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Versatile bonding and coordination modes of ditriazolylidene ligands in rhodium(III) and iridium(III) complexes†

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Metalation of novel ditriazolium salts containing a trimethylene ($-\text{CH}_2\text{CH}_2\text{CH}_2-$) or dimethylether linker ($-\text{CH}_2\text{OCH}_2-$) was probed with different rhodium(III) and iridium(III) precursors. When using $[\text{MCp}^*\text{Cl}_2]_2$, a transmetalation protocol *via* a triazolylidene silver intermediate was effective, while base-assisted metalation with MCl_3 *via* sequential deprotonation of the triazolium salt with KOtBu and addition of the metal precursor afforded homoleptic complexes. The *N*-substituent on the triazole heterocycle directed the metalation process and led to $\text{C}_{\text{trz}}, \text{C}_{\text{trz}}, \text{C}_{\text{Ph}}$ -tridentate chelating ditriazolylidene complexes for *N*-phenyl substituents. With ethyl substituents, only $\text{C}_{\text{trz}}, \text{C}_{\text{trz}}$ -bidentate complexes were formed, while metalation with mesityl substituents was unsuccessful, presumably due to steric constraints. Through modification of the reaction conditions for the metalation step, an intermediate species was isolated that contains a $\text{C}_{\text{trz}}, \text{C}_{\text{Ph}}$ -bidentate chelate *en route* to the formation of the tridentate ligand system. Accordingly, $\text{C}_{\text{phenyl}}-\text{H}$ bond activation occurs prior to formation of the second metal–triazolylidene bond. Stability studies with a $\text{C}_{\text{trz}}, \text{C}_{\text{trz}}, \text{C}_{\text{Ph}}$ -tridentate chelating ditriazolylidene iridium complex towards DCI showed deuterium incorporation at both *N*-phenyl groups and indicate that $\text{C}_{\text{phenyl}}-\text{H}$ bond activation is reversible while the $\text{C}_{\text{trz}}-\text{Ir}$ bond is robust. The flexible linker between the two triazolylidene donor sites provides access to both facial and meridional coordination modes.

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Introduction

The discovery of *N*-heterocyclic carbenes (NHCs) as ligands for transition metals has fundamentally transformed organometallic chemistry¹ and has spurred in particular² the development of new generations of homogeneous catalysts.³ As a consequence of this success, the NHC theme has been varied in all dimensions, including the development of chiral systems,⁴ of non-cyclic analogues,⁵ of carbenes with reduced heteroatom stabilization⁶ and of course the combination of different privileged ligands together with carbenes.⁷ 1,2,3-Triazolylidenes are a subclass of NHCs that have received considerable attention over the last few years,⁸ and which offer vast opportunities for catalysis⁹ and beyond.¹⁰ Their mesoionic character¹¹ and strong σ -donor ability are attractive features for

tailoring the properties of the coordinated metal center.¹² Moreover, these heterocycles are accessible *via* copper(I) catalyzed ‘click’ [2 + 3] cycloaddition of an alkyne and azide (CuAAC),¹³ a reaction that stands out for its versatility and its exceptionally broad functional group tolerance.¹⁴ As a consequence, various donor-functionalized triazolylidene complexes with a wide range of chelating groups have been developed.⁸ Surprisingly however, triazolylidene-based chelating dicarbenes have not been studied extensively, despite the kinetic and thermodynamic stability imparted by chelation. To date, two approaches for linking 1,2,3-triazolium salts *via* either the triazole C4 or N3 position were reported, involving a di-alkyne and a di-azide precursor, respectively. For example, C4-linked ditriazolium salts with rigid aryl-bridges have been metalated with rhodium,¹⁵ ruthenium,¹⁶ nickel,¹⁷ and palladium,¹⁸ leading to bimetallic systems (Fig. 1, A) or CNC-type pincer complexes (B). Directly linked ditriazolylidenes were coordinated to rhodium,¹⁹ iridium, and ruthenium (C).²⁰ Similarly, alkyl- or aryl-linkages *via* N3 have led to bimetallic complexes of ruthenium²¹ and iridium²² in which the ligand adopts a bridging rather than chelating binding mode (D, E).

Trimethylene-linked dicarbene ligands similar to those present in complex E, yet comprised of imidazolylidenes rather than triazolylidene heterocycles, induced alkyl C–H

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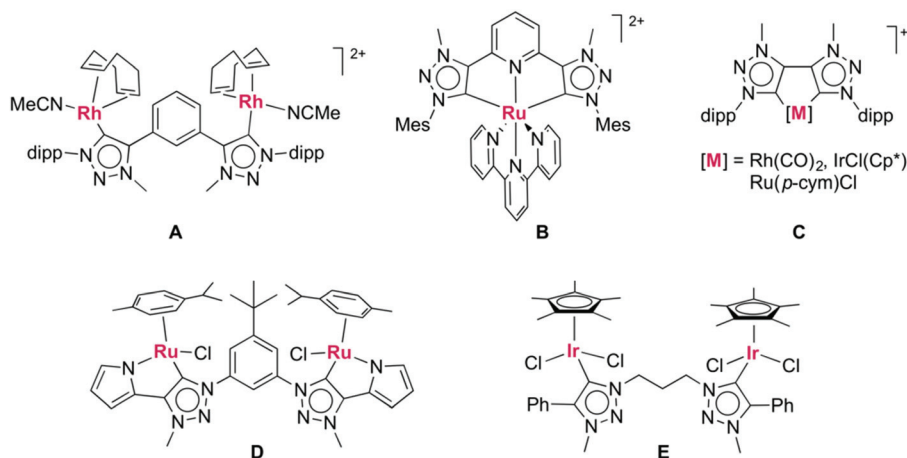


Fig. 1 Known ditriazolylidene complexes including C,C'-linked ditriazolylidene ligands (A, B, C) and N,N'-linked ditriazolylidene scaffolds (D, E).

bond activation of the central methylene unit by rhodium or ruthenium, thus forming a tridentate dicarbene species.²³ The $C_{alkyl}-H$ bond activation was significantly faster when the imidazolylidene is bound to rhodium *via* C4 as a mesoionic carbene rather than in the normal C2-bonding mode.^{23a} Based on these considerations, we were interested to investigate the reactivity of analogous di-1,2,3-triazolylidene systems that are mesoionic as well. In addition, heteroatoms can easily be introduced into the triazolylidene linker, which may provide further reactivity patterns. Here, we report the synthesis of chelating ditriazolylidene rhodium(III) and iridium(III) complexes which contain flexible C,C'-linked ditriazolylidenes. The flexibility accommodates both facial and meridional coordination modes and the peripheral substituents at the heterocycle dictate the coordination mode of the triazolylidenes, thus demonstrating strong reactivity control by ligand design.

Results and discussion

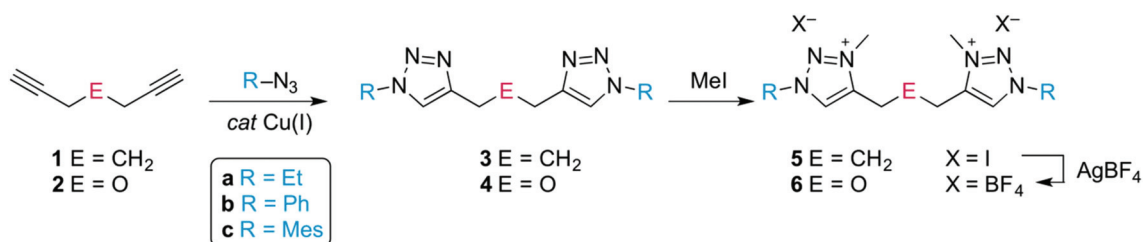
Synthesis of the ligand precursors

The C,C'-linked ditriazoles **3** and **4** were synthesised in good to excellent yields (71–95%) *via* the 'click' cycloaddition of the commercially available diynes **1** and **2**, and the corresponding azide, (Scheme 1). The alkyl linker was identified by a characteristic triplet for the $C_{trz}CH_2$ group and a quintet for the central methylene unit. For example for compound **3a**, these

multiplets appeared at δ_H 2.67 and 1.94 in the 1H NMR spectrum respectively, while the ether linker showed as a singlet, *e.g.* at δ_H 4.71 for **4a**. The versatility of the 'click' reaction allows for the facile variation of the N-bound substituent in the ligand precursor. This versatility is beneficial for the steric and electronic tailoring of the ligand environment when bound to the metal which is particularly useful for bond activation reactions. Alkylation of the ditriazoles with methyl iodide gave the ditriazolium salts **5(I)** and **6(I)** in good yields (Scheme 1). After quaternization, the 1H NMR signal of the heterocyclic proton shifted downfield by almost 1 ppm. For example the $C_{trz}-H$ in **5a(I)** appeared as a singlet at δ_H 8.87 compared to δ_H 7.54 ppm in the precursor **3a**. In addition, a new signal emerged in the 1H and ^{13}C NMR spectrum for the N-bound methyl group (δ_H 4.20, δ_C 38.2 for **5a(I)**). Anion substitution with $AgBF_4$ afforded the corresponding ditriazolium salts **5(BF₄)** and **6(BF₄)**. Successful anion exchange was indicated by a diagnostic ~ 0.5 ppm upfield shift of the $C_{trz}-H$ resonance in the 1H NMR spectrum, presumably due to less pronounced $X\cdots H$ hydrogen bonding.²⁴

Metalation of ditriazolium salts with $[MCp^*Cl_2]_2$

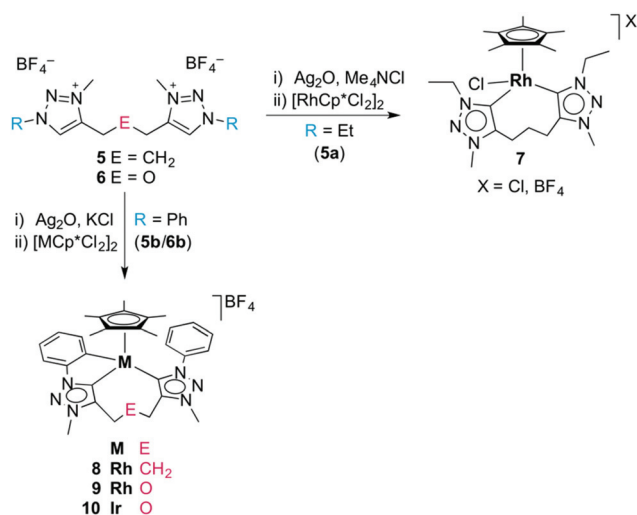
In an initial set of experiments, the well-established transmetalation procedure involving the formation of a triazolylidene silver(I) intermediate was utilised for the formation of triazolylidene rhodium(III) and iridium(III) complexes.^{8d,25} Successful



Scheme 1 Ligand precursor synthesis *via* 'click' cycloaddition and alkylation.

metalation of the triazolium salts using Ag_2O in the presence of KCl was surmised by the disappearance of the ^1H NMR signal of the $\text{C}_{\text{trz}}\text{-H}$ unit, and by the appearance of a mass signal which is in agreement with the $[\text{Ag}(\text{ditriazolyldiene})]^+$ fragment. The ^1H NMR spectrum of the triazolyldiene silver complexes showed a symmetric linker which suggests a dimeric $[\text{Ag}_2(\text{trz}^+\text{E}^-\text{trz})_2]^{2+}$ species rather than a chelating $[\text{Ag}(\text{trz}^+\text{E}^-\text{trz})]^+$ monomer, in agreement with results by Crudden and co-workers.¹⁵ The formation of the silver triazolyldiene proceeded at elevated temperatures when using the *N*-ethyl triazolium salts (refluxing MeCN), while *N*-aryl triazolium salts reacted under milder conditions and provided the desired triazolyldiene silver intermediate at room temperature. Triazolyldiene silver complexes were also formed in the absence of a chloride additive, though significant decomposition was observed and yields were typically much lower, presumably because the triazolyldiene silver unit is less stabilized by tetrafluoroborate as compared to chlorides.^{9e,21,26} Likewise, the triazolyldiene silver intermediates were accessible also from the triazolium iodide salts **5(I)**, but in agreement with previous reports,²⁷ the reaction was generally less clean than when starting from **5(BF₄)**. Carbene silver complexes are known to exist in an equilibrium between ionic species of type $[\text{Ag}(\text{carbene})_2][\text{AgX}_2]$ and the neutral isomer $[\text{AgX}(\text{carbene})]$,²⁸ which is delicately dependent on conditions and will lead to oligo- or polymeric systems with ditopic carbenes as used here. Due to this fluxionality, no attempts have been made to structurally characterize these intermediates.

The triazolyldiene silver complexes were used without further purification for transmetalation with $[\text{MCp}^*\text{Cl}_2]_2$ ($\text{M} = \text{Rh}, \text{Ir}$), and afforded the chelating ditriazolyldiene complexes **7–10** (Scheme 2). All complexes were air- and moisture stable and were isolated by standard column chromatography as red (**7, 8**) or orange solids (**9, 10**) that are moderately soluble in CH_2Cl_2 and readily soluble in MeCN.



Scheme 2 Formation of complexes **7–10** by transmetalation via a silver carbene intermediate.

Chelation in complex **7** was indicated by the presence of symmetry-related triazolyldiene units and the pertinent 5 : 2 integral ratio of the resonances due to the Cp^* protons and the N-CH_3 unit. The carbenic ^{13}C NMR resonance is deshielded and appears at δ_{C} 154.4 as a doublet due to characteristic ^{103}Rh coupling ($^1J_{\text{CRh}} = 50.3$ Hz). Furthermore, chelation led to diastereotopic methylene protons in the ethyl wingtip group as indicated by the two doublet of quartets at δ_{H} 4.81 and 4.42 ($^2J_{\text{HH}} = 12.9$ Hz, $^3J_{\text{HH}} = 7.2$ Hz). Similarly, the triazolyldiene bound CH_2 group of the trimethylene linker appeared as two doublets of doublets of doublets ($^2J_{\text{HH}} = 14.9$ Hz, $^3J_{\text{HH}} = 8.6$ Hz, $^4J_{\text{HH}} = 4.6$ Hz). Of note, a multiplet in the 1.88–1.69 ppm range integrated for two protons and was attributed to the central CH_2 group of the linker, thus suggesting that the linker has not been affected. This reactivity differs from that of related rhodium(III) complexes containing mesoionic diimidazolyldiene ligands, in which C–H bond activation of the linker methylene group is spontaneous.²³ X-ray crystallographic analysis of complex **7** unambiguously confirmed the ligand bonding mode surmised from spectroscopic studies (Fig. 2). The complex cation shows the typical three-legged piano-stool geometry with two triazolyldienes and one chloride ligand site forming the ‘legs’. The carbene bite angle is relatively wide, $\text{C}_{\text{trz}}\text{-Rh-C}_{\text{trz}} = 91.21(9)^\circ$.²⁹ While the triazolyldiene units are symmetrical in solution, the $\text{C}_{\text{trz}}\text{-Rh}$ bond lengths of complex **7** differ considerably in the solid state (C1-Rh 2.026(2) Å, C11-Rh 2.082(2) Å). This difference may be a direct consequence of the different orientation of the triazolyldiene heterocycles in the solid state with respect to the rhodium coordination geometry, e.g. the Cl-Rh-C-N dihedral angle is $48.4(2)^\circ$ for the heterocycle containing C1 and $71.1(2)^\circ$ for the heterocycle containing C7. In solution, these distinct arrangements average out as indicated by the symmetric NMR pattern observed for this complex.

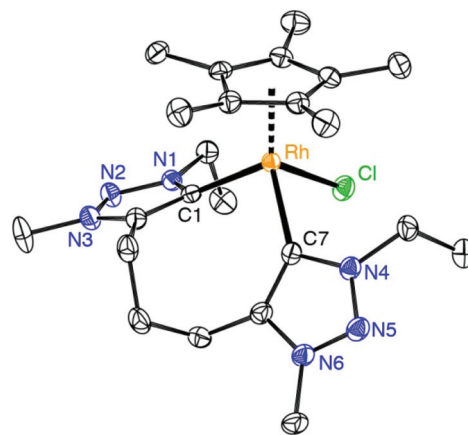


Fig. 2 ORTEP representation of the complex cation complex **7** (50% probability ellipsoids, hydrogens omitted for clarity). Selected bond lengths: Rh-C1 2.026(2) Å, Rh-C7 2.082(2) Å, Rh-Cl 2.410(4) Å, $\text{Rh-Cp}_{\text{centroid}}$ 1.862(4) Å; selected bond angles: C1-Rh-C7 91.21(9)°, C1-Rh-Cl 96.16(6)°, C7-Rh-Cl 84.74(7)°.

It is worth noting that the analogous rhodation of the ether-linked ditriazolium salt **6a**(BF₄) has failed in our hands so far. Formation of the carbene silver intermediate was confirmed by the pertinent NMR and MS data, though substantial amounts of impurities were observed. Possibly, the ether linkage interacts with the silver ion and destabilizes this intermediate under the applied reaction conditions.

The presence of phenyl substituents at the triazole heterocycle altered the outcome of the reaction and induced cyclometalation through activation of one of the *ortho* C_{phenyl}–H bonds in **5b** and **6b** to yield complexes **8–10** containing a C,C,C-tridentate coordinated ditriazolylidene ligand (Scheme 2). Similar C–H bond activation was observed previously in mono-triazolylidene complexes containing N-bound phenyl-substituents.³⁰ Apparently the C_{phenyl}–H bond activation process is preferred over heteroatom coordination and is spontaneous even at –30 °C both with rhodium and iridium precursors. No trace of a coordinated triazolylidene with a non-cyclometalated phenyl group was observed by NMR spectroscopy. Cyclometalation was indicated by the ligand desymmetrization as revealed by the presence of seven distinct phenyl proton resonances in the low-field section of the ¹H NMR spectrum integrating for 9 protons. While one set features the typical 2 : 2 : 1 pattern of a pristine phenyl group, the second set is constituted of four signals that are characteristic for a *ortho* disubstituted phenylene system, with two doublets and two multiplets that are correlated and integrating for one proton each. Ligand desymmetrization was also apparent from the two distinct singlets due to inequivalent NCH₃ groups. Similarly, the OCH₂ groups of the linker of complexes **9** and **10** were inequivalent and appeared as two sets of AB doublets with characteristic ²J_{HH} coupling constants around 15 Hz. Three low-field ¹³C signals were observed in the ¹³C{¹H} NMR spectrum for all three complexes **8–10** and were attributed to the two metal-bound carbenic carbons and the phenyl carbon. For example, the rhodium complex **8** showed three doublets at δ_C 164.2 (C_{trz}, ¹J_{CRh} = 47.0 Hz), 159.5 (C_{phenyl}, ¹J_{CRh} = 36.2 Hz) and 158.2 (C_{trz}, ¹J_{CRh} = 50.3 Hz). The smaller ¹J_{CRh} coupling constant was attributed to the Rh–C_{phenyl} bond,^{30b,f} and the larger coupling constants to Rh–C_{trz} interactions. The larger coupling constant at δ_C 158.2 is identical to the coupling observed in complex **7** (¹J_{CRh} = 50.3 Hz, *vide supra*), therefore suggesting this resonance to be due to the triazolylidene unit that contains the non-cyclometalated phenyl substituent. Accordingly, the resonance at δ_C 164.2 with a slightly smaller coupling constant was tentatively attributed to the carbenic carbon of the triazolylidene containing the metal-bound phenylene fragment.

Further evidence for the tridentate bonding of the ligand was obtained by single crystal X-ray diffraction of complexes **8** and **9** (Fig. 3, Table 1). Both structures are identical within errors and unambiguously reveal a Rh–C_{phenyl} bond in addition to the dicarbene bonding. All three Rh–C bond lengths are within expectation and in the 2.00–2.06 Å range. The average carbene bite angle is 81.5(2)° and thus considerably more acute than in the bidentate carbene complex **7** (C_{trz}–Rh–C_{trz} = 91.21(9)°).

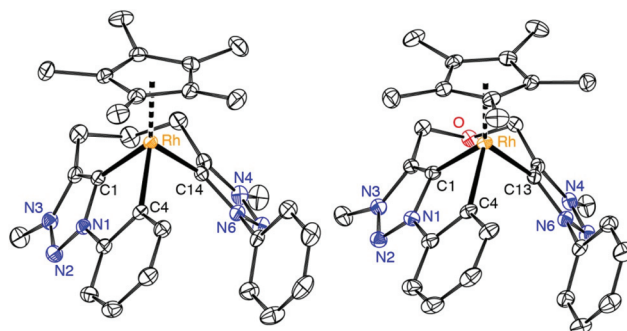


Fig. 3 ORTEP representation of the complex cations of **8** (a), **9** (50% probability ellipsoids, hydrogen atoms omitted for clarity).

Table 1 Selected bond lengths (Å) and angles (°) for **8** and **9**

	8	9
Rh–C1	2.026(12)	2.004(2)
Rh–C13/14	2.033(12)	2.054(2)
Rh–C4	2.050(12)	2.057(2)
Rh–C _{pcentroid}	1.889(1)	1.899(2)
C1–Rh–C13/14	81.62(5)	81.43(8)
C1–Rh–C4	78.97(5)	78.86(9)
C4–Rh–C13/14	92.85(5)	92.92(8)

Minor by-products were observed in the crude reaction mixture of the iridium complex **10** by ¹H NMR spectroscopy, which revealed the characteristic pattern of a cyclometalated phenyl group. Separation by column chromatography yielded traces of the bimetallic complex **11** (Fig. 4), in which both *N*-phenyl groups are *ortho*-metalated to different iridium centers. The ¹H NMR spectrum indicated symmetry-related triazolylidene and phenyl groups, and a diagnostic 2 : 1 Cp*/ligand ratio. The bridging coordination mode was further supported by the single AB doublet (²J_{HH} = 12.6 Hz) for the OCH₂ group, while the chelating complex **10** featured two AB doublets because of the lack of symmetry in the ligand. The carbonyl resonance appeared at δ_C 153.2 in the ¹³C{¹H} NMR spectrum. A high field resonance at δ_C 114.0, attributed to the C_{phenyl}–H nucleus *ortho* to the N_{trz} (*i.e.* formally C3 of the phenylene unit), is diagnostic for cyclometalation. In the chelate complexes **8–10**, this nucleus appears at essentially the same frequency (approximately 113.5 ppm). While NMR studies strongly support the bridging coordination mode of the bis(triazolylidene) ligand, we were unable to purify this

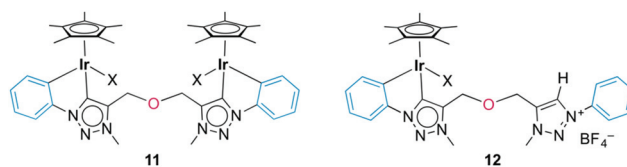


Fig. 4 Complexes **11** and **12** as minor products from transmetalation reaction.



complex sufficiently for elemental analysis or X-ray diffraction analysis, which has prevented the unambiguous identification of the spectator ligand so far. Attempts to selectively form the bimetallic complex by adding the preformed triazolyldiene silver complex dropwise to a concentrated solution of $[\text{IrCp}^*\text{Cl}_2]_2$ cleanly produced complex **10** together with unreacted $[\text{IrCp}^*\text{Cl}_2]_2$, yet no bimetallic species was observed.

When reacting **6b**(BF_4), Ag_2O , and $[\text{IrCp}^*\text{Cl}_2]_2$ simultaneously rather than sequentially (*vide supra*), a yellow mixture was obtained. NMR analysis of this crude mixture identified four distinct species including complexes **10** and **11** and two species, which were isolated by successive precipitation. Spectroscopic analysis indicated a mixture of two strongly related species in approximate 2:1 molar ratio and with a general bonding pattern that is in agreement with the one depicted for complex **12** (Fig. 4). The two species were tentatively assigned as the chloro and the solvento analogues ($\text{X} = \text{Cl}$, NCMe). Both species feature a low-field resonance (δ_{H} 9.10 and 8.87) for the triazolium proton and two AB systems for the OCH_2 groups, indicating desymmetrization of the linker.³¹ Likewise, the NCH_3 groups appeared as distinct singlets. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of this mixture showed two C_{trz} -Ir signals at δ_{C} 153.4 or 146.6 and two C_{trz} -H carbon resonances (δ_{C} 128.9 or 128.8). Heteronuclear multiple bond correlation (HMBC) spectroscopy identified for each of the two species an interaction of one OCH_2 AB set with the iridium-bound triazolyldiene unit, and a correlation of the second OCH_2 resonances with the triazolium C_{trz} -H unit. While the aromatic region in the ^1H NMR spectrum was inconclusive due to significant signal overlap, two high field aryl ^{13}C NMR resonances at δ_{C} 114.7 and 114.0 are in agreement with cyclometalation of the phenyl ring and $\text{C}_{\text{trz}}, \text{C}_{\text{phenyl}}$ -bidentate coordination of the ligand. In addition, two resonances at δ_{C} 138.6 and 138.5 have been attributed to the iridium-bound C_{phenyl} nucleus (*cf.* δ_{C} 139.5 in **10**). Mass spectrometry was consistent with the NMR data and showed a m/z signal at 344 amu, in line with formation of complex **12** (expected m/z for $[\text{C}_{30}\text{H}_{35}\text{IrN}_6\text{O}]^{2+}$ is 344.12 amu). The isolation of $\text{C}_{\text{trz}}, \text{C}_{\text{phenyl}}$ -bidentate ligated complex **12** in combination with the absence of any $\text{C}_{\text{trz}}, \text{C}_{\text{trz}}$ -bidentately bound iridium complex akin to complex **7** strongly suggests that C_{phenyl} -H bond activation is spontaneous. Formation of complex **12** may be a consequence of incomplete triazolyldiene silver formation or due to partial hydrolysis of the semi-transmetalated intermediate prior to chelation of the second carbene unit.

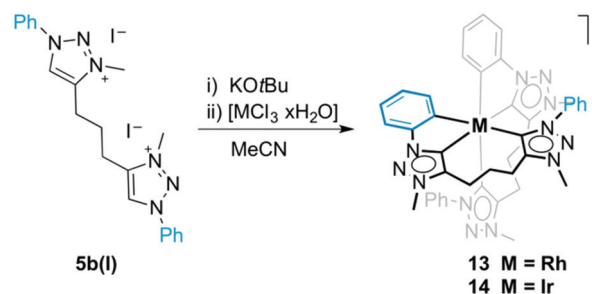
The C_{phenyl} -H bond activation is reversible. Under acidic conditions (20 equiv. DCl in CD_3CN) and at room temperature, the iridium complex **10** incorporated approximately 7% deuterium at the *ortho* positions of both the cyclometalated and the non-cyclometalated phenyl group (24 h). Heating accelerates this isotope exchange, reaching 27% deuterium incorporation at 50 °C (16 h) and up to 60% when heated to 80 °C for 10 h. Gradual decomposition to the triazolium salt was observed under these relatively harsh conditions, and the reaction was therefore aborted after 10 h, presumably due to hydrolysis of the Rh-C_{trz} bond. Deuteration of the *ortho* positions of both

phenyl rings occur initially to the same extent (*e.g.* 27% D-incorporation in the cyclometalated phenyl group *vs.* 26% H/D exchange in the non-cyclometalated residue after 16 h at 50 °C). At higher conversion, the incorporation in the non-cyclometalated ring is slightly higher (68% *vs.* 54% in the cyclometalated phenyl group). The isotope exchange on both phenyl groups indicates that cyclometalation is reversible, involving a bidentate ditriazolyldiene species with two free phenyl groups as a potential transient intermediate which undergoes cyclometalation of either of the two phenyl groups. Attempts to isolate this species have not been successful so far, suggesting that H(D)Cl elimination and cyclometalation are thermodynamically favoured. It is worth noting that the rhodium analogue **9** is much less stable under acidic conditions and rapidly decomposes to the triazolium salt and an inorganic rhodium species.

Transmetalation of the silver triazolyldiene with *N*-mesityl substituents derived from **5c**(BF_4) and **6c**(BF_4) with $[\text{RhCp}^*\text{Cl}_2]_2$ did not proceed. While the formation of a white precipitate and a color change from dark red to orange suggested transfer of the carbene to rhodium, ^1H NMR analysis of the crude product showed broad resonances which were not conclusive. Unambiguous identification of the species was not achieved due to rapid decomposition of the product, both in solution and in the solid state, yielding triazolium starting material. Presumably the mesityl group inhibits chelation of the ditriazolyldiene ligand because of steric interactions with the Cp^* ligand. With *N*-phenyl substituents, such instability issues are circumvented through C-H bond activation and cyclometalation.

Base-mediated metalation

When ligand precursor **5b**(**I**) was reacted directly with MCl_3 ($\text{M} = \text{Rh}$ or Ir) in the presence of KOtBu as base to deprotonate the triazolium salt, the Cp^* -free bis(homoleptic) complexes **13** and **14** were obtained (Scheme 3). Chelation of the triazolyldiene was supported by the desymmetrization of the linker CH_2 groups, which appeared as multiplets between 3.1 and 2.0 ppm in the ^1H NMR spectrum. Similarly to complexes **8–10**, two sets of signals for the phenyl groups indicated that one phenyl substituent is cyclometalated while the other is



Scheme 3 Synthesis of complex **13** and **14** by base-mediated metalation.



not. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the rhodium complex **13** showed three doublet resonances in the low field region. Based on the larger coupling constant, the most deshielded signals at δ_{C} 176.2 and 171.3 ($^1J_{\text{CRh}} = 34.3$ and 30.2 Hz, respectively) were attributed to the triazolylidene carbon, while the resonance at δ_{C} 164.9 ($^1J_{\text{CRh}} = 25.7$ Hz) was assigned to the cyclometalated phenyl carbon. The Rh–C coupling constants for **13** are smaller than those of **8**, which is probably a direct consequence of the stronger *trans* influence of the C,C,C-tridentate ligand in octahedral **13** as compared to Cp* in complex **8**. A meridional coordination mode of the ligand is tentatively surmised from the small chemical shift difference of the central methylene group in the linker (multiplet at δ_{H} 2.08). When coordinating facially as in complex **8**, these protons are magnetically more distinct and appear at 2.33 and 1.62 ppm. The ^1H NMR spectrum of **14** is very similar to that of **13** although the H_{ortho} and H_{meta} signals are broad for **14**. The metal-bound carbons are more shielded than those of **13** and resonate at δ_{C} 158.9 and 152.4 (C_{trz}) and at δ_{C} 147.9 (C_{phenyl}).

A single crystal structure determination of complex **13** confirmed the bis-homoleptic structure with a cyclometalated phenyl group for each ditriazolylidene ligand, thus producing a distorted octahedral geometry around the rhodium center (Fig. 5). In contrast to complexes **8**–**10** with a facially coordinating dicarbene ligand, the same ligand now adopts a meridional coordination mode in complex **13** with the two cyclometalated phenyl units in mutual *cis* position. The cyclometalated phenyl ring is coplanar with the adjacent triazolylidene heterocycle. The $\text{C}_{\text{trz}}\text{--Rh}$ bond *trans* to C_{phenyl} is 0.05 Å longer than the $\text{C}_{\text{trz}}\text{--Rh}$ bond *trans* to a carbene, which is presumably imposed by steric constraints imparted by the chelating bonding mode rather than distinct *trans* influences. One

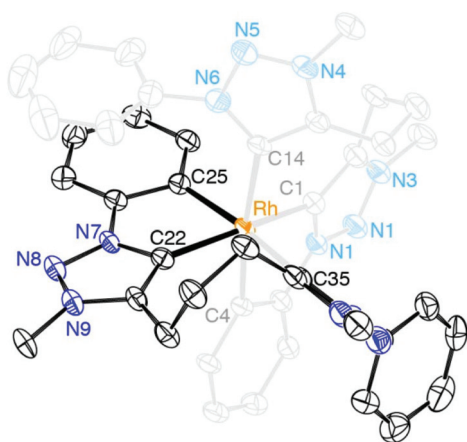


Fig. 5 ORTEP representation of complex **13** (50% probability ellipsoids, I^- counterion, hydrogen atoms, and co-crystallized CH_2Cl_2 molecule omitted for clarity); selected bond lengths: Rh–C1 2.041(3) Å, Rh–C14 2.071(3) Å, Rh–C25 2.098(3) Å; selected bond angles: C1–Rh–C14 80.22(13)°, C1–Rh–C25 91.79(14)°, C14–Rh–C25 171.87(13)°, C1–Rh–C25 164.32(13)°.

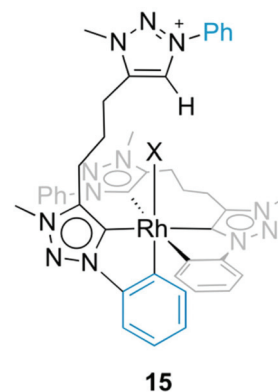


Fig. 6 Intermediate species **15** with a $\text{C}_{\text{trz}},\text{C}_{\text{ph}}$ -bidentate coordinating ligand containing a pendant triazolium unit.

triazolylidene ring is substantially more constrained by the rigid five-membered metalacycle, while the other carbene is part of a more flexible eight-membered metalacyclic motif.

Formation of complex **13** was investigated in more detail by performing the synthesis at different temperatures. When the reaction was carried out at room temperature instead of MeCN reflux temperature, the triazolium salt **5b(I)** was the only species observed by ^1H NMR spectroscopy after 18 h. Upon heating to 60 °C, complex **13** started to form, and in addition, an intermediate was detected by NMR spectroscopy that was identified as complex **15** (Fig. 6). The triazolium proton of **15** appeared in the ^1H NMR spectrum at δ_{H} 8.79 while the phenyl proton signals showed the diagnostic signature of both a pending phenyl group and an *ortho*-metalated phenylene unit, which were in equal intensity yet at distinct chemical shift from the C_{phenyl} resonances of the tridentate ligand. Moreover, mass spectrometry showed a signal at 409 amu, which corroborates the calculated mass for the dicationic fragment of $[\text{15-X}]^{2+}$ ($m/z = 409.4$ calculated for $[\text{C}_{42}\text{H}_{43}\text{RhN}_{12}]^{2+}$).³² Upon further heating, this intermediate **15** evolved to the bis(homoleptic) complex **13** exclusively. Complex **15** is related to intermediate **12** detected *en route* to the tridentate coordinating dicarbene iridium complex **10** (*cf.* Fig. 4). The formation of a $\text{C}_{\text{trz}},\text{C}_{\text{phenyl}}$ -bidentate coordinated complex with a pendant triazolium species supports our previous observation that cyclometalation and $\text{C}_{\text{phenyl}}\text{--H}$ bond activation take place prior to coordination of the second triazolylidene ligand. Cyclometalation may be a key driver in the formation of complex **13**, since the base-mediated metalation reaction did not proceed with the *N*-ethyl or *N*-mesityl analogues **5a(I)** and **5c(I)**, respectively under otherwise identical conditions. Instead, only triazolium starting materials were observed by NMR spectroscopy.

Conclusions

A series of ditriazolylidene rhodium and iridium complexes containing alkyl- or ether-linkers between the triazolylidene bonding sites were derived from commercially available



diynes. Ligand parameters and specifically the *N*-substituents on the triazole heterocycle critically dictate the bonding mode of the dicarbene ligand. In particular, *N*-phenyl substituted triazolyldienes lead in all cases to *ortho*-metalation of one of the phenyl rings and to a C_{trz}C_{trz}C_{Ph}-tridentate ligand coordination mode. The C_{Ph}-H bond activation process is spontaneous and the isolation of a C_{trz}C_{Ph}-bidentate intermediate suggests that this bond activation occurs prior to chelation of the second carbene. Stability studies under acidic conditions involving the C_{trz}C_{trz}C_{Ph}-tridentate coordinated iridium complex indicate that the Ir-C_{trz} bonds are robust while the Ir-C_{Ph} bond is kinetically labile and formed reversibly. Moreover, depending on the applied metalation procedure, the ligand coordinates either meridionally or facially. This coordinative flexibility paired with the hemilability of the C_{Ph}-Ir bond are attractive features for catalysis. The potential of these complexes as catalysts in, for example, hydrogen transfer reactions is currently under investigation.

Experimental section

General comments

All reagents were used as received from commercial suppliers. Unless specified, NMR spectra were recorded at 25 °C on Varian spectrometers operating at 300, 400 or 500 MHz (¹H NMR) and 75, 100 or 125 MHz (¹³C{¹H} NMR) respectively. Chemical shifts (δ in ppm, coupling constants *J* in Hz) were referenced to external SiMe₄ (¹H, ¹³C{¹H}). Assignments are based on homo- and hetero-nuclear shift correlation spectroscopy. High-resolution mass spectrometry was carried out with a Micromass/Waters Corp. USA liquid chromatography with an electrospray source. Elemental analyses were performed at UCD Microanalytic Laboratory using an Exeter Analytical CE-440 elemental analyser. Residual solvents were identified by NMR spectroscopy.

General procedure for the synthesis of ditriazoles 3 and 4

Method A: A mixture of the corresponding diyne (1 mol equiv.), azide (2.2 mol equiv.), CuSO₄ (2 mol%) and sodium ascorbate (20 mol%) in a 1 : 1 mixture of THF : H₂O was irradiated in a microwave reactor at 100 °C for 2 h using high absorption. The THF was removed under reduced pressure and the organics were extracted with CH₂Cl₂ (2 × 50 mL). The combined organics were washed with dilute (NH₄)(OH) (aq., 50 mL), water (2 × 50 mL) and saturated NaCl solution (aq. 1 × 40 mL), dried over anhydrous Na₂SO₄, filtered and all volatiles removed under reduced pressure yielding the ditriazole product.

Method B: EtI (1 mol equiv.) and NaN₃ (4 mol equiv.) were added to a microwave vessel with 1 : 1 of THF : H₂O (20 mL) and stirred at room temperature for 48 h. To this mixture the corresponding diyne (0.33 mol equiv.), CuSO₄ (14 mol%) and copper powder (5 mol%) were added and the mixture was irradiated in a microwave reactor at 100 °C for 2 h using high absorption. The THF was removed under reduced pressure and the organic residue was extracted with CH₂Cl₂ (2 × 50 mL).

The crude reaction mixture was filtered through a short column of silica with a CH₂Cl₂/acetone solution (1 : 1, 300 mL) until all product was collected as indicated by TLC. The solvent was removed under reduced pressure giving the ditriazole product as an oil.

Synthesis of 3a. According to method B, EtI (2.8 g, 18 mmol), NaN₃ (4.8 g, 74 mmol), THF (5 mL), H₂O (5 mL), 1,6-heptadiyne (0.62 mL, 5.4 mmol), CuSO₄ (0.189 g, 0.756 mmol) and copper powder (0.017 g, 0.270 mmol) were reacted in a microwave reactor for 2 h. After purification, the product was obtained as a yellow oil (0.92 g, 72%). ¹H NMR (CD₃CN, 400 MHz): δ 7.54 (s, 2H, H_{trz}), 4.30 (q, 4H, ³J_{HH} = 7.3 Hz, NCH₂), 2.67 (t, 4H, ³J_{HH} = 7.5 Hz, C_{trz}CH₂), 1.94 (quintet, 2H, ³J_{HH} = 7.5 Hz, C_{trz}CH₂CH₂), 1.41 (t, 6H, ³J_{HH} = 7.3 Hz, NCH₂CH₃). ¹³C{¹H} NMR (CD₃CN, 100 MHz): δ 148.1 (C_{trz}), 121.8 (C_{trz}-H), 45.7 (NCH₂), 30.0 (CCH₂CH₂), 25.6 (CCH₂CH₂), 15.8 (NCH₂CH₃). ESI-MS (*m/z*): 235.1676, calcd for [C₁₁H₁₉N₆]⁺ 235.1671.

Synthesis of 3b. According to method A, 1,6-heptadiyne (0.53 mL, 4.62 mmol), phenyl azide (1.38 g, 11.56 mmol), CuSO₄ (0.015 g, 94 μmol), sodium ascorbate (0.183 g, 0.924 mmol), THF (8 mL) and H₂O (8 mL) were reacted in a microwave reactor for 2 h. After purification, the product was obtained as an off-white solid (1.83 g, 95%). Analytically pure product was obtained by recrystallization from minimal amounts of THF/cyclohexane (1 : 1). ¹H NMR (CDCl₃, 400 MHz): δ 7.80 (s, 2H, H_{trz}), 7.70–7.66 (m, 4H, H_{ortho}), 7.49–7.43 (m, 4H, H_{meta}), 7.37 (tt, 2H, ³J_{HH} = 7.4 Hz, ⁴J_{HH} = 1.2 Hz, H_{para}), 2.89 (t, 4H, ³J_{HH} = 7.4 Hz, C_{trz}CH₂), 2.18 (quintet, 2H, ³J_{HH} = 7.4 Hz, CCH₂CH₂). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 148.3 (C_{trz}), 137.2 (C_{ipso}), 129.7 (C_{meta}), 128.5 (C_{para}), 120.4 (C_{ortho}), 119.4 (C_{trz}-H), 29.0 (C_{trz}CH₂CH₂), 24.9 (C_{trz}CH₂). ESI-MS (*m/z*): 331.1677, calcd for [C₁₉H₁₉N₆]⁺ 331.1671. Anal calcd for C₁₉H₁₈N₆ (330.39): C, 69.07; H, 5.49; N, 25.44%. Found: C, 68.58; H, 5.49; N, 25.19%.

Synthesis of 3c. According to method A, 1,6-heptadiyne (0.13 mL, 1.13 mmol), mesityl azide (0.40 g, 2.48 mmol), CuSO₄ (0.004 g, 23 μmol), sodium ascorbate (0.045 g, 0.23 mmol), THF (9 mL) and H₂O (9 mL) were reacted in a microwave reactor for 2 h. After purification, the product was obtained as an off-white solid (0.37 g, 80%). Analytically pure material was obtained by recrystallization from hot cyclohexane (30 mL) with a minimum amount of THF.

¹H NMR (CDCl₃, 400 MHz): δ 7.41 (s, 2H, H_{trz}), 6.96 (s, 4H, H_{Mes}), 2.92 (t, 4H, ³J_{HH} = 7.6 Hz, C_{trz}CH₂), 2.33 (s, 6H, CH_{3-para}), 2.23 (quintet, 2H, ³J_{HH} = 7.6 Hz, CCH₂CH₂), 1.95 (s, 12H, CH_{3-ortho}). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 147.3 (C_{trz}), 139.9 (C_{para}), 135.2 (C_{ortho}), 133.8 (C_{ipso}), 129.1 (C_{meta}), 123.0 (C_{trz}-H), 29.3 (CCH₂CH₂), 25.1 (C_{trz}CH₂), 21.2 (CH_{3-para}), 17.4 (CH_{3-ortho}). ESI-MS (*m/z*): 415.2600, calcd for [C₂₅H₃₁N₆]⁺ 415.2610. Anal calcd for C₂₅H₃₀N₆ (414.55): C, 72.43; H, 7.29; N, 20.27%. Found: C, 72.12; H, 7.38; N, 19.99%.

Synthesis of 4a. According to method B, EtI (624 mg, 4 mmol), NaN₃ (1 g, 16 mmol), THF (9 mL), H₂O (9 mL), propargyl ether (0.21 mL, 2 mmol), CuSO₄ (100 mg, 0.4 mmol) and copper powder (70 mg, 0.1 mmol) were reacted in a micro-



wave reactor for 2 h. Purification was carried out as per method A giving the product as a red oil (0.34 g, 71%). ^1H NMR (CDCl_3 , 400 MHz): δ 7.59 (s, 2H, H_{trz}), 4.71 (s, 4H, OCH_2), 4.40 (q, 4H, $^3J_{\text{HH}} = 7.4$ Hz, NCH_3), 1.55 (t, 4H, $^3J_{\text{HH}} = 7.4$ Hz, NCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 144.8 (C_{trz}), 122.2 ($\text{C}_{\text{trz-H}}$), 63.8 (OCH_2), 45.4 (NCH_3), 15.6 (NCH_2CH_3). ESI-MS (m/z): 237.1473, calcd for $[\text{C}_{10}\text{H}_{17}\text{N}_6\text{O}]^+$ 237.1464. The oily nature prevented full purification to micro-analytical standards.

Synthesis of 4b. According to method A, propargyl ether (0.6 mL, 5.82 mmol), phenyl azide (1.73 g, 14.5 mmol), CuSO_4 (0.019 g, 0.12 mmol), sodium ascorbate (0.230 g, 1.16 mmol), THF (8 mL) and H_2O (8 mL) were reacted in a microwave reactor for 2 h. After purification, the product was obtained as an off-white solid (1.45 g, 95%). Analytically pure product was obtained by recrystallization from minimum amounts of THF/cyclohexane (1 : 1). ^1H NMR (CDCl_3 , 400 MHz): δ 8.05 (s, 2H, H_{trz}), 7.73–7.69 (m, 4H, H_{ortho}), 7.52–7.47 (m, 4H, H_{meta}), 7.44–7.39 (m, 2H, $^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, H_{para}), 4.84 (s, 4H, OCH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 145.4 (C_{trz}), 137.0 (C_{ipso}), 129.8 (C_{meta}), 128.9 (C_{para}), 121.3 ($\text{C}_{\text{trz-H}}$), 120.6 (C_{ortho}), 63.7 (OCH_2). ESI-MS (m/z): 333.1473, calcd for $[\text{C}_{18}\text{H}_{17}\text{N}_6\text{O}]^+$ 333.1464. Anal calcd for $\text{C}_{18}\text{H}_{16}\text{N}_6\text{O}$ (332.36): C, 65.05; H, 4.85; N, 25.29%. Found: C, 64.64; H, 4.58; N, 24.97%.

Synthesis of 4c. According to method A, propargyl ether (0.12 mL, 1.13 mmol), mesityl azide (0.4 g, 2.48 mmol), CuSO_4 (4 mg, 0.023 mmol), sodium ascorbate (45 mg, 0.23 mmol), THF (8 mL) and H_2O (8 mL) were reacted in a microwave reactor for 2 h. After solvent evaporation, the crude product was obtained as an amber oil (0.4 g, 85%). It was purified by column chromatography (SiO_2 ; Et_2O , then CH_2Cl_2). An analytically pure sample was obtained by recrystallization from minimum quantities of THF/cyclohexane (1 : 1). ^1H NMR (CDCl_3 , 400 MHz): δ 7.67 (s, 2H, H_{trz}), 6.98 (s, 4H, H_{Mes}), 4.87 (s, 4H, OCH_2), 2.34 (s, 6H, $\text{CH}_3\text{-para}$), 1.96 (s, 12H, $\text{CH}_3\text{-ortho}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 144.6 (C_{trz}), 140.1 (C_{para}), 135.2 (C_{ortho}), 133.5 (C_{ipso}), 129.2 (C_{meta}), 124.9 ($\text{C}_{\text{trz-H}}$), 63.8 (OCH_2), 21.2 ($\text{CH}_3\text{-para}$), 17.4 ($\text{CH}_3\text{-ortho}$). ESI-MS (m/z): 417.2398, calcd for $[\text{C}_{24}\text{H}_{29}\text{N}_6\text{O}]^+$ 417.2403. Anal calcd for $\text{C}_{24}\text{H}_{28}\text{N}_6\text{O}$ (416.52): C, 69.21; H, 6.78; N, 20.18%. Found: C, 69.44; H, 6.90; N, 19.93%.

General procedure for alkylation of ditriazoles (5a–c(I), 6a–c(I))

A mixture of ditriazole (1 mol equiv.) and MeI (excess) were added to a pressure tube with MeCN (10 mL). The mixture was heated for a set time at reflux. After cooling to room temperature the product was precipitated by addition of Et_2O (80 mL) and the ditriazolium salt was isolated by centrifugation. The crude product was suspended in MeCN (10 mL) and precipitated again with Et_2O (80 mL) and isolated by centrifugation. This purification procedure was repeated once more.

Synthesis of 5a(I). According to the general procedure, 3a (0.55 g, 2.35 mmol) and MeI (3.33 g, 23.5 mmol) and after 21 h of reflux, the product was obtained as a dark red waxy solid (1.08 g, 89%). ^1H NMR (CD_3CN , 400 MHz): δ 8.87 (s, 2H, H_{trz}), 4.59 (q, 4H, $^3J_{\text{HH}} = 7.3$ Hz, NCH_2), 4.20 (s, 6H, NCH_3),

3.06 (t, 4H, $^3J_{\text{HH}} = 7.7$ Hz, $\text{C}_{\text{trz}}\text{CH}_2$), 2.22 (quintet, 2H, $^3J_{\text{HH}} = 7.7$ Hz, $\text{C}_{\text{trz}}\text{CH}_2\text{CH}_2$), 1.59 (t, 6H, $^3J_{\text{HH}} = 7.3$ Hz, NCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 100 MHz): δ 143.4 (C_{trz}), 128.6 ($\text{C}_{\text{trz-H}}$), 49.3 (NCH_2), 38.2 (NCH_3), 24.3 ($\text{C}_{\text{trz}}\text{CH}_2\text{CH}_2$), 22.4 ($\text{C}_{\text{trz}}\text{CH}_2\text{CH}_2$), 13.9 (NCH_2CH_3). ESI-MS (m/z): 132.0580, calcd for $[\text{C}_{13}\text{H}_{24}\text{N}_6]^{2+}$ 132.1031. Because of the oily consistency of the product, we were unable to obtain satisfactory microanalysis even after repeated precipitations (see also ESI†).

Synthesis of 5b(I). Compound 3b (0.50 g, 1.51 mmol) and MeI (0.94 mL, 15.1 mmol) were refluxed in MeCN for 20 h according to the general procedure. The formed precipitate was collected on a sintered funnel and washed twice with Et_2O (3×40 mL). After solvent evaporation, the product was obtained as a white solid (0.663 g, 71%). A microanalytically pure sample was obtained by slow diffusion of Et_2O into a MeCN solution containing the ditriazolium salt. ^1H NMR ($(\text{CD}_3)_2\text{SO}$, 400 MHz): δ 9.56 (s, 2H, H_{trz}), 8.05–8.02 (m, 4H, H_{ortho}), 7.80–7.73 (m, 6H, H_{Ph}), 4.39 (s, 6H, NCH_3), 3.15 (t, 4H, $^3J_{\text{HH}} = 7.5$ Hz, $\text{C}_{\text{trz}}\text{CH}_2$), 2.32 (quintet, 2H, $^3J_{\text{HH}} = 7.5$ Hz, CCH_2CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR ($(\text{CD}_3)_2\text{SO}$, 100 MHz): δ 144.1 (C_{trz}), 134.8 (C_{ipso}), 131.7 (C_{para}), 130.5 (C_{meta}), 127.0 ($\text{C}_{\text{trz-H}}$), 121.3 (C_{ortho}), 38.2 (NCH_3), 23.1 (CCH_2CH_2), 21.8 ($\text{C}_{\text{trz}}\text{CH}_2$). ESI-MS (m/z): 180.0987, calcd for $[\text{C}_{21}\text{H}_{24}\text{N}_6]^{2+}$ 180.1031. Anal calcd for $\text{C}_{21}\text{H}_{24}\text{N}_6\text{I}_2$ (614.26): C, 41.06; H, 3.94; N, 13.68%. Found: C, 41.05; H, 3.88; N, 13.64%.

Synthesis of 5c(I). Compound 3c (0.34 g, 0.82 mmol) and MeI (0.51 mL, 8.13 mmol) were refluxed in MeCN for 48 h and purified according to the general procedure, yielding 5c(I) as a yellow solid (0.45 g, 79%). The product was recrystallized by slow diffusion of Et_2O into an MeCN solution of the compound. ^1H NMR (CD_3CN , 400 MHz): δ 9.04 (s, 2H, H_{trz}), 7.15 (s, 4H, H_{Mes}), 4.32 (s, 6H, NCH_3), 3.17 (t, 4H, $^3J_{\text{HH}} = 7.8$ Hz, $\text{C}_{\text{trz}}\text{CH}_2$), 2.48 (quintet, 2H, $^3J_{\text{HH}} = 7.8$ Hz, CCH_2CH_2), 2.37 (s, 6H, $\text{CH}_3\text{-para}$), 2.10 (s, 12H, $\text{CH}_3\text{-ortho}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 100 MHz): δ 145.4 (C_{trz}), 143.5 (C_{para}), 135.7 (C_{ortho}), 132.4 (C_{ipso}), 132.1 ($\text{C}_{\text{trz-H}}$), 130.6 (C_{meta}), 39.7 (NCH_3), 24.6 (CCH_2CH_2), 23.9 ($\text{C}_{\text{trz}}\text{CH}_2$), 21.2 ($\text{CH}_3\text{-para}$), 17.8 ($\text{CH}_3\text{-ortho}$). ESI-MS (m/z): 222.1477, calcd for $[\text{C}_{27}\text{H}_{36}\text{N}_6]^{2+}$ 222.1500. Anal calcd for $\text{C}_{27}\text{H}_{36}\text{I}_2\text{N}_6$ (698.42): C, 46.43; H, 5.20; N, 12.03%. Found: C, 46.11; H, 5.06; N, 11.94%.

Synthesis of 6a(I). Compound 4a (0.85 g, 3.6 mmol) and MeI (0.9 mL, 14.4 mmol) were refluxed for 3 days in MeCN. After purification as described in the general procedure, the product was obtained as an off-white solid (1.44 g, 77%), and further purified by recrystallization from MeCN/ Et_2O . ^1H NMR (CD_3CN , 400 MHz): δ 8.92 (s, 2H, H_{trz}), 5.05 (s, 4H, OCH_2), 4.64 (q, 4H, $J_{\text{HH}} = 7.3$ Hz, NCH_2), 4.26 (s, 6H, NCH_3), 1.60 (t, 6H, $J_{\text{HH}} = 7.3$ Hz, NCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 100 MHz): δ 140.3 (C_{trz}), 130.9 ($\text{C}_{\text{trz-H}}$), 61.4 (OCH_2), 50.5 (NCH_2), 39.8 (NCH_3), 14.7 (NCH_2CH_3). ESI-MS (m/z): 133.0876, calcd for $[\text{C}_{12}\text{H}_{22}\text{N}_6\text{O}]^{2+}$ 133.0928. Anal calcd for $\text{C}_{12}\text{H}_{22}\text{N}_6\text{I}_2\text{O}$ (520.15): C, 27.71; H, 4.26; N, 16.16%. Found: C, 27.74; H, 4.06; N, 15.93%.

Synthesis of 6b(I). Compound 4b (0.59 g, 1.78 mmol) and MeI (0.44 mL, 7.10 mmol) were refluxed in MeCN for 20 h. After purification according to the general procedure, the



product was obtained as a white solid (0.84 g, 77%), which was recrystallized by slow diffusion of Et₂O into an MeCN solution of the ditriazolium salt. ¹H NMR ((CD₃)₂SO, 400 MHz): δ 9.62 (s, 2H, H_{trz}), 8.04–8.00 (m, 4H, H_{ortho}), 7.78–7.74 (m, 6H, H_{Ph}), 5.12 (s, 4H, OCH₂), 4.43 (s, 6H, NCH₃). ¹³C{¹H} NMR ((CD₃)₂SO, 100 MHz): δ 140.3 (C_{trz}), 134.8 (C_{ipso}), 132.0 (C_{para}), 130.6 (C_{meta}), 128.6 (C_{trz}-H), 121.7 (C_{ortho}), 60.1 (OCH₂), 38.9 (NCH₃). ESI-MS (*m/z*): 180.0915, calcd for [C₂₀H₂₂N₆O]²⁺ 180.0928. Anal calcd for C₂₀H₂₂N₆I₂O (615.99): C, 38.98; H, 3.60; N, 13.64%. Found: C, 38.88; H, 3.37; N, 13.52%.

Synthesis of 6c(I). Compound **4c** (0.38 g, 0.91 mmol) and MeI (0.12 mL, 2.00 mmol) were refluxed for 2 days. After purification (see general procedure), the product was obtained as an off-white solid (0.44 g, 69%). Subsequent recrystallization from MeCN/Et₂O yielded pure compound **6c(I)**. ¹H NMR (CD₃CN, 400 MHz): δ 8.89 (s, 2H, H_{trz}), 7.17 (s, 4H, H_{Mes}), 5.14 (s, 4H, OCH₂), 4.39 (s, 6H, NCH₃), 2.38 (s, CH_{3-para}), 2.09 (CH_{3-ortho}). ¹³C{¹H} NMR (CD₃CN, 100 MHz): δ 143.8 (C_{para}), 141.5 (C_{trz}), 135.6 (C_{ortho}), 133.0 (C_{trz}-H), 131 (broad, C_{ipso}), 130.7 (C_{meta}), 62.1 (OCH₂), 40.5 (NCH₃), 21.2 (CH_{3-para}), 17.6 (CH_{3-ortho}). ESI-MS (*m/z*): 222.1308, calcd for [C₂₆H₃₄N₆O]²⁺ 223.1397. Anal calcd for C₂₆H₃₄N₆I₂O (700.40) × 0.5 Et₂O: C, 45.60; H, 5.33; N, 11.40%. Found: C, 45.94; H, 4.93; N, 11.66%.

General procedure for halide exchange and formation of ditriazolium salts 5(BF₄) and 6(BF₄)

The ditriazolium iodide was suspended in MeCN (10 mL) and AgBF₄ (2 mol equiv.) was added. The reaction mixture was stirred at room temperature for a set time. The crude reaction mixture was filtered through a short pad of Celite and evaporated to dryness.

Synthesis of 5a(BF₄). According to the general procedure from **5a(I)** (0.22 g, 0.42 mmol) and AgBF₄ (0.18 g, 0.93 mmol) for 16 h, the product was obtained as a waxy yellow solid (0.182 g, quantitative). ¹H NMR (CD₃CN, 400 MHz): δ 8.28 (s, 2H, H_{trz}), 4.54 (q, 4H, ³J_{HH} = 7.3 Hz, NCH₂), 4.13 (s, 6H, NCH₃), 2.93 (t, 4H, ³J_{HH} = 7.8 Hz, C_{trz}CH₂CH₂), 2.11 (quintet, 2H, ³J_{HH} = 7.8 Hz, C_{trz}CH₂CH₂), 1.56 (t, 6H, ³J_{HH} = 7.3 Hz, NCH₂CH₃). ¹³C{¹H} NMR (CD₃CN, 100 MHz): δ 144.2 (C_{trz}), 128.5 (C_{trz}-H), 50.0 (NCH₂), 38.1 (NCH₃), 24.7 (C_{trz}CH₂CH₂), 22.7 (C_{trz}CH₂CH₂), 14.4 (NCH₂CH₃). ESI-MS (*m/z*): 132.0949, calcd for [C₁₃H₂₄N₆] 132.1031. The high viscosity of the product precluded removing of all solvent for satisfactory microanalysis even after repeated precipitations, irrespective of the solvent combinations used (see also ESI†).

Synthesis of 5b(BF₄). According to the general procedure from **5b(I)** (110 mg, 0.179 mmol) and AgBF₄ (70 mg, 0.358 mmol) for 1 h, the product was obtained as an off-white solid (96 mg, quantitative). Recrystallization from MeCN/Et₂O gave microanalytically pure material by slow diffusion of solution of the compound. ¹H NMR (CD₃CN, 400 MHz): δ 8.77 (s, 2H, H_{trz}), 7.90–7.87 (m, 4H, H_{ortho}), 7.74–7.71 (m, 6H, H_{Ph}), 4.28 (s, 6H, NCH₃), 3.08 (t, 4H, ³J_{HH} = 7.7 Hz, C_{trz}CH₂), 2.30 (quintet, 2H, ³J_{HH} = 7.7 Hz, CCH₂CH₂). ¹³C{¹H} NMR (CD₃CN, 100 MHz): δ 145.2 (C_{trz}), 136.0 (C_{ipso}), 132.9 (C_{para}), 131.5 (C_{meta}), 127.5 (C_{trz}-H), 122.5 (C_{ortho}), 38.8 (NCH₃), 24.6

(C_{trz}CH₂CH₂), 22.9 (C_{trz}CH₂). ESI-MS (*m/z*): 180.1006, calcd for [C₂₁H₂₄N₆]²⁺ 180.1031. Anal calcd for C₂₁H₂₄B₂F₈N₆ (534.06): C, 47.23; H, 4.53; N, 15.74%. Found: C, 47.12; H, 4.27; N, 15.67%.

Synthesis of 5c(BF₄). According to the general procedure from **5c(I)** (0.28 g, 0.4 mmol) and AgBF₄ (0.17 g, 0.88 mmol) for 16 h, the product was obtained as an off-white solid (0.25 g, quantitative). A microanalytically pure sample was obtained by slow diffusion of Et₂O into an MeCN solution of the compound. ¹H NMR (CD₃CN, 400 MHz): δ 8.42 (s, 2H, H_{trz}), 7.17 (s, 4H, H_{Mes}), 4.28 (s, 6H, NCH₃), 3.09 (t, 4H, ³J_{HH} = 7.9 Hz, C_{trz}CH₂), 2.39 (s, 6H, CH_{3-para}), 2.31 (quintet, 2H, ³J_{HH} = 7.9 Hz, CCH₂CH₂), 2.06 (s, 12H, CH_{3-ortho}). ¹³C{¹H} NMR (CD₃CN, 100 MHz): δ 145.3 (C_{trz}), 143.5 (C_{para}), 135.6 (C_{ortho}), 132.3 (C_{ipso}), 131.1 (C_{trz}-H), 130.5 (C_{meta}), 38.9 (NCH₃), 24.2 (C_{trz}CH₂CH₂), 23.2 (C_{trz}CH₂), 21.1 (CH_{3-para}), 17.1 (CH_{3-ortho}). ESI-MS (*m/z*): 222.1485, calcd for [C₂₇H₃₆N₆]⁺ 222.1500. Anal calcd for C₂₇H₃₆B₂F₈N₆ (618.22): C, 52.45; H, 5.87; N, 13.59%. Found: C, 52.38; H, 5.81; N, 13.56%.

Synthesis of 6a(BF₄). According to the general procedure from the triazolium iodide **6a(I)** (0.50 g, 0.96 mmol) and AgBF₄ (0.41 g, 2.11 mmol) for 2 h, the product was obtained as an off-white solid (0.42 g, quantitative). Microanalytically pure material was obtained by slow diffusion of Et₂O into an MeCN solution of the ditriazolium salt. ¹H NMR (CD₃CN, 400 MHz): δ 8.44 (s, 2H, H_{trz}), 4.86 (s, 4H, OCH₂), 4.58 (q, 4H, ³J_{HH} = 7.3 Hz, NCH₂), 4.19 (s, 6H, NCH₃), 1.57 (t, 6H, ³J_{HH} = 7.3 Hz, NCH₂CH₃). ¹³C{¹H} NMR (CD₃CN, 100 MHz): δ 140.2 (C_{trz}), 130.1 (C_{trz}-H), 60.8 (OCH₂), 50.3 (NCH₂), 39.0 (NCH₃), 14.4 (NCH₂CH₃). ESI-MS (*m/z*): 133.0871, calcd for [C₁₂H₂₂N₆O]²⁺ 133.0928. Anal calcd for C₁₂H₂₂N₆B₂F₈O (439.95) × 0.2 H₂O: C, 32.49; H, 5.09; N, 18.95%. Found: C, 32.49; H, 4.75; N, 18.59%.

Synthesis of 6b(BF₄). According to the general procedure from the triazolium iodide **6b(I)** (0.43 g, 0.70 mmol) and AgBF₄ (0.41 g, 2.11 mmol) for 1 h, the product was obtained as an off-white solid (0.38 g, quantitative). Microanalytically pure material was obtained by slow diffusion of Et₂O into an MeCN solution of the compound. ¹H NMR (CD₃CN, 400 MHz): δ 8.92 (s, 2H, H_{trz}), 7.91–7.87 (m, 4H, H_{ortho}), 7.74–7.70 (m, 6H, H_{Ph}), 5.02 (s, 4H, OCH₂), 4.36 (s, 6H, NCH₃). ¹³C{¹H} NMR (CD₃CN, 100 MHz): δ 141.2 (C_{trz}), 135.9 (C_{ipso}), 133.0 (C_{para}), 131.4 (C_{meta}), 129.1 (C_{trz}-H), 122.7 (C_{ortho}), 61.0 (OCH₂), 39.6 (NCH₃). ESI-MS (*m/z*): 180.0900, calcd for [C₂₀H₂₂N₆O]²⁺ 180.0928. Anal calcd for C₂₀H₂₂N₆B₂F₄O (536.04): C, 44.81; H, 4.14; N, 15.68%. Found: C, 44.50; H, 3.93; N, 15.48%.

Synthesis of 6c(BF₄). According to the general procedure from the triazolium iodide **6c(I)** (0.40 g, 0.57 mmol) and AgBF₄ (0.22 g, 1.14 mmol) for 16 h, the product was obtained as an off-white solid (0.35 g, quantitative). Microanalytically pure material was obtained by slow diffusion of Et₂O into an MeCN solution of the compound. ¹H NMR (CD₃CN, 400 MHz): δ 8.62 (s, 2H, H_{trz}), 7.16 (s, 4H, H_{Mes}), 5.06 (s, 4H, OCH₂), 4.36 (s, 6H, NCH₃), 2.37 (CH_{3-para}), 2.05 (CH_{3-ortho}). ¹³C{¹H} NMR (CD₃CN, 100 MHz): δ 143.6 (C_{para}), 141.4 (C_{trz}), 135.6 (C_{ortho}), 132.6 (C_{trz}-H), 132.1 (C_{ipso}), 130.5 (C_{meta}), 61.6 (OCH₂), 39.8 (NCH₃), 21.1 (CH_{3-para}), 17.1 (CH_{3-ortho}). ESI-MS (*m/z*): 223.1395, calcd for



$[\text{C}_{26}\text{H}_{34}\text{N}_6\text{O}]^{2+}$ 223.1397. Anal. calcd for $\text{C}_{26}\text{H}_{34}\text{N}_6\text{B}_2\text{F}_8\text{O}$ (620.21) \times 0.5 CH_2Cl_2 : C, 47.87; H, 5.14; N, 12.61%. Found: C, 48.03; H, 5.32; N, 12.68%.

Synthesis of 7. Triazolium salt **5a**(BF_4) (68 mg, 0.16 mmol), Me_4NCl (296 mg, 1.55 mmol) and Ag_2O (72 mg, 0.31 mmol) were refluxed in MeCN (10 mL) for 1 h. After cooling to room temperature the suspension was filtered through Celite and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 mL) and filtered through cotton to remove Me_4NCl by washing with CH_2Cl_2 (2×10 mL). Then $[\text{Cp}^*\text{RhCl}_2]_2$ (47 mg, 0.076 mmol) was dissolved in CH_2Cl_2 (10 mL) and the solution was frozen. The silver triazolyldiene solution (10 mL) was added dropwise to the frozen rhodium solution and the solution was allowed to warm to room temperature. The mixture was stirred at room temperature for 1 h. After filtration through Celite and removal of the solvent under reduced pressure the residue was purified by column chromatography (SiO_2 ; CH_2Cl_2 then $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$, 9 : 1) yielding the title complex as an orange solid (75 mg, 85%). Crystals of **7** suitable for X-ray diffraction studies were obtained by diffusion of pentane into a $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (20 : 1) solution of the complex.

^1H NMR (CD_3CN , 400 MHz): δ 4.81, 4.42 ($2 \times \text{dq}$, 2H, $^2J_{\text{HH}} = 12.9$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, NCH_2), 4.06 (s, 6H, NCH_3), 2.70, 2.40 ($2 \times \text{ddd}$, 2H, $^2J_{\text{HH}} = 14.9$ Hz, $^3J_{\text{HH}} = 8.6$ Hz, $^3J_{\text{HH}} = 4.6$ Hz, $\text{C}_{\text{trz}}\text{CH}_2$), 1.88–1.69 (m, 2H, CCH_2CH_2) 1.45 (t, 6H, $^3J_{\text{HH}} = 7.1$ Hz, NCH_2CH_3), 1.43 (s, 15H, Cp-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 100 MHz): δ 154.4 (d, $^1J_{\text{CRh}} = 50.3$ Hz, $\text{C}_{\text{trz-Rh}}$), 145.5 (d, $^2J_{\text{CRh}} = 3.3$ Hz, C_{trz}), 100.2 (d, $^1J_{\text{CRh}} = 5.2$ Hz, C_{CP}), 50.2 (NCH_2), 37.5 (NCH_3), 24.4 (CCH_2CH_2), 22.5 ($\text{C}_{\text{trz}}\text{CH}_2$), 17.0 (NCH_2CH_3), 9.5 (Cp-CH_3). ESI-MS (m/z): 535.1844, calcd for $[\text{C}_{23}\text{H}_{37}\text{N}_6\text{RhCl}]^+$ 535.1823. Anal. calcd for $\text{C}_{23}\text{H}_{37}\text{B}_{0.21}\text{F}_{0.84}\text{Cl}_{1.79}\text{N}_6\text{Rh}$ (582.17) \times 0.3 CH_2Cl_2 : C, 46.05; H, 6.24; N, 13.83%. Found: C, 46.44; H, 5.85; N, 13.44%.

Synthesis of 8. The triazolium salt **5b**(BF_4) (177 mg, 0.33 mmol) and Ag_2O (298 mg, 1.29 mmol) were stirred at room temperature in MeCN (100 mL) for 2 days under exclusion of light. The mixture was filtered through Celite and all volatiles were removed under reduced pressure. The residual crystalline white solid was suspended in CH_2Cl_2 (200 mL) and $[\text{Cp}^*\text{RhCl}_2]_2$ (50 mg, 0.08 mmol) was added. The mixture was stirred for 10 minutes and filtered through Celite. After solvent evaporation, the residue was purified by column chromatography (SiO_2 ; CH_2Cl_2 then $\text{CH}_2\text{Cl}_2/\text{acetone}$, 1 : 1) yielding the title complex as a yellow solid (38 mg, 35%). Crystals of **8** suitable for X-ray diffraction studies were obtained by diffusion of Et_2O into a CH_2Cl_2 solution of the complex.

^1H NMR (CD_3CN , 400 MHz): δ 7.47 (tt, 1H, $^3J_{\text{HH}} = 7.5$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, H_{Ph}), 7.37 (dd, 1H, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, $\text{H}_{\text{Ph-Rh}}$), 7.28 (t, $^3J_{\text{HH}} = 7.9$ Hz, 2H, H_{Ph}), 6.82 (ddd, 1H, $^3J_{\text{HH}} = 7.8$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, $\text{H}_{\text{Ph-Rh}}$), 6.64 (d, 2H, $^3J_{\text{HH}} = 7.3$ Hz, H_{Ph}), 6.59 (d, 1H, $^3J_{\text{HH}} = 7.7$ Hz, $\text{H}_{\text{Ph-Rh}}$), 6.46 (dt, 1H, $^3J_{\text{HH}} = 7.5$ Hz, $^4J_{\text{HH}} = 1.4$ Hz, $\text{H}_{\text{Ph-Rh}}$), 4.01, 3.86 ($2 \times \text{s}$, 3H, NCH_3), 3.32–3.11 (m, 4H, $\text{C}_{\text{trz}}\text{CH}_2$), 2.38–2.29 (m, 1H, $\text{C}_{\text{trz}}\text{CH}_2\text{CH}_2$), 1.76 (s, 15H, Cp-CH_3), 1.68–1.56 (m, 1H, $\text{C}_{\text{trz}}\text{CH}_2\text{CH}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 100 MHz): δ 164.2 (d,

$^1J_{\text{CRh}} = 47.0$ Hz, $\text{C}_{\text{trz-Rh}}$), 159.5 (d, $^1J_{\text{CRh}} = 36.2$ Hz, $\text{C}_{\text{Ph-Rh}}$), 158.2 (d, $^1J_{\text{CRh}} = 50.3$ Hz, $\text{C}_{\text{trz-Rh}}$), 149.6 (d, $^2J_{\text{CRh}} = 1.4$ Hz, C_{trz}), 146.2 (d, $^2J_{\text{CRh}} = 3.7$ Hz, C_{trz}), 144.0 ($\text{C}_{\text{Ph-Rh}}$), 141.3 (C_{Ph}), 139.6 ($\text{C}_{\text{Ph-Rh}}$), 130.4 (C_{Ph}), 129.9 (C_{Ph}), 127.9 (d, $^3J_{\text{CRh}} = 1.7$ Hz, $\text{C}_{\text{Ph-Rh}}$), 126.5 (C_{Ph}), 122.5 ($\text{C}_{\text{Ph-Rh}}$), 113.4 (d, $^3J_{\text{CRh}} = 1.2$ Hz, $\text{C}_{\text{Ph-Rh}}$), 99.2 (d, $J = 4.1$ Hz, C_{CP}), 37.1, 37.0 ($2 \times \text{NCH}_3$), 26.4 ($\text{C}_{\text{trz}}\text{CH}_2\text{CH}_2$), 26.0, 25.7 ($2 \times \text{C}_{\text{trz}}\text{CH}_2$), 10.7 (Cp-CH_3). ESI-MS (m/z): 595.2040, calcd for $[\text{C}_{31}\text{H}_{36}\text{N}_6\text{Rh}]^+$ 595.2056. Anal. calcd for $\text{C}_{31}\text{H}_{36}\text{BF}_4\text{N}_6\text{Rh}$ (595.56) \times 0.2 CH_2Cl_2 : C, 53.58; H, 5.25; N, 12.02%. Found: C, 53.69; H, 5.13; N, 11.95%.

Synthesis of 9. The triazolium salt **6b**(BF_4) (0.20 g, 0.37 mmol), Ag_2O (0.35 g, 1.49 mmol), and KCl (0.28 g, 3.73 mmol) were stirred at room temperature in MeCN (80 mL) for 2 days under exclusion of light. The mixture was filtered through Celite and all volatiles were removed under reduced pressure. The resulting white solid was suspended in CH_2Cl_2 (200 mL) and cooled to -30°C . Then, $[\text{Cp}^*\text{RhCl}_2]_2$ (0.12 g, 0.19 mmol) in CH_2Cl_2 (5 mL) was added dropwise while stirring. Stirring was continued for 2 h at -30°C and for 16 h at room temperature. After filtration through Celite, the crude product was purified by column chromatography (SiO_2 ; CH_2Cl_2 then $\text{CH}_2\text{Cl}_2/\text{acetone}$, 9 : 1) yielding complex **9** as a pale yellow solid (93 mg, 36%). Crystals suitable for X-ray diffraction studies were obtained by diffusion of Et_2O into a CH_2Cl_2 solution of the complex.

^1H NMR (CD_3CN , 400 MHz): δ 7.50 (tt, 1H, $^3J_{\text{HH}} = 7.5$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, H_{Ph}), 7.37 (dd, 1H, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, H_{Ph}), 7.34–7.29 (t, $^3J_{\text{HH}} = 8.0$ Hz, 2H, H_{Ph}), 6.86 (ddd, 1H, $^3J_{\text{HH}} = 7.9$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, $\text{H}_{\text{Ph-Rh}}$), 6.70 (dd, 2H, $^3J_{\text{HH}} = 8.3$ Hz, $^4J_{\text{HH}} = 1.1$ Hz, H_{Ph}), 6.57 (d, 1H, $^3J_{\text{HH}} = 7.7$ Hz, $\text{H}_{\text{Ph-Rh}}$), 6.50 (dt, 1H, $^3J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{HH}} = 1.4$ Hz, $\text{H}_{\text{Ph-Rh}}$), 5.12 (d, 1H, $^2J_{\text{HH}} = 14.7$ Hz, OCH_2), 5.10, 4.99 ($2 \times \text{d}$, 1H, $^2J_{\text{HH}} = 14.9$ Hz, OCH_2), 4.96 (d, 1H, $^2J_{\text{HH}} = 14.7$ Hz, OCH_2), 4.08, 3.95 ($2 \times \text{s}$, 3H, NCH_3), 1.75 (s, 15H, Cp-CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 100 MHz): δ 167.9 (d, $^1J_{\text{CRh}} = 46.9$ Hz, $\text{C}_{\text{trz-Rh}}$), 160 ($\text{C}_{\text{trz-Rh}}$), 158.7 (d, $^1J_{\text{CRh}} = 46.9$ Hz, $\text{C}_{\text{Ph-Rh}}$), 147.1 (d, $^2J_{\text{CRh}} = 1.3$ Hz, C_{trz}), 144.1 (d, $^2J_{\text{CRh}} = 3.8$ Hz, C_{trz}), 144.0 ($\text{C}_{\text{Ph-Rh}}$), 140.9 (C_{Ph}), 139.5 ($\text{C}_{\text{Ph-Rh}}$), 130.7 (C_{Ph}), 129.4 (C_{Ph}), 128.0 (d, $^3J_{\text{CRh}} = 1.6$ Hz, $\text{C}_{\text{Ph-Rh}}$), 126.6 (C_{Ph}), 122.8 ($\text{C}_{\text{Ph-Rh}}$), 113.6 (d, $^3J_{\text{CRh}} = 1.3$ Hz, $\text{C}_{\text{Ph-Rh}}$), 99.4 (d, $J = 4.0$ Hz, C_{CP}), 65.3, 64.8 ($2 \times \text{OCH}_2$), 37.4, 37.3 ($2 \times \text{NCH}_3$), 10.6 (Cp-CH_3). ESI-MS (m/z): 597.1878, calcd for $[\text{C}_{30}\text{H}_{34}\text{N}_6\text{ORh}]^+$ 597.1849. Anal. calcd for $\text{C}_{30}\text{H}_{34}\text{BF}_4\text{N}_6\text{ORh}$ (684.34) \times 0.25 CH_2Cl_2 : C, 51.49; H, 4.93; N, 11.91%. Found: C, 51.53; H, 4.88; N, 11.84%.

Synthesis of 10. According to the procedure described for the synthesis of **9**, complex **10** was obtained from **6b**(BF_4) (0.20 g, 0.37 mmol), Ag_2O (0.35 g, 1.49 mmol) and KCl (0.28 g, 3.73 mmol) and $[\text{Cp}^*\text{IrCl}_2]_2$ (0.14 g, 0.18 mmol). Purification by column chromatography (SiO_2 ; CH_2Cl_2 then $\text{CH}_2\text{Cl}_2/\text{acetone}$, 2 : 1) yielded complex **10** as a pale yellow solid (113 mg, 39%).

^1H NMR (CD_3CN , 400 MHz): δ 7.50 (tt, 1H, $^3J_{\text{HH}} = 7.5$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, H_{Ph}), 7.37 (dd, 1H, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, $\text{H}_{\text{Ph-Ir}}$), 7.33–7.28 (m, 2H, H_{Ph}), 6.85–6.80 (m, 1H, $\text{H}_{\text{Ph-Ir}}$), 6.70–6.67 (m, 2H, H_{Ph}), 6.51 (dd, 1H, $^3J_{\text{HH}} = 7.7$ Hz, $^4J_{\text{HH}} = 1.1$ Hz, $\text{H}_{\text{Ph-Ir}}$), 6.46–6.41 (m, 1H, $\text{H}_{\text{Ph-Ir}}$), 5.12 (d, 1H, $^2J_{\text{HH}} = 14.7$



Hz, OCH₂), 5.11, 4.90 (2 × d, 1H, ²J_{HH} = 14.9 Hz, OCH₂), 4.82 (d, 1H, ²J_{HH} = 14.7 Hz, OCH₂), 4.09, 3.95 (2 × s, 3H, NCH₃), 1.81 (s, 15H, Cp-CH₃). ¹³C{¹H} NMR (CD₃CN, 100 MHz): δ 149.0 (C_{trz}), 148.8 (C_{trz}-Ir), 143.9 (C_{Ph}-Ir), 143.1 (C_{trz}), 141 (C_{trz}-Ir), 140.7 (C_{Ph}), 139.5, 138.6 (2 × C_{Ph}-Ir), 130.7 (C_{Ph}), 129.9 (C_{Ph}), 128.4 (C_{Ph}-Ir), 126.7 (C_{Ph}), 121.9, 113.5 (2 × C_{Ph}-Ir), 93.9 (C_{Cp}), 65.2, 64.3 (2 × OCH₂), 37.5, 37.3 (2 × NCH₃), 10.3 (Cp-CH₃). ESI-MS (*m/z*): 687.2411, calcd for [C₃₀H₃₄N₆OIr]⁺ 687.2424. Anal calcd for C₃₀H₃₄BF₄N₆OIr (773.65): C, 46.57; H, 4.43; N, 10.86%. Found: C, 46.15; H, 4.31; N, 10.60%.

Synthesis of 13. Triazolium iodide **5b(I)** (180 mg, 0.293 mmol) and KO^tBu (55 mg, 0.49 mmol) were suspended in dry, degassed MeCN (5 mL). The mixture was stirred at room temperature for 10 minutes. To the pink suspension, RhCl₃·3H₂O (26 mg, 0.098 mmol) was added and the mixture was heated to reflux for 16 h. After cooling to room temperature, the mixture was filtered in air through Celite, and all volatiles were evaporated. The residue was purified by column chromatography (SiO₂; CH₂Cl₂ then NaI, CH₂Cl₂/acetone, 1 : 1), which afforded complex **13** as a pale yellow solid (52 mg, 56%). Crystals suitable for X-ray diffraction studies were obtained by layering a CH₂Cl₂/MeCN (2 : 1) solution with Et₂O.

¹H NMR (CD₃CN, 400 MHz): δ 7.23 (t, 2H, ³J_{HH} = 7.5 Hz, H_{Ph}), 6.92 (t, 4H, ³J_{HH} = 7.5 Hz, H_{Ph}), 6.75 (d, 2H, ³J_{HH} = 7.6 Hz, H_{Ph}-Rh), 6.57, 6.45 (2 × t, 2H, ³J_{HH} = 7.6 Hz, H_{Ph}-Rh), 6.25 (br, 4H, H_{Ph}), 6.08 (d, 2H, ³J_{HH} = 7.6 Hz, H_{Ph}-Rh), 4.15, 4.03 (2 × s, 6H, H_H), 3.06–2.97, 2.94–2.87, 2.61–2.54, 2.48–2.38 (4 × m, 2H, C_{trz}-CH₂), 2.12–2.04 (m, 4H, C_{trz}-CH₂-CH₂). ¹³C{¹H} NMR (CD₃CN, 100 MHz): δ 176.2 (¹J_{CRh} = 34.3 Hz, C_{trz}-Rh), 171.3 (¹J_{CRh} = 30.2 Hz, C_{trz}-Rh), 164.9 (¹J_{CRh} = 25.7 Hz, C_{Ph}-Rh), 146.7 (C_{Ph}-Rh), 145.5 (C_{trz}), 143.9 (C_{trz}), 139.9 (C_{Ph}), 137.1 (C_{Ph}-Rh), 129.2 (C_{Ph}), 128.8 (C_{Ph}), 126.7 (C_{Ph}-Rh), 126.2 (C_{Ph}), 121.3, 115.0 (2 × C_{Ph}-Rh), 36.8, 36.5 (2 × NCH₃), 26.2 (CCH₂CH₂), 22.6, 21.3 (2 × C_{trz}-CH₂). ESI-MS (*m/z*): 817.2750, calcd for [C₄₂H₄₂N₁₂Rh]⁺ 817.2710. Anal calcd for C₄₂H₄₂IN₁₂Rh (944.67) × 0.75 CH₂Cl₂: C, 50.92; H, 4.35; N, 16.67%. Found: C, 50.95; H, 4.28; N, 16.37%.

Synthesis of 14. Following the same procedure as for the synthesis of **13**, the triazolium salt **5b(I)** (125 mg, 0.203 mmol) and KO^tBu (38 mg, 0.339 mmol) and IrCl₃·3H₂O (24 mg, 0.068 mmol) yielded crude complex **14**, which was purified by column chromatography (SiO₂; CH₂Cl₂ then CH₂Cl₂/acetone, 1 : 1) to give the title complex as a pale yellow solid (12 mg, 17%). Complex **14** decomposes upon extended time in solution. Because of this behaviour and due to the low yield and quantity, we did not succeed in purifying the compound to analytical purity (see also ESI[†]).

¹H NMR (CD₃CN, 400 MHz): δ 7.22 (tt, 2H, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 1.1 Hz, H_{Ph}), 6.90 (br, 4H, H_{Ph}), 6.72 (dd, 2H, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.1 Hz, H_{Ph}-Ir), 6.55 (m, 2H, H_{Ph}-Ir), 6.42 (td, 2H, ³J_{HH} = 7.3 Hz, ⁴J_{HH} = 1.3 Hz, H_{Ph}-Ir), 6.25 (br, 4H, H_{Ph}), 6.07 (dd, 2H, ³J_{HH} = 7.3 Hz, ⁴J_{HH} = 1.1 Hz, H_{Ph}-Ir), 4.15, 4.03 (2 × s, 6H, NCH₃), 3.05–2.87 (m, 4H, C_{trz}-CH₂), 2.67–2.60, 2.46–2.36 (2 × m, 2H, C_{trz}-CH₂), 2.11–2.01 (m, 4H, CCH₂CH₂). ¹³C{¹H} NMR (CD₃CN, 100 MHz): δ 158.9 (C_{trz}-Ir), 152.4 (C_{trz}-Ir), 147.9 (C_{Ph}-Ir), 146.9 (C_{trz}), 146.7 (C_{Ph}-Ir), 143.3 (C_{trz}), 139.9 (C_{Ph}),

136.6 (C_{Ph}-Ir), 129.1 (C_{Ph}), 128.6 (C_{Ph}), 127.3, 120.7, 115.1 (3 × C_{Ph}-Ir), 36.9, 36.5 (2 × NCH₃), 25.8 (CCH₂CH₂), 22.8, 21.1 (2 × C_{trz}-CH₂), one C_{Ph} not resolved. ESI-MS (*m/z*): 907.3322, calcd for [C₄₂H₄₂N₁₂Ir]⁺ 907.3285.

Crystal structure determinations

Crystal data for **7–9**, and **13** were collected using a Rigaku (former Agilent Technologies) Oxford Diffraction SuperNova A diffractometer fitted with an Atlas detector and using monochromated Mo-K_α radiation (0.71073 Å) (**7–9**) or Cu-K_α (1.54184 Å) (**13**). A complete dataset was collected, assuming that the Friedel pairs are not equivalent. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares fitting on *F*² for all data using SHELXL-97.³³ Hydrogen atoms were added at calculated positions and refined by using a riding model. Anisotropic thermal displacement parameters were used for all non-disordered nonhydrogen atoms. The solvent in **13** could not be modelled in terms of atomic sites. The SQUEEZE option as incorporated in PLATON³⁴ was used to compensate for the spread electron density. The B–F bonds of the tetrafluoroborate anion in **7** were restrained to be equal using SADI. Further crystallographic details are compiled in Tables S1–S3.[†] Crystallographic data (excluding structure factors) for all three complexes have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1477830 (**7**), 1477829 (**8**), 1477828 (**9**) and 1477827 (**13**).

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References

- (a) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122; (b) A. J. Arduengo and G. Bertrand, *Chem. Rev.*, 2009, **109**, 3209; (c) D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39.
- (a) A. Kascatan-Nebioglu, M. J. Panzner, C. A. Tessier, C. L. Cannon and W. J. Youngs, *Coord. Chem. Rev.*, 2007, **251**, 884; (b) M.-L. Teyssot, A.-S. Jarrousse, M. Manin, A. Chevy, S. Roche, F. Norre, C. Beaudoin, L. Morel, D. Boyer, R. Mahiou and A. Gautier, *Dalton Trans.*, 2009, 6894; (c) L. Mercs and M. Albrecht, *Chem. Soc. Rev.*, 2010, **39**, 1903; (d) R. Visbal and M. C. Gimeno, *Chem. Soc. Rev.*, 2014, **43**, 3551.
- (a) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; (b) N-Heterocyclic Carbenes in Transition Metal Catalysis, in *Topics in Organometallic Chemistry*, ed. F. Glorius, Springer, Berlin, 2007; (c) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612; (d) M. Poyatos, J. A. Mata and E. Peris, *Chem. Rev.*, 2009, **109**, 3677;



- (e) C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247; (f) R. H. Crabtree, *Coord. Chem. Rev.*, 2007, **251**, 595; (g) *N-Heterocyclic Carbenes: from Laboratory Curiosities to Efficient Synthetic Tools*, ed. S. Díez-González, RSC Publishing, Cambridge, 2011; (h) *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*, ed. C. S. J. Cazin, Springer, Berlin, 2011.
- 4 (a) M. C. Perry and K. Burgess, *Tetrahedron: Asymmetry*, 2003, **14**, 951; (b) J. J. Van Veldhuizen, J. E. Campbell, R. E. Giudici and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2005, **127**, 6877; (c) E. P. Kündig, T. M. Seidel, Y. X. Jia and G. Bernardinelli, *Angew. Chem., Int. Ed.*, 2007, **46**, 8484.
- 5 J. Vignolle, X. Cattoën and D. Bourissou, *Chem. Rev.*, 2009, **109**, 3333.
- 6 (a) K. Ofele, E. Tosh, C. Taubmann and W. A. Herrmann, *Chem. Rev.*, 2009, **109**, 3408; (b) O. Schuster, L. Yang, H. G. Raubenheimer and M. Albrecht, *Chem. Rev.*, 2009, **109**, 3445; (c) M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 8810.
- 7 See for examples: (a) A. T. Normand and K. J. Cavell, *Eur. J. Inorg. Chem.*, 2008, 2781; (b) E. Peris and R. H. Crabtree, *Coord. Chem. Rev.*, 2004, **248**, 2239; (c) J. F. Lefebvre, M. Lo, D. Leclercq and S. Richeter, *Chem. Commun.*, 2011, **47**, 2976; (d) K. Farrell and M. Albrecht, in *The Privileged Pincer-Metal Platform: Coordination Chemistry & Applications, Topics in Organometallic Chemistry*, ed. G. van Koten and R. A. Gossage, Springer, Berlin, 2016, p. 45.
- 8 (a) P. Mathew, A. Neels and M. Albrecht, *J. Am. Chem. Soc.*, 2008, **130**, 13534; (b) G. Guisado-Barrios, J. Bouffard, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 4759; (c) J. D. Crowley, A. Lee and K. J. Kilpin, *Aust. J. Chem.*, 2011, **64**, 1118; (d) K. F. Donnelly, A. Petronilho and M. Albrecht, *Chem. Commun.*, 2013, **49**, 1145; (e) B. Schulze and U. S. Schubert, *Chem. Soc. Rev.*, 2014, **43**, 2522.
- 9 For selected and recent examples, see: (a) J. Bouffard, B. K. Keitz, R. Tonner, V. Lavallo, G. Guisado-Barrios, G. Frenking, R. H. Grubbs and G. Bertrand, *Organometallics*, 2011, **30**, 2617; (b) B. K. Keitz, J. Bouffard, G. Bertrand and R. H. Grubbs, *J. Am. Chem. Soc.*, 2011, **133**, 8498; (c) E. C. Keske, O. V. Zenkina, R. Wang and C. M. Crudden, *Organometallics*, 2012, **31**, 6215; (d) D. Canseco-Gonzalez, A. Petronilho, H. Müller-Bunz, K. Ohmatsu, T. Ooi and M. Albrecht, *J. Am. Chem. Soc.*, 2013, **135**, 13193; (e) J. R. Wright, P. C. Young, N. T. Lucas, A.-L. Lee and J. D. Crowley, *Organometallics*, 2013, **32**, 7065; (f) I. Corbucci, A. Petronilho, H. Müller-Bunz, L. Rocchigiani, M. Albrecht and A. Macchioni, *ACS Catal.*, 2015, **5**, 2714; (g) R. Heath, H. Müller-Bunz and M. Albrecht, *Chem. Commun.*, 2015, **51**, 8699; (h) S. Hohloch, S. Kaiser, F. L. Duecker, A. Bolje, R. Maity, J. Košmrlj and B. Sarkar, *Dalton Trans.*, 2015, **44**, 686; (i) M. Valencia, H. Müller-Bunz, R. A. Gossage and M. Albrecht, *Chem. Commun.*, 2016, **52**, 3344.
- 10 (a) D. G. Brown, N. Sanguantrakun, B. Schulze, U. S. Schubert and C. P. Berlinguette, *J. Am. Chem. Soc.*, 2012, **134**, 12354; (b) V. Leigh, W. Ghattas, R. Lalrempuia, H. Müller-Bunz, M. T. Pryce and M. Albrecht, *Inorg. Chem.*, 2013, **52**, 5395; (c) D. G. Brown, P. A. Schauer, J. Borau-Garcia, B. R. Fancy and C. P. Berlinguette, *J. Am. Chem. Soc.*, 2013, **135**, 1692.
- 11 (a) According to the IUPAC Golden Book, mesoionic compounds are “Dipolar five- (possibly six-) membered heterocyclic compounds in which both the negative and the positive charge are delocalized, for which a totally covalent structure cannot be written, and which cannot be represented satisfactorily by any one polar structure. The formal positive charge is associated with the ring atoms, and the formal negative charge is associated with ring atoms or an exocyclic nitrogen or chalcogen atom. Mesoionic compounds are a subclass of betains.” IUPAC. Compendium of Chemical Terminology, 2nd ed. (the “Gold Book”) compiled by McNaught AD and Wilkinson A. Blackwell Oxford, UK: Scientific Publications; 1997. See also: (b) S. Araki, Y. Wanibe, F. Uno, A. Morikawa, K. Yamamoto, K. Chiba and Y. Butsugan, *Chem. Ber.*, 1993, **12**, 1149.
- 12 (a) R. H. Crabtree, *Coord. Chem. Rev.*, 2013, **257**, 755; (b) M. Albrecht, *Adv. Organomet. Chem.*, 2014, **62**, 111.
- 13 (a) R. Huisgen, *Angew. Chem., Int. Ed.*, 1963, **2**, 565; (b) H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004; (c) V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596; (d) F. Himo, T. Lovell, R. Hilgraf, V. V. Rostovtsev, L. Noodleman, K. B. Sharpless and V. V. Fokin, *J. Am. Chem. Soc.*, 2005, **127**, 210.
- 14 (a) V. D. Bock, H. Hiemstra and J. H. Van Maarseveen, *Eur. J. Org. Chem.*, 2006, 51; (b) M. Meldal and C. W. Tornøe, *Chem. Rev.*, 2008, **108**, 2952; (c) J. E. Hein and V. V. Fokin, *Chem. Soc. Rev.*, 2010, **39**, 1302.
- 15 E. C. Keske, O. V. Zenkina, R. Wang and C. M. Crudden, *Organometallics*, 2012, **31**, 456.
- 16 (a) B. Schulze, D. Escudero, C. Friebe, R. Siebert, H. Goerls, U. Koehn, E. Altuntas, A. Baumgaertel, M. D. Hager, A. Winter, B. Dietzek, J. Popp, L. Gonzalez and U. S. Schubert, *Chem. – Eur. J.*, 2011, **17**, 5494; (b) S. Sinn, B. Schulze, C. Friebe, D. G. Brown, M. Jäger, E. Altuntaş, J. Kübel, O. Guntner, C. P. Berlinguette, B. Dietzek and U. S. Schubert, *Inorg. Chem.*, 2014, **53**, 2083.
- 17 D. I. Bezuidenhout, G. Kleinhans, G. Guisado-Barrios, D. C. Liles, G. Ung and G. Bertrand, *Chem. Commun.*, 2014, **50**, 2431.
- 18 M. T. Zamora, M. J. Ferguson and M. Cowie, *Organometallics*, 2012, **31**, 5384.
- 19 G. Guisado-Barrios, J. Bouffard, B. Donnadieu and G. Bertrand, *Organometallics*, 2011, **30**, 6017.
- 20 S. Hohloch, L. Suntrup and B. Sarkar, *Organometallics*, 2013, **32**, 7376.
- 21 J. Cai, X. Yang, K. Arumugam, C. W. Bielawski and J. L. Sessler, *Organometallics*, 2011, **30**, 5033.
- 22 A. Petronilho, J. A. Woods, S. Bernhard and M. Albrecht, *Eur. J. Inorg. Chem.*, 2014, 708.



- 23 (a) A. Krüger, L. J. L. Häller, H. Müller-Bunz, O. Serada, A. Neels, S. A. Macgregor and M. Albrecht, *Dalton Trans.*, 2011, **40**, 9911; (b) A. Krüger, A. Neels and M. Albrecht, *Chem. Commun.*, 2010, **46**, 315; (c) J. A. Cabeza, M. Damonte, P. Garcia-Alvarez and E. Perez-Carreno, *Chem. Commun.*, 2013, **49**, 2813.
- 24 (a) K. M. Mullen, J. Mercurio, C. J. Serpell and P. D. Beer, *Angew. Chem., Int. Ed.*, 2009, **48**, 4781; (b) J. Dupont, P. A. Z. Suarez, R. F. De Souza, R. A. Burrow and J.-P. Kintzinger, *Chem. – Eur. J.*, 2000, **6**, 2377.
- 25 (a) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang and I. J. B. Lin, *Chem. Rev.*, 2009, **109**, 3561; (b) J. C. Garrison and W. J. Youngs, *Chem. Rev.*, 2005, **105**, 3978.
- 26 (a) T. Nakamura, T. Terashima, K. Ogata and S.-I. Fukuzawa, *Org. Lett.*, 2011, **13**, 620; (b) S. Hohloch, L. Hettmanczyk and B. Sarkar, *Eur. J. Inorg. Chem.*, 2014, 3164.
- 27 M. Iglesias, D. J. Beetstra, J. C. Knight, L.-L. Ooi, A. Stasch, S. Coles, L. Male, M. B. Hursthouse, K. J. Cavell, A. Dervisi and I. A. Fallis, *Organometallics*, 2008, **27**, 3279.
- 28 (a) H.-L. Su, L. M. Pérez, S.-J. Lee, J. H. Reibenspies, H. S. Bazzi and D. E. Bergbreiter, *Organometallics*, 2012, **31**, 4063–4071; (b) E. Caytan and S. Roland, *Organometallics*, 2014, **33**, 2115–2118.
- 29 For a related system with imidazol-2-ylidene ligands and smaller bite angles, see: J. A. Mata, A. R. Chianese, J. R. Miecznikowski, M. Poyatos, E. Peris, J. W. Faller and R. H. Crabtree, *Organometallics*, 2004, **23**, 1253.
- 30 (a) R. Lalrempuia, N. D. McDaniel, H. Mueller-Bunz, S. Bernhard and M. Albrecht, *Angew. Chem., Int. Ed.*, 2010, **49**, 9765; (b) A. Poulain, D. Canseco-Gonzalez, R. Hynes-Roche, H. Müller-Bunz, O. Schuster, H. Stoeckli-Evans, A. Neels and M. Albrecht, *Organometallics*, 2011, **30**, 1021; (c) R. Saravanakumar, V. Ramkumar and S. Sankararaman, *Organometallics*, 2011, **30**, 1689; (d) L. Bernet, R. Lalrempuia, W. Ghattas, H. Mueller-Bunz, L. Vigara, A. Llobet and M. Albrecht, *Chem. Commun.*, 2011, **47**, 8058; (e) A. Petronilho, M. Rahman, J. A. Woods, H. Al-Sayyed, H. Müller-Bunz, J. M. Don MacElroy, S. Bernhard and M. Albrecht, *Dalton Trans.*, 2012, **41**, 13074; (f) K. F. Donnelly, R. Lalrempuia, H. Müller-Bunz and M. Albrecht, *Organometallics*, 2012, **31**, 8414; (g) K. Ogata, S. Inomata and S. Fukuzawa, *Dalton Trans.*, 2013, **42**, 2362.
- 31 W. A. Herrmann and M. G. Gardiner, *Organometallics*, 1999, **18**, 4082.
- 32 Further attempts to characterize complex **15** included trapping of this species with PPh₃. The appearance of a doublet in the ³¹P NMR spectrum (δ_{P} 15.2, $^1J_{\text{PRh}}$ = 92 Hz) as well as a MS signal at confirmed phosphine coordination to rhodium, however, crystallization efforts to obtain structural information have been unsuccessful.
- 33 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112.
- 34 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

