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

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Metallation of novel ditriazolium salts containing a trimethylene (−CH2CH2CH2−) or dimethylether linker (−CH2OCH2−) was probed with different rhodium(III) and iridium(III) precursors. When using [MCP*Cl2]3, a transmetalation protocol via a triazolylidene silver intermediate was effective, while base-assisted metalation with MCl3 via sequential deprotonation of the triazolium salt with KOTBu and addition of the metal precursor afforded homeoleptic complexes. The N-substituent on the triazole heterocycle directed the metalation process and led to Ctrz,Ctrz,CPh-tridentate chelating ditriazolylidene complexes for N-phenyl substituents. With ethyl substituents, only Ctrz,Ctrz-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 Ctrz,CPh-bidentate chelate en route to the formation of the tridentate ligand system. Accordingly, Cphenyl=H bond activation occurs prior to formation of the second metal–triazolylidene bond. Stability studies with a Ctrz,Ctrz,CPh-tridentate chelating ditriazolylidene iridium complex towards DCI showed deuterium incorporation at both N-phenyl groups and indicate that Cphenyl=H bond activation is reversible while the Ctrz=Ir bond is robust. The flexible linker between the two triazolylidene donor sites provides access to both facial and meridional coordination modes.

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 di-carbenes 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-azole precursor, respectively. For example, C4-linked ditriazolium salts with rigid aryl-bridges have been metalated with rhodium,5 ruthenium,616 nickel,17 and palladium,18 leading to bimetallic systems (Fig. 1, A) or CNC-type pincer complexes (B). Directly linked ditriazolylidene were coordinated to rhodium,19 iridium, and ruthenium (C).20 Similarly, alkyl- or aryl-linkages via N3 have led to bimetalllic complexes of ruthenium11 and iridium15 in which the ligand adopts a bridging rather than chelating binding mode (D, E).

Trimethylene-linked dicarbone ligands similar to those present in complex E, yet comprised of imidazolylidenes rather than triazolylidene heterocycles, induced alkyl C–H
bond activation of the central methylene unit by rhodium or ruthenium, thus forming a tridentate dicarbene species.\textsuperscript{23} The C\textsubscript{alkyl}-H bond activation was significantly faster when the imidazolylidene is bound to rhodium via C\textsubscript{4} as a mesoionic carbene rather than in the normal C\textsubscript{2}-bonding mode.\textsuperscript{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 che-lating ditriazolylidene rhodium(III) and iridium(III) complexes which contain flexible C,\textsubscript{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,\textsubscript{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\textsubscript{trz}CH\textsubscript{2} group and a quintet for the central methylene unit. For example for compound 3\textsubscript{a}, these multiplets appeared at \(\delta\textsubscript{H} 2.67\) and \(1.94\) in the \(^1\text{H}\) NMR spectrum respectively, while the ether linker showed as a singlet, \(e.g.\) at \(\delta\textsubscript{H} 4.71\) for 4\textsubscript{a}. 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 \(^1\text{H}\) NMR signal of the heterocyclic proton shifted downfield by almost 1 ppm. For example the C\textsubscript{trz}-Hi in 5\textsubscript{a}(I) appeared as a singlet at \(\delta\textsubscript{H} 8.87\) compared to \(\delta\textsubscript{H} 7.54\) ppm in the precursor 3\textsubscript{a}. In addition, a new signal emerged in the \(^1\text{H}\) and \(^1\text{C}\) NMR spectrum for the N-bound methyl group (\(\delta\textsubscript{H} 4.20, \delta\textsubscript{C} 38.2\) for 5\textsubscript{a}(I)). Anion substitution with AgBF\textsubscript{4} afforded the corresponding ditriazolium salts 5(BF\textsubscript{4}) and 6(BF\textsubscript{4}). Successful anion exchange was indicated by a diagnostic ~0.5 ppm upfield shift of the C\textsubscript{trz}-H resonance in the \(^1\text{H}\) NMR spectrum, presumably due to less pronounced X⋯H hydrogen bonding.\textsuperscript{24}

Metalation of ditriazolium salts with [MCp*Cl\textsubscript{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(m) and iridium(m) complexes.\textsuperscript{8d,25} Successful

![Scheme 1](image-url)
metatation of the triazolium salts using Ag₂O in the presence of KCl was surmised by the disappearance of the ³H NMR signal of the Cₜrz–H unit, and by the appearance of a mass signal which is in agreement with the [Ag(ditriazolylidene)]⁺ fragment. The ³H NMR spectrum of the triazolylidene silver complexes showed a symmetric linker which suggests a dimeric [Ag₂(ttrz⁻E⁻trz)₂]²⁺ species rather than a chelating [Ag(ttrz⁻E⁻trz)]⁺ monomer, in agreement with results by Crudden and co-workers.¹⁵ The formation of the silver triazolylidene proceeded at elevated temperatures when using the N-ethyl triazolium salts (refluxing MeCN), while N-aryl triazolylidene salts reacted under milder conditions and provided the desired triazolylidene silver intermediate at room temperature. Triazolylidene 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 triazolylidene silver unit is less stabilized compared to chlorides.⁹

Triazolylidene silver complexes were used without further purification for transmetatation with [MCp*Cl₂]₂ (M = Rh, Ir), and afforded the chelating ditriazolylidene 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 CH₂Cl₂ and readily soluble in MeCN.

Chelation in complex 7 was indicated by the presence of symmetry-related triazolylidene units and the pertinent 5:2 integral ratio of the resonances due to the Cp* protons and the N–CH₃ unit. The carbenic ¹³C NMR resonance is deshielded and appears at δ_C 154.4 as a doublet due to characteristic ¹⁰³Rh coupling (J_{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 (J_HH = 12.9 Hz, J_{CH} = 7.2 Hz). Similarly, the triazolylidene bound CH₂ group of the trimethylene linker appeared as two doublets of doublets of doublets (J_HH = 14.9 Hz, J_{CH} = 8.6 Hz, J_{CH} = 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 CH₂ 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 diimidazolylidene 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 triazolylidenes and one chloride ligand site forming the ‘legs’. The carbene bite angle is relatively wide, Cₜrz–Rh–Cₜrz = 91.21(9)°.²⁹ While the triazolylidene units are symmetrical in solution, the Cₜrz–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 triazolylidene 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)° for the heterocycle containing C₁ and 71.1(2)° for the heterocycle containing C₇. In solution, these distinct arrangements average out as indicated by the symmetric NMR pattern observed for this complex.

Scheme 2  Formation of complexes 7–10 by transmetatation via a silver carbene intermediate.
It is worth noting that the analogous rhodium of the ether-linked dmitrazolium salt \( \text{6a} \cdot \text{BF}_4 \) 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 Cphenyl–H bonds in \( \text{5b} \) and \( \text{6b} \) to yield complexes \( \text{8} \)–\( \text{10} \) containing a \( \text{C} \cdot \text{C} \cdot \text{C} \)-tridentate coordinated dmitrazolylidene ligand (Scheme 2). Similar C–H bond activation was observed previously in monodmitrazolylidene complexes containing N-bound phenyl-substituents.\(^{30}\) Apparently the Cphenyl–H bond activation process is preferred over heteroatom coordination and is spontaneous even at \(-30^\circ \text{C}\) 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 \( ^1 \text{H} \) 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 NCH\(_3\) groups. Similarly, the \( \text{OCH}_2 \) groups of the linker of complexes \( \text{9} \) and \( \text{10} \) were inequivalent and appeared as two sets of AB doublets with characteristic \( ^1J_{\text{HH}} \) coupling constants around 15 Hz. Three low-field \( ^{13} \text{C} \) signals were observed in the \( ^{13} \text{C} \{^1 \text{H}\} \) NMR spectrum for all three complexes \( \text{8} \)–\( \text{10} \) and were attributed to the two metal-bound carbene carbons and the phenyl carbon. For example, the rhodium complex \( \text{8} \) showed three doublets at \( \delta_c 164.2 \) \( \text{(Ctrz, } ^1J_{\text{Crh}} = 47.0 \text{ Hz}) \), 159.5 \( \text{(Cphenyl, } ^1J_{\text{Crh}} = 36.2 \text{ Hz}) \) and 158.2 \( \text{(Crh centroid, } ^1J_{\text{Crh}} = 50.3 \text{ Hz}) \). The smaller \( ^1J_{\text{Crh}} \) coupling constant was attributed to the Rh–Cphenyl bond,\(^{30b,}\) and the larger coupling constants to Rh–Ctrz interactions. The larger coupling constant at \( \delta_c 158.2 \) is identical to the coupling observed in complex \( \text{7} \) \( (^1J_{\text{Crh}} = 50.3 \text{ Hz, vide supra}) \), therefore suggesting this resonance to be due to the triazolylidene unit that contains the non-cyclometalated phenyl substituent. Accordingly, the resonance at \( \delta_c 164.2 \) with a slightly smaller coupling constant was tentatively attributed to the carbene 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 \( \text{8} \) and \( \text{9} \) (Fig. 3, Table 1). Both structures are identical within errors and unambiguously reveal a Rh–Cphenyl bond in addition to the dicarbene bonding. All three Rh–C bond lengths are within expectation and in the 2.00–2.06 \( \text{Å} \) range. The average carbene bite angle is 81.5(2)° and thus considerably more acute than in the bidentate carbene complex \( \text{7} \) \( (\text{Ctrz–Rh–Ctrz} = 91.21(9)°) \).

Minor by-products were observed in the crude reaction mixture of the iridium complex \( \text{10} \) by \( ^1 \text{H} \) NMR spectroscopy, which revealed the characteristic pattern of a cyclometalated phenyl group. Separation by column chromatography yielded traces of the bimetallic complex \( \text{11} \) (Fig. 4), in which both N-phenyl groups are ortho-metalated to different iridium centers. The \( ^1 \text{H} \) NMR spectrum indicated symmetry-related triazolylidene and phenyl groups, and a diagnostic 2 : 1 \( \text{Cp}^* \) ligand ratio. The bridging coordination mode was further supported by the single AB doublet \( (^1J_{\text{HH}} = 12.6 \text{ Hz}) \) for the \( \text{OCH}_2 \) group, while the chelating complex \( \text{10} \) featured two AB doublets because of the lack of symmetry in the ligand. The carbonic resonance appeared at \( \delta_c 153.2 \) in the \( ^{13} \text{C} \{^1 \text{H}\} \) NMR spectrum. A high field resonance at \( \delta_c 114.0 \), attributed to the Cphenyl–H nucleus ortho to the \( \text{Ntrz} \) (i.e. formally C3 of the phenylene unit), is diagnostic for cyclometalation. In the chelate complexes \( \text{8} \)–\( \text{10} \), 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

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**Table 1**

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

**Fig. 4** Complexes \( \text{11} \) and \( \text{12} \) 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 triazolylidene silver complex dropwise to a concentrated solution of [IrCp*Cl2]2 cleanly produced complex 10 together with unreacted [IrCp*Cl2]2, yet no bimetallic species was observed.

When reacting 6b(BF4), Ag2O, and [IrCp*Cl2]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 (X = Cl, NCMe). Both species feature a low-field resonance (δH 9.10 and 8.87) for the triazolyl proton and two AB systems for the OCH3 groups, indicating desymmetrization of the linker.31 Likewise, the NCH3 groups appeared as distinct singlets. The 13C{1H} NMR spectrum of this mixture showed two Ctrz-Ir signals at δC 153.4 or 146.6 and two Ctrz-H carbon resonances (δC 128.9 or 128.8). Heteronuclear multiple bond correlation (HMBC) spectroscopy identified for each of the two species an interaction of one of the OCH3, AB set with the iridium-bound triazolylidene unit, and a correlation of the second OCH3 resonances with the triazolium Ctrz-H unit. While the aromatic region in the 1H NMR spectrum was inconclusive due to significant signal overlap, two high field aryl 13C NMR resonances at δC 114.7 and 114.0 are in agreement with cyclometalation of the phenyl ring and Ctrz,Cphenyl-bidentate coordination of the ligand. In addition, two resonances at δC 138.6 and 138.5 have been attributed to the iridium-bound Cphenyl nucleus (cf. δC 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 [C10H13IrN6O]2+ is 344.12 amu). The isolation of Ctrz,Cphenyl-bidentate ligated complex 12 in combination with the absence of any Ctrz,Ctrz-bidentately bound iridium complex akin to complex 7 strongly suggests that Cphenyl-H bond activation is spontaneous. Formation of complex 12 may be a consequence of incomplete triazolylidene silver formation or due to partial hydrolysis of the semi-transmetaled intermediate prior to chelation of the second carbene unit.

The Cphenyl-H bond activation is reversible. Under acidic conditions (20 equiv. DCl in CD3CN) 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-Ctrz 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-cyclometallated 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 diriazolylidene 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 triazolylidene with N-mesityl substituents derived from 5c(BF4) and 6c(BF4) with [RhCp*Cl2] 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 diriazolylidene 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 MCl3 (M = 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 triazolylidene was supported by the desymmetrization of the linker CH2 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
not. The $^{13}$C($^1$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 $\delta_\text{C}$ 176.2 and 171.3 ($J_{\text{Crh}} = 34.3$ and 30.2 Hz, respectively) were attributed to the triazolylidene carbon, while the resonance at $\delta_\text{C}$ 164.9 ($J_{\text{Crh}} = 25.7$ 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-triazolyldene 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 $\delta_{\text{H}}$ 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 $^1$H NMR spectrum of 14 is very similar to that of 13 although the H$_\text{ortho}$ and H$_\text{meta}$ signals are broad for 14.

The metal-bound carbons are more shielded than those of 13 and resonate at $\delta_\text{C}$ 158.9 and 152.4 (C$_\text{trz}$) and at $\delta_\text{C}$ 147.9 (C$_\text{phenyl}$).

A single crystal structure determination of complex 13 confirmed the bis-homoleptic structure with a cyclometalated phenyl group for each ditriazoylidene 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 C$_\text{trz}$–Rh bond trans to C$_\text{phenyl}$ is 0.05 Å longer than the C$_\text{trz}$–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 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 $^1$H 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 rhodium proton of 15 appeared in the $^1$H NMR spectrum at $\delta_{\text{H}}$ 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$_\text{phenyl}$ resonances of the tridentate ligand. Moreover, mass spectrometry showed a signal at 409 amu, which corroborates the calculated mass for the dicaticonic fragment of [15–X]$^{2+}$ ($m/z$ 409.4 calculated for [C$_4$H$_8$RhN$_2$]$_2^{2+}$).

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 C$_\text{trz}$–C$_\text{phenyl}$ bidentate coordinated complex with a pendant triazolium species supports our previous observation that cyclometalation and C$_\text{phenyl}$–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 metatation reaction did not proceed with the N-ethyl or N-mesityl analogues 5a(I) and 5e(I), respectively under otherwise identical conditions. Instead, only triazolium starting materials were observed by NMR spectroscopy.

Fig. 6 Intermediate species 15 with a C$_\text{trz}$–C$_\text{phenyl}$–two bidentate coordinating ligand containing a pendant triazolium unit.

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 triazolylidenes lead in all cases to ortho-metalation of one of the phenyl rings and to a Ctrz,Ctrz,CPh-tridentate ligand coordination mode. The Cph–H bond activation process is spontaneous and the isolation of a Ctrz,Cph-bidentated intermediate suggests that this bond activation occurs prior to chelation of the second carbene. Stability studies under acidic conditions involving the Ctrz,Ctrz,Cph-tridentate coordinated iridium complex indicate that the Ir–Ctrz bonds are robust while the Ir–

Cph bond is kinetically labile and formed reversibly. Moreover, depending on the applied metatation procedure, the ligand coordinates either meridionally or facially. This coordinative flexibility paired with the hemilability of the Cph–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 (20 mL) was reacted 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 x 50 mL). The combined organics were washed with dilute (NH4)2(OH) (aq., 50 mL), water (2 x 50 mL) and saturated NaCl solution (aq. 1 x 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 x 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, Htrz), 4.30 (q, JHH = 7.3 Hz, CH2), 2.67 (t, 4H, JHH = 7.5 Hz, CtrzCH2), 1.94 (quintet, 2H, JHH = 7.5 Hz, CtrzCH2CH2), 1.41 (t, 6H, JHH = 7.3 Hz, NCH2CH2). 13C{1H} NMR (CD3CN, 100 MHz): δ 148.1 (Ctrz), 121.8 (Ctrz-H), 45.7 (NCH2), 30.0 (CCH2CH2), 25.6 (CCH2CH2), 15.8 (NCH2CH2). ESI-MS (m/z): 235.1676, calef for [C13H16N4]+ 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, Htrz), 7.70–7.66 (m, 4H, Hortho), 7.49–7.43 (m, 4H, Hmeta), 7.37 (tt, 2H, JHH = 7.4 Hz, JHH = 1.2 Hz, Hpara), 2.89 (t, 4H, JHH = 7.4 Hz, CtrzCH2), 2.18 (quintet, 2H, JHH = 7.4 Hz, CCH2CH2). 13C{1H} NMR (CDCl3, 100 MHz): δ 148.3 (Ctrz), 137.2 (Cipso) 129.7 (Cmeta), 128.5 (Cpara), 120.4 (Cortho), 119.4 (Cipso-H), 29.0 (CCH2CH2), 24.9 (Cipso-H). ESI-MS (m/z): 331.1677, calef for [C19H19N6]+ 331.1671. Anal. Calcd for C19H19N6: C, 72.12; H, 7.38; N, 19.99%. 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, Htrz), 6.96 (s, 4H, Hmeta), 2.92 (t, 4H, JHH = 7.6 Hz, CtrzCH2), 2.33 (s, 6H, CH3-para), 2.23 (quintet, 2H, JHH = 7.6 Hz, CCH2CH2), 1.95 (s, 12H, CH2-ortho). 13C{1H} NMR (CDCl3, 100 MHz): δ 147.3 (Ctrz), 139.9 (Cpara), 135.2 (Cortho), 133.8 (Cipso), 129.1 (Cortho), 120.3 (Cipso-H), 29.3 (CCH2CH2), 25.1 (Cipso-H), 21.2 (CH3-para), 17.4 (CH2-ortho). ESI-MS (m/z): 415.2600, calef for [C25H31N6]+ 415.2610. Anal. Calcd for C25H31N6: C, 69.07; H, 5.49; N, 25.44%. Found: C, 68.47; H, 5.49; N, 25.19%.

**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 (CDCl3, 400 MHz): δ 7.59 (s, 2H, Htrz), 4.71 (s, 4H, OCH2), 4.40 (q, 4H, JHH = 7.4 Hz, NCH3), 1.55 (t, 4H, JHH = 7.4 Hz, NCH2CH3).

13C{1H} NMR (CDCl3, 100 MHz): δ 144.8 (Ctrz), 122.2 (Ctrz-H), 63.8 (OCH2), 45.4 (NCH3), 15.6 (NCH2CH3).

ESI-MS (m/z): 237.1473, calcld for [C10H12N4O]+ 237.1464. The oily nature prevented full purification to microanalytical standards.

**Synthesis of 4b.** According to method A, propargyl ether (0.6 mL, 5.82 mmol), phenyl azide (1.73 g, 14.5 mmol), CuSO4 (0.12 mL, 1.13 mmol), mesityl azide (0.4 g, 2.48 mmol), CuSO4 (0.6 mL, 5.82 mmol) were refluxed in MeCN for 20 h. After solvent evaporation, the product was obtained as an amber oil (0.4 g, 85%). It was purified by recrystallization from minimum amounts of THF/H2O (3 × 40 mL). After purification according to the general procedure, the product was obtained as a dark red waxy solid (1.08 g, 89%).

1H NMR (CD3CN, 400 MHz): δ 7.62 (s, 2H, Htrz), 7.73-7.69 (m, 4H, Hortho), 7.52-7.47 (m, 4H, Hmeta), 7.44-7.39 (m, 2H, JHH = 7.4 Hz, JHH = 1.2 Hz, Hpara), 4.84 (s, 4H, OCH2), 13.2 (C(OCH2), 129.8 (Cmeta), 128.9 (Cpara), 121.3 (Ctrz-H), 60.5 (Cortho), 63.7 (OCH2).

ESI-MS (m/z): 333.1473, calcld for [C21H17N6O]+ 333.1464. Anal. calcld for C46.43; H, 5.20; N, 12.03%. Found: C, 46.50; H, 4.83; N, 25.29%. Compound 1H NMR (CD3CN, 400 MHz): δ 9.04 (s, 2H, Htrz), 7.15 (s, 4H, HMes), 4.32 (s, 6H, NCH3), 3.17 (t, 4H, JHH = 7.8 Hz, CtrzCH2), 2.48 (quintet, 2H, JHH = 7.8 Hz, CCH2CH3), 2.37 (s, 6H, CH3-para), 2.10 (s, 12H, CH3-ortho).

**Synthesis of 6b.** According to the general procedure, 2,4-dinitrophenylhydrazine (0.59 g, 1.78 mmol) and CuSO4 (0.51 mL, 8.13 mmol) were refluxed in MeCN for 48 h and purified according to the general procedure, yielding 5e as a yellow solid (0.45 g, 79%). The product was recrystallized by slow diffusion of EtO into a MeCN solution of the compound. 1H NMR (CD3CN, 400 MHz): δ 9.04 (s, 2H, Htrz), 7.15 (s, 4H, HMes), 4.32 (s, 6H, NCH3), 3.17 (t, 4H, JHH = 7.8 Hz, CtrzCH2), 2.48 (quintet, 2H, JHH = 7.8 Hz, CCH2CH3), 2.37 (s, 6H, CH3-para), 2.10 (s, 12H, CH3-ortho). 13C{1H} NMR (CD3CN, 100 MHz): δ 145.1 (Ctrz), 143.5 (Cpara), 130.6 (Cortho), 123.4 (Cipso), 154.2 (Ctrz-H), 130.6 (Cmeta), 93.7 (NCH3), 24.6 (CCH2CH3), 23.9 (Cortho), 17.8 (Cortho).

ESI-MS (m/z): 222.1477, calcld for [C21H17N6]+ 222.1500. Anal. calcld for C21H17N6 (614.26): C, 27.74; H, 4.06; N, 12.03%. Found: C, 27.74; H, 4.06; N, 15.93%.

**Synthesis of 6a.** According to the general procedure, 3a (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/EtO. 1H NMR (CD3CN, 400 MHz): δ 8.92 (s, 2H, Htrz), 5.05 (s, 4H, OCH2), 4.64 (q, 4H, JHH = 7.3 Hz, NCH3), 4.26 (s, 6H, NCH3), 1.60 (t, 4H, JHH = 7.8 Hz, NCH2CH3), 13C{1H} NMR (CD3CN, 100 MHz): δ 140.3 (Ctrz), 130.9 (Cortho-H), 61.4 (OCH2), 50.5 (NCH3), 39.8 (NCH3), 14.7 (NCH2CH3). ESI-MS (m/z): 133.0876, calcld for [C21H17N6O]2+ 133.0928. Anal. calcld for [C21H17N6O]2+ 133.0928. Anal. calcld for [C4H2N2O]2+ 520.15: C, 77.71; H, 4.26; N, 16.16%. Found: C, 77.74; H, 4.06; N, 15.93%.

**Synthesis of 6b.** According to method A, propargyl ether (0.9 mL, 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/EtO. 1H NMR (CD3CN, 400 MHz): δ 8.92 (s, 2H, Htrz), 5.05 (s, 4H, OCH2), 4.64 (q, 4H, JHH = 7.3 Hz, NCH3), 4.26 (s, 6H, NCH3), 1.60 (t, 4H, JHH = 7.8 Hz, NCH2CH3), 13C{1H} NMR (CD3CN, 100 MHz): δ 140.3 (Ctrz), 130.9 (Cortho-H), 61.4 (OCH2), 50.5 (NCH3), 39.8 (NCH3), 14.7 (NCH2CH3). ESI-MS (m/z): 133.0876, calcld for [C21H17N6O]2+ 133.0928. Anal. calcld for [C4H2N2O]2+ 520.15: C, 77.71; H, 4.26; N, 16.16%. Found: C, 77.74; H, 4.06; N, 15.93%.
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/ESI-TO yielded pure compound 6c(I). 1H NMR (CD3CN, 400 MHz): δ 8.89 (s, 2H, Htrz), 7.17 (s, 4H, HMes), 5.14 (s, 4H, OCH2), 4.39 (s, 6H, NCH2), 2.38 (s, CH3para), 2.09 (CH3ortho). 13C{1H} NMR (CD3CN, 100 MHz): δ 143.8 (Cpara), 141.5 (Ctrz), 135.6 (Cortho), 133.0 (Cortho), 131 (broad, Cpip), 130.7 (Cmeta), 62.1 (OCH), 40.5 (NCH2), 21.2 (CH3para), 17.6 (CH3ortho). ESI-MS (m/z): 222.1308, calculated for [C26H14N4O2]+ 222.1397. Anal calcd for C26H14N4O2 (700.4) × 0.5 Et2O: C, 45.60; H, 5.33; N, 11.40%. Found: C, 45.94; H, 4.93; N, 11.66%.

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 triazolium salt. 1H NMR (CD3CN, 400 MHz): δ 8.44 (s, 2H, Htrz), 4.86 (s, 4H, OCH2), 4.58 (q, 4H, JHH = 7.3 Hz, NCH2), 4.19 (s, 6H, NCH2), 1.57 (t, 6H, JHH = 7.3 Hz, NCH2CH2). 13C{1H} NMR (CD3CN, 100 MHz): δ 140.2 (Ctrz), 130.1 (Cortho), 60.8 (OCH2), 50.3 (NCH2), 39.0 (NCH1), 14.4 (NCH3), CH3ESI-MS (m/z): 133.0871, calculated for [C13H20N12O]+ 133.0928. Anal calcd for C13H20N12BF4O (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 5b(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, Htrz), 7.91–7.87 (m, 4H, Hortho), 7.74–7.70 (m, 6H, HHtrz), 5.02 (s, 4H, OCH2), 4.36 (s, 6H, NCH2), 4.33 (C{1H} NMR (CD3CN, 100 MHz): δ 141.2 (Cortho), 135.9 (Cpip), 130.3 (Cpara), 131.4 (Cmeta), 129.1 (Cortho), 122.7 (Cortho), 61.0 (OCH2), 39.6 (NCH3). ESI-MS (m/z): 180.0900, calculated for [C20H12N6O2]+ 180.0928. Anal calcd for C20H12N6BF4O (356.04): C, 44.81; H, 4.14; N, 15.68%. Found: C, 44.50; H, 3.93; N, 15.48%.

Synthesis of 3c(BF4). According to the general procedure from the triazolium iodide 3e(I) (0.40 g, 0.57 mmol) and AgBF4 (0.22 g, 1.14 mmol) for 1 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, Htrz), 7.16 (s, 4H, Hmeses), 5.06 (s, 4H, OCH2), 4.36 (s, 6H, NCH2), 2.37 (CH3para), 2.05 (CH3ortho). 13C{1H} NMR (CD3CN, 100 MHz): δ 143.6 (Cpara), 141.4 (Cpip), 135.6 (Cortho) 132.6 (Cortho), 132.1 (Cpip), 130.5 (Cpara), 61.6 (OCH2), 39.8 (NCH3), 21.1 (CH3para), 17.1 (Cortho). ESI-MS (m/z): 223.1395, calculated for 223.1401.
Synthesis of 7. Triazolium salt 5a(BF$_4$) (68 mg, 0.16 mmol), Me$_3$NCl (296 mg, 1.55 mmol) and Ag$_2$O (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$_2$Cl$_2$ (10 mL) and filtered through cotton to remove Me$_3$NCl by washing with CH$_2$Cl$_2$ (2 × 10 mL). Then [Cp*RhCl$_2$]$_2$ (47 mg, 0.076 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL) and the solution was frozen. The silver triazolylidene solution (10 mL) was added dropwise to the frozen rhodium solution and the solution was allowed to warm to room temperature. After filtration through Celite and removal of the solvent under reduced pressure the residue was purified by column chromatography (SiO$_2$; CH$_2$Cl$_2$ then CH$_2$Cl$_2$/acetone, 1 : 1) yielding the title complex as a yellow solid (75 mg, 85%). Crystals of 7 suitable for X-ray diffraction studies were obtained by diffusion of pentane into a CH$_2$Cl$_2$/MeCN (20 : 1) solution of the complex.

Synthesis of 8. The triazolium salt 5b(BF$_4$) (177 mg, 0.33 mmol) and Ag$_2$O (298 mg, 1.29 mmol) were stirred at room temperature in MeCN (100 mL) for 2 days under exclusion of light. 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$_2$Cl$_2$ then CH$_2$Cl$_2$/CH$_3$OH, 9 : 1) yielding the title complex as an orange solid (75 mg, 85%). Crystals of 8 suitable for X-ray diffraction studies were obtained by diffusion of pentane into a CH$_2$Cl$_2$/MeCN (20 : 1) solution of the complex.

Synthesis of 9. The triazolium salt 6b(BF$_4$) (0.20 g, 0.37 mmol), Ag$_2$O (0.53 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$_2$Cl$_2$ (200 mL) and cooled to −30 °C. Then, [Cp*RhCl$_2$]$_2$ (0.12 g, 0.19 mmol) in CH$_2$Cl$_2$ (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$_2$Cl$_2$ then CH$_2$Cl$_2$/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$_2$O into a CH$_2$Cl$_2$ solution of the complex.

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$_2$O (0.35 g, 1.49 mmol) and KCl (0.28 g, 3.73 mmol) and [Cp*RhCl$_2$]$_2$ (0.14 g, 0.18 mmol). Purification by column chromatography (SiO$_2$; CH$_2$Cl$_2$ then CH$_2$Cl$_2$/acetone, 2 : 1) yielded complex 10 as a pale yellow solid (113 mg, 39%).
Hz, OCH$_3$), 5.11, 4.90 (2 × d, 1H, $^2$J$_{HH}$ = 14.9 Hz, OCH$_3$), 4.82 (d, 1H, $^2$J$_{HH}$ = 14.7 Hz, OCH$_3$), 4.09, 3.95 (2 × s, 3H, NCH$_3$), 1.81 (s, 15H, Cp-CH$_3$). $^{13}$C(1H) NMR (CD$_3$CN, 100 MHz): $^\alpha$C(CPh), 128.4 (CPh), 128.3 (CPh), 128.0 (CPh), 121.9, 113.5 (2 × CPh–), 93.9 (C(Cp), 65.2, 64.3 (2 × OCH$_2$), 37.5, 37.3 (2 × NCH$_3$), 10.3 (Cp–CH$_3$). ESI-MS (m/z): 867.2411, calcd for [C$_{30}$H$_{34}$BF$_4$N$_6$OIr]+ 817.2750.

Found: C, 50.92; H, 4.38; N, 16.67%. Found: C, 50.92; H, 4.35; N, 16.67%. Found: C, 50.95; H, 4.28; N, 16.37%.

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$_\alpha$ radiation (0.71073 Å) (7–9) or Cu-K$_\alpha$ (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. 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 PLATON$^\dagger$ 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.$^\dagger$ 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


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.


32 Further attempts to characterize complex 15 included trapping of this species with PPh₃. The appearance of a doublet in the 3¹P NMR spectrum (δₚ 15.2, JₚRh = 92 Hz) as well as a MS signal at confirmed phosphine coordination to rhodium, however, crystallization efforts to obtain structural information have been unsuccessful.
