ORGANOMETALLICS

Di-Mesoionic Carbene-Bridged Complexes of Rh₂, Ir₂, and RhIr: A Stepwise Metalation Strategy for the Synthesis of di-MIC-Bridged Mixed-Metal Systems

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Supporting Information



ABSTRACT: A meta-substituted benzene-bridged ditriazolium salt has been prepared using copper-catalyzed azide—alkyne cycloaddition (CuAAC or "click" chemistry) and methylation protocols. Metalation of this dicationic species by basic-ligand-containing $[Rh(\mu-OMe)(COD)]_2$ and $[Ir(\mu-OMe)(COD)]_2$ precursors provides homobimetallic complexes of Rh and Ir bridged by a 1,2,3-triazol-5-ylidene-type di-mesoionic carbene (di-MIC) via an "internal-base" strategy. By using only $1/_2$ equiv of the internal-base precursor, mononuclear MIC-anchored/pendent-triazolium intermediates have been isolated, in which only one end of the ditriazolium salt has been deprotonated and attached to Rh or Ir. Reaction of these pendent intermediates with another $1/_2$ equiv of an internal-base precursor affords either the aforementioned homobimetallic products or an analogous di-MIC-bridged, mixed-metal Ir/Rh complex.

INTRODUCTION

Although Arduengo's seminal synthesis of a free N-heterocyclic carbene (NHC, Figure 1a, for example)¹ marked a spectacular



Figure 1. Imidazol-2-ylidene-type NHC (a) and MICs based on imidazol-2-ylidene (b), *r*NHC (c), and 1,2,3-triazol-5-ylidene (d) frameworks.

rise in popularity for the use of carbenes as ancillary ligands,^{2–8} Crabtree's report^{9,10} describing an "abnormal" carbene (aNHCs, with a lone pair on the C-4 or C-5 carbon instead of C-2, Figure 1b)^{11–14} sparked an interest in *different* carbenes based on *N*-heterocycles, such as "remote" NHCs (*r*NHCs, Figure 1c).^{15–20} Since no reasonable resonance forms containing a carbene moiety can be drawn for either of these free ligands without additional charges (unlike the case for "normal" NHCs^{11,14,21}), they are often referred to as "mesoionic carbenes" (or MICs).

While still in their infancy, MIC ligands have experienced a surge in popularity owing to the development of convenient routes to deprotonated "free" mesoions.^{21–23} MICs have been shown to be even stronger electron donors (and weaker π acceptors) than NHCs, which opens up interesting perspectives for their applications.^{11–14,24} Furthermore, the significant steric bulk required to stabilize most free carbenes is less vital in MICs because there have been no reported dimerizations of *a*NHCs or *r*NHCs.²¹ As a result, the scope of possible substituents is broadened significantly, making a wide variety of substituted carbenes possible.

Transition-metal complexes containing 1,2,3-triazol-5-ylidene MICs (Figure 1d, herein referred to as MICs for simplicity) have been shown to be active catalysts in many different reactions, such as alcohol oxidation,²⁵ hydroarylation of alkynes,²⁶ Suzuki–Miyaura cross-coupling,^{27–31} hydroalkoxylation of allenes,³² and olefin metathesis.^{23,33} These examples illustrate the versatility of MICs, which can be generated using a wide range of different functionalities on N-1, N-3, and C-4. In all cases, these complexes exhibit catalytic activities similar to those of well-developed NHC-based systems.

Albrecht^{34,35} and Bertrand²¹ have developed routes for the synthesis of 1,2,3-triazol-5-ylidene-based MICs through deprotonation of 1,2,3-triazolium salt precursors. The parent

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triazole can be prepared from a copper-catalyzed azide–alkyne cycloaddition (CuAAC, or "click" chemistry³⁶⁻³⁸), which is then followed by alkylation to afford the readily deprotonated triazolium salt (Scheme 1), although other routes for the

Scheme 1. Triazolium Synthesis using the CuAAC and Methyl Trifluoromethanesulfonate Approach



arylation at this position by the formal 1,3-dipolar cycloaddition between 1,3-diaza-2-azoniaallene salts and alkynes have also been reported.^{23,39–41} With a wide range of alkynes and azides available, 1,2,3-triazol-5-ylidenes are highly tunable MICs, as is obvious from the assortment of functional groups on the precatalysts noted above.^{23,25–33}

Our studies of binuclear complexes, in order to exploit the concept of metal-metal cooperativity, have usually been based on diphosphines such as bis(diphenylphosphino)methane (Ph₂PCH₂PPh₂, dppm) as bridging groups in order to maintain the integrity of these species during the reactions of interest.⁴² However, we have recently extended these studies to dicarbene ligands, capable of bridging pairs of identical⁴³ or different⁴⁴ metal atoms. With the recent popularity surrounding MIC ligands, we were interested in the use of linked pairs of MICs (much like the ubiquitous di-NHCs) as strongly donating bridging groups. Surprisingly, only one bidentate di-MIC had been reported at the time this work began,³² with two examples reported subsequently by Bertrand ("i-bitz" di-MICs,⁴⁵ similar to Crabtree's "bitz" ligands⁴⁶) and recently by Crudden et al.⁴⁷

In this paper we report our studies on the preparation of 1,2,3-triazol-5-ylidene-type di-MIC ligands and the use of internal-base-containing metal precursors for their attachment to transition metals—a process established by Wanzlick⁴⁸ and Herrmann⁴⁹ for the metalation of NHCs. We utilize this strategy for the controlled stepwise metalation of the ditriazolium precursors, generating first the MIC-anchored/ pendent-triazolium complexes of Rh and Ir, followed by a second metalation to give di-MIC-bridged complexes of Rh₂ and Ir2. Furthermore, the potential application of the MICanchored/pendent-triazolium complexes as precursors to di-MIC-bridged, mixed-metal complexes is outlined. The current study represents part of an ongoing investigation into the possible use of dicarbene-bridged mixed-metal complexes in tandem catalysis.^{50–52} With two different metals combined into one catalyst, heterobimetallic complexes such as these can potentially mediate two mechanistically different catalytic processes in one pot with high atom economy. One of our previously reported di-NHC-bridged Pd/Rh species⁴⁴ is currently being studied as a potential Suzuki-Miyaura/transfer hydrogenation tandem catalyst, and we sought to compare this reactivity with that of other mixed-metal complexes linked by other types of dicarbenes.

RESULTS AND COMPOUND CHARACTERIZATION

Symmetrical di-MIC ligands, in which the two linked MIC groups are identical, are possible as two attachment isomers, both of which can, in principle, be prepared using the CuAAC protocol noted above. An N,N'-linked di-MIC, in which the

MIC rings are connected to the linker at N-1 (Figure 2a, di-MIC $_{N\!,N'}$), should be possible using linked azide groups (N_3–



Figure 2. Different di-MIC isomers possible depending on N-1 (a) or C-4 (b) linkage.

(linker)– N_3), whereas C,C'-linked di-MICs (Figure 2b, di-MIC_{C,C'}) would require linked alkynes (HC \equiv C-(linker)– C \equiv CH). Unsymmetrical di-MICs, in which one MIC is Cbound to the linker unit while the second MIC is N-bound, are also possible, although probably synthetically more challenging.

Attempted Synthesis of Dicationic Precursors to di-MICs. Although diazides appear to be the easiest route to ditriazoles, we did not attempt to generate simple alkyl-bridged diazides (i.e., $N_3 - (CH_2)_n - N_3$, n = 1, 2) to form di-MICs analogous to our previously reported di-NHCs,⁴⁴ owing to the shock-sensitive hazards associated with azides having a low carbon-to-nitrogen ratio.53 We instead chose a linker of higher molecular weight (ortho-, meta-, and para-substituted benzene rings) to bridge both azide components (Scheme 2). Although this linker is significantly different than those examined in our di-NHC studies,44 substituted benzene rings satisfy our criterion of allowing a reasonable metal-metal proximity (once transformed into carbenes and attached to transition metals), and therefore other differences (i.e., linker shape, size, electronic arrangement, etc.) were not expected to interfere with our studies.

The diazides (1) can be prepared using previously reported syntheses;^{54–60} however, several problems arose in preparing the respective ditriazole species (compound 3; Scheme 2). In all attempts, an incomplete triazole/azide product (2) precipitated from solution, preventing the second CuAAC reaction required to produce the desired product (although product 3c had previously been reported in low yield⁵⁶). Because of only minimal solubility in all solvents tried, the NMR spectra could not be obtained, although HRMS displayed a signal corresponding to a [triazole–linker–N]⁺ species, presumably a result of N₂ loss during electrospray ionization. Due to our lack of success in producing the N,N'-linked ditriazoles necessary to generate MIC precursors, we abandoned this pursuit in favor of C,C'-linked isomers.

As noted, the synthesis of di-MIC_{C,C'} systems should be possible by the reaction of a dialkyne with 2 equiv of an azide. Dialkyne-substituted benzene rings are relatively inexpensive and should provide the metal—metal proximity required for our studies. Before initiating this study, however, it came to our attention that solubility issues also plagued similar C,C'-linked triazoles when organized in ortho and para substitution patterns;³² therefore, only the meta-substituted C,C'-linked case was investigated.

A diisopropylphenyl-substituted ditriazole (5) can be prepared in high yield using the dialkyne 4 and 2-azido-1,3diisopropylbenzene⁶¹ (DippN₃) (Scheme 3).^{47,62-64} Formation of 5 is obvious from the ¹H NMR spectrum, which displays the expected pattern for a meta-substituted benzene ring (two triplets and a doublet of doublets of 1:1:2 intensity ratios, respectively) and signals typical for a Dipp-substituted triazole





Scheme 3. Synthesis of di-MIC_{C,C'} Precursors Using Dialkyne Route



Figure 3. Free dication (a), bridging (b), and pendent (c) labeling scheme.

Scheme 4. Formation of Homobimetallic di-MIC-Bridged Species



ring, including two doublets for the ^{*i*}Pr methyl groups, most likely due to inhibited $Ar-^{i}Pr$ bond rotation. Additionally, the alkyne proton resonance shifts dramatically from ca. δ 3.0 to δ 8.5, consistent with transformation of **4** into a ditriazole.

The ¹³C{¹H} NMR spectrum also displays typical resonances for a ditriazole group bridged by a benzene ring at the 1,3positions. The resonances corresponding to the carbons in the six-membered rings change only slightly; however, there are significant shifts in the resonances for the alkynyl carbons, consistent with their transformation to triazole rings, shifting from ca. δ 80 (for both) to δ 127.8 for the C–H and δ 139.2 for the quaternary connecting carbon. The resonances corresponding to the carbon atoms in the Dipp groups of **5** also show evidence for inhibited Ar–ⁱPr bond rotation (two different ⁱPr_{Me} environments at δ 22.1 and 22.3, but only one ⁱPr_{C–H} environment, suggesting that N–Dipp rotation is *not* inhibited).

Addition of MeOTf at low temperature results in selective methylation at the distal nitrogen atom, forming the desired ditriazolium salt (6), which was reported recently by Crudden et al., in which alkylation of the ditriazole precursor was carried out using Me_3OBF_4 .⁴⁷ The ¹H and ¹³C{¹H} NMR spectra of 6 are nearly identical with those of its precursor (5), with the exception of an additional signal in both spectra for the methyl

group on N-3 and a slight shift for the now acidic proton and its attached carbon.

Since all di-MICs discussed in this report are of the C,C'linked type (i.e., di-MIC_{C,C'} dicarbenes), they are subsequently referred to as di-MICs for simplicity. In describing metal complexes ligated by di-MICs, we use the abbreviations $[^{Dipp}(Trz(H))_2][X]_2$ for the MIC(H)⁺/MIC(H)⁺ dicationic di-MIC precursors, $(\mu^{-\text{Dipp}}\text{Tr}z_2)[\text{ML}_n]_2$ or $[\text{ML}_n(\mu^{-\text{Dipp}}\text{Tr}z_2)]$ $M'L_n$] for di-MIC-bridged complexes, and $[ML_n(\kappa^{1-Dipp}TrzTrz-$ (H))][X] for the monodentate MIC-anchored/pendenttriazolium intermediates $(MIC/MIC(H)^+)$, all of which are slight modifications of the original nomenclature for di-NHCs used by us previously⁴⁴ and originally suggested by Green et al.,⁶⁵ as shown in Figure 3. In these abbreviations the triazole N-1 substituent (2,6-diisopropylphenyl (Dipp) in this work) on the triazolium/MIC ring appears first, followed by either the dicationic ring $((Trz(H))_2)$, bridging di-MIC (Trz_2) , or anchored-MIC/pendent-triazolium (κ^1 -TrzTrz(H)) notation. These abbreviations are simplified somewhat in this work, in which neither the nature of the linker nor the N-1 or N-3 substituent is altered. Furthermore, in all cases the same substituent (Dipp) is used on both sides of the ligand.

di-MIC-Bridged Homobinuclear Complexes of Rh and Ir. Albrecht et al. have shown that $[Pd(OAc)_2]$ can metalate

1,2,3-triazolium species, although relatively harsh conditions (temperatures of around 120 °C) are required.³⁵ Surprisingly, this reagent failed to metalate the ditriazolium compound 6 at temperatures below 100 °C, while at higher temperatures only decomposition occurred. Furthermore, our initial attempts to obtain the desired di-MIC-bridged homobimetallic Rh₂ complex using the acetate-containing precursor $[Rh(\mu-OAc)-$ (COD)]₂, paralleling our earlier successes in di-NHC-bridged systems,^{43,44} also failed owing to the lower acidity of the dicationic di-MIC precursor. However, metalation of the triazolium moieties is readily achieved under mild heat (80 °C) within 1 h using either $[Rh(\mu-OMe)(COD)]_2$ or $[Ir(\mu-DMe)(COD)]_2$ $OMe)(COD)]_2$ (Scheme 4), yielding the targeted homobimetallic di-MIC-bridged products $(\mu^{-\text{Dipp}}\text{Trz}_2)[\text{RhI}(\text{COD})]_2$ (7) and $(\mu^{-\text{Dipp}}\text{Trz}_2)[IrI(COD)]_2$ (8) and bypassing the need for the generation of a silver-transfer intermediate. An excess of potassium iodide (KI) is added to the reaction mixture in order to force an iodide product upon metalation, allowing us to draw comparisons to our previous work involving Rh-containing di-NHC-bridged systems.43,44

The Rh complex (7) is an interesting neutral analogue to Crudden's dicationic di-Rh complex,⁴⁷ in which an acetonitrile ligand on each metal is replaced by an iodide ion. Formation of the bimetallic product is evident from the disappearance of the acidic protons in the ¹H NMR spectrum and the emergence of a downfield doublet in the ¹³C{¹H} NMR spectrum for 7 (δ 170.7, ¹*J*_{C-Rh} = 47 Hz) and a singlet for 8 (δ 169.5). Elemental analyses and HRMS also imply a bimetallic structure rather than a chelated one. In these cases, both ¹H and ¹³C{¹H} NMR spectra indicate a barrier to Ar–ⁱPr rotation, as was observed in the dicationic precursor.

Single crystals were obtained by slow diffusion of diethyl ether into a CH_2Cl_2 solution of the di-Rh complex 7. The structure of 7, determined by X-ray diffraction techniques, is shown in Figure 4. Although the disorder present (see the Experimental Section) precludes an in-depth discussion of structural parameters, this structural determination is certainly sufficient to confirm the structural assignment determined on the basis of spectral data. It is well-documented that bimetallic species (involving two square-planar systems) bridged by



Figure 4. Three-dimensional representation of the complex $(\mu^{-Dipp}Trz_2)[RhI(COD)]_2$ (7) showing the numbering scheme. Only one of the two disordered COD and Dipp positions is shown. Thermal ellipsoids are shown at the 20% probability level, except for the hydrogens, which are shown artificially small. Hydrogen atoms are omitted from the COD ligands and methyl groups for clarity. Relevant structural parameters for 7 are given as Supporting Information.

dicarbenes can adopt either *meso* (C_s) or *dl* (C_2) symmetry resulting from hindered rotation about the M-carbene bond; for 7 and 8, these possible diastereomers differ by having both iodides pointing in either the *same* or *opposite* direction, respectively.⁶⁶ Although we are unable to determine which diastereomer best describes complexes 7 and 8 through spectroscopy, it is clear from the structure of 7, shown in Figure 4, that this complex adopts the *dl* orientation, which is presumably a result of steric hindrance. The spectral properties of 7 and 8 are extremely similar, which suggests that the Ir analogue adopts the same geometry. The barrier for rotation about the M-C_{MIC} bond is presumably similar to that of M-C_{NHC} bonds, which is too high for this process to occur readily in solution at ambient temperature.⁶⁷

As is also typical of binuclear species bridged by only one bidentate ligand, the dicarbene framework in 7 is twisted in such a way to allow the metal coordination planes to avoid each other. As a result the Rh(1)- - -Rh(2) separation is quite large, at 7.137(1) Å. This skewing about the dicarbene aryl linker is shown clearly in Figure 4 and is evident by the dihedral angle of 70.1(3)° between the two MIC planes. Furthermore, the Dipp rings also adopt a near-perpendicular arrangement compared to each MIC ring, with dihedral angles ranging from 73.6(6)° to 81.2(6)°, for the two disordered groups. Otherwise, all parameters are as expected.

Both species (7 and 8) can be converted into their carbonylated analogues $(\mu^{-\text{Dipp}}\text{Trz}_2)[\text{RhI}(\text{CO})_2]_2$ (9) and $(\mu^{-\text{Dipp}}\text{Trz}_2)[\text{IrI}(\text{CO})_2]_2$ (10) under a gentle purge of carbon monoxide (Scheme 4), although the yields are diminished owing to the generation of a small amount of an additional unidentified product in each case, which slowly appears subsequent to formation of 9 and 10. This decomposition can be halted by the removal of solvent once carbonylation is complete, followed by recrystallization by quick injection of diethyl ether into a dichloromethane solution of 9 or 10 (see the Experimental Section). In addition to the resonances expected for a carbonylated complex in the ¹H NMR spectrum (see below), this additional, more symmetric product is also present for each metal system, having fewer aromatic linker signals and only one N-3 methyl signal and also lacking an acidic proton at high frequency. These additional undesired products are presumably the mononuclear species [MI(CO)-

 $(\kappa^2 C^2, C^{2'}, C^$

These carbonylated bimetallic species 9 and 10 exhibit NMR spectra similar to those of their respective precursors, apart from the absence of signals for the COD protons and the presence of carbonyl signals in the ¹³C{¹H} NMR spectrum. In the case of 9, the CO signals display chemical shifts and C–Rh coupling constants typical for Rh carbonyl ligands trans to a π -donating halide (δ 182.7, ¹J_{C-Rh} = 78 Hz) and trans to a strong σ -donor (δ 188.7, ¹J_{C-Rh} = 54 Hz). In the di-Ir complex, it is interesting to note that the linker of the di-Ir complex 10 exhibits long-range coupling not observed in its precursors, showing coupling of para-oriented protons (⁵J_{H-H} ≈ 1 Hz). For both compounds, the carbonyl vibrations in the infrared spectrum (1988, 2068 cm⁻¹ (9); 1981, 2053 cm⁻¹ (10)) are typical. Unfortunately, these species decompose in solution





over the course of a few hours, precluding an X-ray structure determination.

MIC-Anchored/Pendent-Triazolium Intermediates. Reaction of the ditriazolium salt (6) with $1/_2$ equiv of either of the $[M(\mu-OMe)(COD)]_2$ (M = Rh, Ir) complexes results in metalation of only one end of this dication to give the MICanchored/pendent-triazolium species [MI(COD)- $(\kappa^{1}-DippTrzTrz(H))][I]$ (M = Rh (11), Ir (12)), shown in Scheme 5. This approach has been used by us^{43,44} and others^{52,68–78} for the generation of analogous NHC-anchored/ pendent-imidazolium complexes by metalation of one end of the corresponding diimidazolium salts. Isolation of such intermediates is not possible with silver-transfer protocols and is difficult to control with external base routes, the outcomes of which are frequently serendipitous and hard to predict.^{79,80} The pendent structure of the Rh complex (11) is easily confirmed by the disappearance of the original high-frequency resonance for 6 and the emergence of a different acidic (H_{Trz}) proton resonance in the high-frequency region of the ¹H NMR spectrum as a sharp singlet at δ 9.06 as well as two singlets for the now-inequivalent N-3 methyl substituents. Although it was expected that these complexes would also display evidence for inhibited rotation about the $Ar-^{i}Pr$ bond (for both inequivalent Dipp systems), only two doublets are observed at low frequency, representing the two different Trz and $Trz(H)^+$ environments, as opposed to the expected four. Two signals representing the olefinic COD hydrogens appear in the spectrum at δ 4.73 as a broad multiplet for the group trans to the MIC (which is at a lower frequency than COD signals trans to an NHC⁴⁴) and a broad signal at δ 3.45 for the two protons cis to the carbene. It is worth noting that this resonance for the cis protons is *significantly* broadened (width at half height = 46 Hz) and was difficult to locate (especially if the sample contains even small amounts of Et₂O; δ_{CH_2} 3.42) until an (F_2, F_1) correlation signal $(\delta({}^{1}H), \delta({}^{13}C\{{}^{1}H\}))$ was obtained in 2D gHMQC NMR experiments confirming this location in the ¹H NMR spectrum.

With the symmetry about the aromatic linker being broken, all phenyl-linker protons are inequivalent and appear as four separate resonances with considerable mutual coupling. The use of 2D transverse rotating-frame Overhauser enhancement spectroscopy (TROESY) also helps to distinguish between signals on the "acidic side" of the molecule (owing to NOE interactions with H_{Trz}) and the "coordinated-carbene side". An expansion of the high-frequency region of the ¹H NMR spectrum of 11 is shown in Figure 5. Although there is no



Figure 5. High-frequency region of the ¹H NMR spectrum of complex 11 showing left/right asymmetry.

spectroscopic evidence to confirm that the MIC unit adopts the usual perpendicular orientation with respect to the square plane of the metal, it is presumed to bind in this manner owing to steric considerations.

The ¹³C{¹H} NMR spectrum of **11** indicates formation of a pendent species having a rhodium-bound carbene by the emergence of a high-frequency doublet in the typical carbene region at δ 171.0 (¹J_{C-Rh} = 46 Hz). This chemical shift is at a slightly lower frequency than for the related (COD)Rh–NHC complexes (ca. δ 181)⁴⁴ but is comparable to that for other (COD)Rh–MIC systems reported by the groups of Albrecht³⁵ and Crudden.⁴⁷ Several signals crowd the aromatic region, owing to the asymmetry present, but assignments are established through the use of various 2D NMR experimental techniques. Signals for the olefinic COD carbons (δ 98.8 for trans, δ 71.7 for cis to the MIC) are unusually broad, and as a result, coupling to Rh cannot be resolved. Although the ¹H NMR spectrum implies the presence of only two 'Pr methyl environments, four different signals are observed in the

¹³C{¹H} NMR spectrum, consistent with the lower symmetry. This inconsistency is the result of accidental equivalence of the proton signals, as confirmed by 2D NMR correlation spectroscopy.

The analogous Ir pendent complex $[IrI(COD)-(\kappa^{1}-Dipp}TrzTrz(H))][I]$ (12; Scheme 5) can be prepared using $[Ir(\mu-OMe)(COD)]_2$, much as described for the Rh species. As expected, the ¹H and ¹³C{¹H} NMR spectra are nearly identical with those of its Rh analogue, apart from the absence of Rh coupling in the ¹³C resonance for the carbene, which appears as a singlet at δ 168.4 in the ¹³C{¹H} NMR spectrum.

To further confirm the pendent nature of species 11 and 12, correlation signals ($\delta({}^{1}\text{H})$, $\delta({}^{13}\text{C}\{{}^{1}\text{H}\})$) are observed in both gHSQC and gHMQC 2D NMR spectra for the singlets representing the acidic proton and its attached carbon (C– H_{acid}). Furthermore, the singlet resonances in the ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR spectrum expand to doublets (ca. ${}^{1}J_{C-H} = 162$ Hz) when analyzed by proton-coupled ${}^{13}\text{C}$ NMR spectroscopic methods, while the resonance representing the carbene shows no additional proton coupling.

Although replacement of the COD ligands by CO in compounds 11 and 12 proceeds as expected to yield the analogous dicarbonyl complexes $[RhI(CO)_2(\kappa^{1}-DippTrzTrz-(H))][I]$ (13) and $[IrI(CO)_2(\kappa^{1}-DippTrzTrz(H))][I]$ (14), shown in Scheme 5, the yields are again diminished owing to decomposition to the respective proposed chelate products, as was seen in the generation of 9 and 10. This decomposition process is much more rapid in the case of these monometallic species but can be halted through quick precipitation as conducted with 9 and 10 (see the Experimental Section).

In order to confirm that the pendent [MI(COD)- $(\kappa^{1}_{-}^{\text{Dipp}}\text{TrzTrz}(H))$][I] systems 11 and 12 are intermediates in the formation of the di-MIC-bridged homobimetallic $(\mu^{-}^{\text{Dipp}}\text{Trz}_{2})$ [(COD)MI]₂ complexes, these pendent species were each reacted with another $^{1}/_{2}$ equiv of the appropriate methoxide precursor to afford the expected Rh₂ (7) or Ir₂ complexes (8).

di-MIC-Bridged Heterobinuclear Complexes of Rh and Ir. One of our main goals in dicarbene chemistry has been establishing routes to *hetero*bimetallic complexes through the use of this stepwise metalation and "pendent" strategies. Although, on the basis of our limited attempts to date, we have been unsuccessful in generating Pd/Rh di-MIC systems analogous to those of our di-NHCs,⁴⁴ owing presumably to the lower acidity of the ditriazolium precursors, a Rh/Ir di-MIC-bridged complex (15, Scheme 6) can be generated using this "pendent" strategy through the reaction of ¹/₂ equiv of

Scheme 6. Formation of a Heterobimetallic di-MIC-Bridged Rh/Ir Complex (15) via Two Routes



 $[M(\mu-OMe)(COD)]_2$ (M = Rh, Ir) with a pendent complex of the other metal. Obviously two routes are possible: generation of **15** from the reaction of the Rh-containing **11** with ¹/₂ equiv of $[Ir(\mu-OMe)(COD)]_2$, or a similar reaction of the Ircontaining **12** with ¹/₂ equiv of $[Rh(\mu-OMe)(COD)]_2$. Although each route incorporates the metals in a different order, the symmetric nature of these di-MICs allows for the same resulting mixed-metal complex **15**. Both routes were attempted, and the yields are similar by both paths. Surprisingly, reaction of ¹/₂ equiv of $[M(\mu-OMe)(COD)]_2$ with the carbonylated species **13** or **14**, containing the opposite metal, in attempts to form a $[MI(CO)_2(\mu-DippTrz_2)M'I(COD)]$ hybrid only produced a complex mixture of products which could not be purified.

Although single crystals of 15 suitable for an X-ray diffraction study could not be obtained (and in any case would surely yield crystals in which the metal positions were disordered in a 1/1mix), the spectral data leave little doubt about its formulation. Formation of the bimetallic species is supported by the disappearance of the high-frequency signal representing the acidic proton on the triazolium group. Signals representing groups on the "acidic" side of the precursor shift slightly owing to the transformation from a pendent-triazolium group to a metal-coordinated MIC. Four different olefinic COD signals (two for trans, two for cis) are also present, as well as a significantly crowded region at low frequency owing to eight different aliphatic CH₂ environments of the COD ligands. The ¹H NMR spectrum for **15** is given as Supporting Information. The ${}^{13}C{}^{1}H$ spectrum contains two high-frequency signals, representing two different carbene environments: a doublet at δ 171.0 (${}^{1}J_{C-Rh}$ = 46.7 Hz) representing the carbene coordinated to Rh and a singlet at δ 169.5 for the Ir-MIC group.

With asymmetry about the aromatic linker remaining, most of the proton and carbon atoms remain inequivalent, as was observed in the pendent precursors. Unfortunately, without the presence of a pendent acidic proton we cannot distinguish the signals on the "Rh side" of the molecule from those on the "Ir side", as was achieved with the pendent precursors using TROESY experiments.

DISCUSSION

With the recent increase in popularity of MIC ligands, we set out to design a set of *di*carbenes of this type for the purposes of bridging mixed-metal systems, and we were able to devise simple routes to di-MIC precursors. Unlike the case for di-NHCs, two different "attachment isomers" are possible, depending on the nature of the starting materials. Although attempts to produce $N_{,N'}$ -linked di-MIC_{N,N'} systems failed(through coupling of a diazide with 2 equiv of alkyne), we were $successful in generating a <math>C_{,C'}$ -linked di-MIC_{C,C'}</sub> system starting from an aryl-linked dialkyne and 2 equiv of azide. These two reagents can be coupled using "click" chemistry to produce ditriazoles, which can subsequently be methylated, forming ditriazolium salts which function as direct di-MIC precursors.</sub>

The major difference between the di-MIC ligand system and the related di-NHC ligands is the ease of metalation of the diprotonated precursors, with the latter being significantly more acidic and more-readily metalated. As a result, the acetatebridged complex $[Rh(\mu-OAc)(COD)]_2$, which was effective for metalating the diimidazolium precursors of di-NHCs, is not effective for metalation of the ditriazolium precursors to form the di-MICs. However, $[Rh(\mu-OMe)(COD)]_2$ and $[Ir(\mu-$ OMe)(COD)₂, containing the more basic methoxide ligands, are excellent internal-base precursors for the metalation of the triazolium salts. Throughout much of the Rh carbene literature, $[Rh(\mu-OAc)(COD)]_2$ is frequently used to effect metalation of the carbene precursor; however, we recommend that the aforementioned methoxide-bridged precursor be considered instead in future studies. Significantly milder conditions are required to facilitate metalation, and yields (in our experience) are much more favorable. Gratifyingly, the synthesis of $[Rh(\mu -$ OMe (COD)]₂ is also simpler than that of $[Rh(\mu - OAc) - OAc)$ (COD)₂ and is nearly quantitative from $[Rh(\mu-Cl)(COD)]_2$. In addition to this species being an alternative to the OAcmetalation route, this methoxide species could potentially be more favorable than most silver-transfer transmetalation routes which are frequently used, as these precursors offer a much simpler protocol if the desired attachment is Rh or Ir.

The above challenges caused by the differences in acidity between imidazolium and triazolium salts are clearly seen in our recent, related study⁸² in which $[Pd(OAc)_2]$ succeeded in metalating the imidazolium end of a mixed imidazolium/ triazolium species, yielding the corresponding NHC-anchored/ pendent-triazolium complexes. However, in attempts to produce a [Rh(NHC)/Pd(MIC)] species by metalation of the triazolium end of an NHC-anchored/pendent-triazolium complex of Rh using $[Pd(OAc)_2]$, no reaction was observed below 100 °C, while decomposition occurred at higher temperatures.

One of the major advantages of the internal-base method for metalation of the dicationic precursors is the relative ease of effecting a single metalation to yield the MIC-anchored/ pendent-triazolium species for subsequent metalation by a different metal complex, giving a convenient route to di-MICbridged heterobinuclear complexes. In spite of the fact that we were unsuccessful in generating heterobinuclear Pd/M (M = Rh, Ir) species, owing to the inability of $[Pd(OAc)_2]$ to metalate either the ditriazolium salt or the triazolium arm of a pendent complex, we report success in preparing one example of a Rh/Ir complex by this stepwise route. Our failure to generate a hybrid $[MI(CO)_2(\mu - Dipp Trz_2)M'I(COD)]$ complex using carbonylated pendent systems is perhaps due to the instability of the precursors to the mild heating required for the second metalation step, a property also noted previously in attempts to prepare related di-NHC-bridged, carbonylated complexes.⁴⁴ Presumably other mixed-metal combinations can be achieved if more robust complexes with stabilities similar to that of the pendent COD-coordinated precursors reported here are employed. Investigations in this area are currently underway.

EXPERIMENTAL SECTION

General Comments. Deuterated solvents used for NMR experiments were freeze–pump–thaw degassed and stored under argon over appropriate molecular sieves. Unless otherwise specified, reactions were carried out at ambient temperature. Potassium iodide was purchased from ACP, cycloocta-1,5-diene, 2,6-diisopropylaniline, methyl trifluoromethanesulfonate, and 1,3-diethynylbenzene (4) were purchased from Aldrich, triethylamine was purchased from Anachemia, sodium nitrite and potassium hydroxide were purchased from Caledon Laboratory Chemicals, sodium azide was purchased from J.T. Baker Chemical Co., copper(I) iodide was purchased from Pressure Chemical Co., and ammonium hexachloroiridate(IV) was purchased from Strem. All chemicals were used without further purification, with the exception of potassium iodide, which was

purified by repetitive melting under dynamic vacuum before use. o_{7}^{59} m_{7}^{58} and *p*-diazidobenzene $(1a-c)^{83}$ have been previously reported, although all were synthesized on the basis of the diazotization procedure.⁶¹ 1,2-Bis(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzene (3c) has previously been reported (in low yield).⁵⁶ 2-Azido-1,3-diisopropyl-benzene (DippN₃),⁶¹ bis(cycloocta-1,5-diene)bis(μ -chloro)dirhodium ([Rh(μ -Cl)(COD)]₂),^{84,85} bis(cycloocta-1,5-diene)bis(μ -methoxo)dirhodium ([Rh(μ -OMe)(COD)]₂),⁸¹ and bis(cycloocta-1,5-diene)-bis(μ -methoxo)diiridium ([Ir(μ -OMe)(COD)]₂)⁸¹ were prepared as reported previously. Caution! Organic azides are potentially explosive substances that can decompose readily upon exposure to heat, light, or pressure. Appropriate safety precautions should be exercised (i.e., proper lab protection, blast shields, etc.) to prevent serious injury. A bis(tetrafluoroborate) analogue of our dicationic di-MIC precursor 4,4'-(1,3-phenylene)bis(1-(2,6-diisopropylphenyl)-3-methyl-1H-1,2,3triazol-3-ium) trifluoromethanesulfonate, [DippTrz(H)Trz(H)][OTf]2 (6), and its precursor (5) were reported⁴⁷ while this paper was in preparation, but our slightly different synthetic protocols are shown here. The ¹H and ¹³C{¹H} NMR spectra were recorded on a dual cold probe equipped Varian DirectDrive 500 MHz, iNova-500, iNova-400, or Varian iNova-300 spectrometer operating at the resonance frequencies of the NMR nuclei given below in the spectroscopic data. Chemical shifts are reported in parts per million (δ). The ¹H and $^{13}C{^{1}H}$ chemical shifts are referenced to TMS, and the $^{19}F{^{1}H}$ chemical shift for 6 is referenced to CFCl₃. The ${}^{19}F{}^{1}H$ NMR spectra were recorded on an iNova-400 spectrometer operating at the resonance frequency given below in the spectroscopic data. The following abbreviations are used in describing NMR couplings: (s) singlet, (d) doublet, (t) triplet, (q) quartet, and (br) broad. Resonances within a group are separated by commas and separated from other groups by semicolons. The group is identified in parentheses for the last resonance given for the group. Mass spectrometric analyses were performed by the departmental Mass Spectrometry Laboratory using positive ion electrospray ionization on an Agilent Technologies 6220 accurate-mass TOF LC/MS. Infrared spectra were obtained using a Nicolet Avatar 370DGTS instrument.

Preparation of Compounds. (a). Attempted Synthesis of 1,2-Bis(4-phenyl-1H-1,2,3-triazol-1-yl)benzene (3a). A 20 mL portion of MeOH/H₂O (1/1) was added to a flask containing 1a (0.416 g, 2.60 mmol) and phenylacetylene (0.61 mL, 5.6 mmol). The resulting solution was stirred for 5 min, and then CuI (0.046 g, 0.24 mmol, 9.3 mol %) and NEt₃ (0.36 mL, 2.58 mmol) were quickly added, at which point the solution turned dark green and was stirred at room temperature overnight. The solution was filtered, and the product was extracted with chloroform. The solution was dried with MgSO4 and decanted, and the solvent was removed under reduced pressure, followed by washing of the crude product with 5×20 mL portions of n-pentane before drying in vacuo, giving 0.614 g of a dark yellow powder. ¹H NMR (299.97 MHz, chloroform-d, 27.5 °C): δ 8.01 (s, 1H, H_{Trz}); 7.84 (m, 2H), 7.60–7.41 (m, 7H, Ar). IR (solution, cm⁻¹): 2111 (N₃, asymm). These spectral data indicated that the product was the intermediate species 2a and not the targeted compound. Attempts to convert 2a to 3a did not succeed; therefore, this work was not pursued further.

(b). Attempted Synthesis of 1,3-Bis(4-phenyl-1H-1,2,3-triazol-1yl)benzene (**3b**). The monotriazole product was prepared as described for **3a**, using **1b** (0.435 g, 2.72 mmol), phenylacetylene (0.63 mL, 5.74 mmol), CuI (0.050 g, 0.26 mmol, 9.7 mol %), and NEt₃ (0.39 mL, 2.8 mmol). The solution changed from yellow to dark green instantly and was stirred overnight. The crude product was purified as described for **3a** and isolated as a dark yellow powder (0.621 g). ¹H NMR (299.97 MHz, chloroform-*d*, 27.5 °C): δ 8.11 (s, 1H, H_{Trz}); 7.76 (m, 3H), 7.50–7.31 (m, 5H), 7.01 (m, 1H, Ar). IR (solution, cm⁻¹): 2107 (N₃, asymm.). These spectral data indicated that the product was the intermediate species **2b** and not the targeted compound. Attempts to convert **2b** to **3b** did not succeed; therefore, this work was not pursued further.

(c). Attempted Synthesis of 1,4-Bis(4-phenyl-1H-1,2,3-triazol-1yl)benzene (**3c**). The monotriazole product was prepared as described for **3a**, using **1c** (0.950 g, 5.93 mmol), phenylacetylene (1.252 g, 11.40 mmol), CuI (0.548 g, 2.88 mmol, 48.5 mol %), and NEt₃ (1.254 g, 8.99 mmol). The solution changed from yellow to dark green instantly and was stirred overnight. The crude product was purified as described for **3a** and isolated as a bright yellow powder (1.477 g). ¹H NMR (299.97 MHz, chloroform-*d*, 27.5 °C): δ 8.21 (s, 1H, H_{Trz}); 7.94 (m, 2H), 7.84 (m, 2H), 7.57–7.41 (m, 3H), 7.31–7.23 (m, 2H, Ar). IR (solution, cm⁻¹): 2111 (N₃, asymm). These spectral data indicated that the product was the intermediate species **2c** and not the targeted complex. Attempts to convert **2c** to **3c** did not succeed; therefore, this work was not pursued further.

(d). 1,3-Bis(1-(2,6-Diisopropylphenyl)-1H-1,2,3-triazol-4-yl)benzene (5). The ditriazole product was prepared as described for the attempted preparation of 3a, using DippN₃ (20.961 g, 103.11 mmol), 4 (5.215 g, 41.34 mmol), CuI (3.202 g, 16.81 mmol, 20.3 mol %), and NEt₃ (4.192 g, 30.06 mmol). The solution changed from yellow to dark green instantly and was stirred for 1 h. The crude product was purified as described for the attempts to prepare 3a and recrystallized from CH2Cl2 and pentane as a light beige powder (17.383 g, 79%). ¹H NMR (498.12 MHz, acetonitrile- d_3 , 26.1 °C): δ 8.43 (s, 2H, H_{Trz}); 8.60 (td, 1H, ${}^{4}J_{H-H}$ = 1.8 Hz, ${}^{5}J_{H-H}$ = 0.4 Hz), 8.01 (dd, 2H, ${}^{3}J_{H-H}$ = 7.8 Hz, ${}^{4}J_{H-H}$ = 1.8 Hz), 7.64 (td, 1H, ${}^{3}J_{H-H}$ = 7.8 Hz, ${}^{5}J_{H-H} = 0.5$ Hz, Ar_{link}); 7.61 (t, 2H, ${}^{3}J_{H-H} = 7.9$ Hz), 7.44 (d, 4H, ${}^{3}J_{H-H} = 7.9$ Hz, Ar_{Dipp}); 2.34 (qq, 4H, ${}^{3}J_{H-H} = 6.9$ Hz, ${}^{3}J_{H-H} = 6.9$ Hz, $^{1}\text{Pr}_{\text{C-H}}$); 1.19 (d, 12H, $^{3}J_{\text{H-H}}$ = 6.9 Hz), 1.16 (d, 12H, $^{3}J_{\text{H-H}}$ = 6.9 Hz, ⁱPr_{Me}). ¹³C{¹H} NMR (125.69 MHz, acetonitrile-*d*₃, 27.7 °C): δ 146.8 (s, 2C, Trz_{quat}); 124.1 (s, 2C, Trz_{C-H}); 146.1 (s, 4C, Ar_{quat}-^{*i*}Pr); 133.3 (s, 2C, Ar_{quat} -N); 124.0 (s, 4C), 131.1 (s, 2C, Ar_{C-H}); 131.6 (s, 2C, hr_{quat} -N); 124.0 (s, 4C), 131.1 (s, 2C, Ar_{C-H}); 131.6 (s, 2C, $hr_{r_{quat}}$); 129.7 (s, 1C), 125.3 (s, 2C, $hr_{r_{c-H}}$); 122.7 (s, 1C, $hr_{r_{c-H}}$); 122.7 (s, 1C, $hr_{r_{c-H}}$); 122.7 (s, 1C, $hr_{r_{c-H}}$); 23.4 (s, 4C), 23.1 $(s, 4\dot{C}, {}^{i}Pr_{Me}).$

(e). 4,4'-(1,3-Phenylene)bis(1-(2,6-diisopropylphenyl)-3-methyl-1H-1,2,3-triazol-3-ium) Trifluoromethanesulfonate, (^{Dipp}Trz(H)Trz-(H)][OTf]₂ (6). A 40 mL portion of CH₂Cl₂ was added to a flask containing 5 (0.711 g, 1.33 mmol) under an inert $Ar_{(g)}$ atmosphere. The resulting solution was stirred for 10 min and cooled to -78 °C, and then MeOTf (0.4 mL, 3.65 mmol) was quickly injected, resulting in a cloudy discharge above the solution. The solution was warmed to room temperature and then stirred overnight, yielding a slightly darker beige solution. The solvent was then removed under reduced pressure, and the crude product was washed with 5 \times 20 mL portions of *n*pentane before drying in vacuo and was recrystallized from CH₂Cl₂ and Et₂O as a very fine white powder (0.837 g, 73%). ¹H NMR (399.79 MHz, acetonitrile-d₃, 26.5 °C): δ 8.90 (s, 2H, H_{Trz}); 8.19 (td, 1H, ${}^{4}J_{H-H}$ = 1.8 Hz, ${}^{5}J_{H-H}$ = 0.7 Hz), 8.12 (dd, 2H, ${}^{3}J_{H-H}$ = 7.8 Hz, ${}^{4}J_{H-H} = 1.8 \text{ Hz}$, 8.03 (td, 1H, ${}^{3}J_{H-H} = 7.8 \text{ Hz}$, ${}^{5}J_{H-H} = 0.7 \text{ Hz}$, Ar_{link}); 7.77 (t, 2H, ${}^{3}J_{H-H}$ = 7.8 Hz), 7.56 (d, 4H, ${}^{3}J_{H-H}$ = 7.8 Hz, Ar_{Dipp}); 4.45 (s, 6H, N-CH₃); 2.50 (qq, 4H, ${}^{3}J_{H-H} = 6.8$ Hz, ${}^{3}J_{H-H} = 6.8$ Hz, ${}^{i}Pr_{C-H}$; 1.27 (d, 12H, ${}^{3}J_{H-H}$ = 6.8 Hz), 1.24 (d, 12H, ${}^{3}J_{H-H}$ = 6.8 Hz, ⁱPr_{Me}). ¹³C{¹H} NMR (125.69 MHz, acetonitrile-*d*₃, 27.7 °C): δ 142.8 (s, 2C, Trz_{quat}); 131.7 (s, 2C, Trz_{C-H}); 145.7 (s, 4C, Ar_{quat}-^{*i*}Pr); 130.8 (5) 2C, Ar_{quat} , N; 133.2 (s, 2C), 124.9 (s, 4C, Ar_{C-H}); 123.6 (s, 2C, $linkAr_{quat}$); 131.1 (s, 1C), 133.2 (s, 2C, $linkerAr_{C-H}$); 130.8 (s, 1C, $linkAr_{quat}$); 131.1 (s, 1C), 133.2 (s, 2C, $linkerAr_{C-H}$); 130.8 (s, 1C, $linkAr_{quat}$, $linkAr_{quat}$, $linkAr_{quat}$, $linkAr_{quat}$, $linkAr_{quat}$; 121.1 (q, 2C, $^{3}J_{C-F}$ = 319.9 Hz, OTf); 39.5 (s, 2C, N-CH₃); 28.4 (s, 4C, ⁱPr_{C-H}); 23.6 (s, 4C), 22.9 (s, 4C, ⁱPr_{Me}). ¹⁹F{¹H} NMR (376.15 MHz, acetonitrile-*d*₃, 26.1 °C): δ –79.3 (s, 2F, OTf). HRMS: m/z calcd for $C_{38}H_{46}N_6O_3S$ (M⁺ – OTf ⁻) 711.3299, found 711.3293 (M⁺ – OTf⁻); m/z calcd for C₃₈H₄₆N₆ $(M^{2+} - 2 \text{ OTf}^{-})$ 281.1886, found 281.1889 $(M^{+} - 2 \text{ OTf}^{-})$. Anal. Calcd for C38H46F6N6O6S2: C, 53.01; H, 5.39; N, 9.76. Found: C, 52.90; H, 5.47; N, 9.53. The ¹H NMR spectrum of this compound is given in the Supporting Information (Figure S1).

(f). 4,4'-(1,3-Phenylene)bis(1-(2,6-diisopropylphenyl)-3-methyl-1H-1,2,3-triazol-5-yl)($\eta^{2}:\eta^{2}$ -cycloocta-1,5-diene)iodidorhodium(l), [Rhl(COD)]₂($\mu^{-Dipp}Trz_{2}$) (7). A 10 mL portion of acetonitrile was added to a solid mixture containing 6 (0.432 g, 0.50 mmol), [Rh(μ -OMe)(COD)]₂ (0.503 g, 1.04 mmol), and KI (0.502 g, 3.02 mmol) under an inert Ar_(g) atmosphere. The resulting solution was stirred for 1 h at 80 °C in a sealed container and cooled to room temperature. The solvent was then removed under reduced pressure, and the crude product was redissolved in 3 mL of acetonitrile and filtered through Celite. A 45 mL portion of diethyl ether was added to precipitate a yellow solid, and the mother liquor was removed via cannula. The precipitate was washed with 5×20 mL portions of *n*-pentane before drying in vacuo, giving an orange powder (0.515 g, 83%). ¹H NMR (498.12 MHz, acetonitrile- d_3 , 26.1 °C): δ 8.51 (t, 1H, ${}^{4}J_{H-H} = 1.5$ Hz), 8.42 (dd, 2H, ${}^{3}J_{H-H} = 7.6$ Hz, ${}^{4}J_{H-H} = 1.5$ Hz), 7.90 (t, 1H, ${}^{3}J_{H-H} = 7.6$ Hz, Ar_{link}); 7.61 (t, 2H, ${}^{3}J_{H-H} = 8.0$ Hz), 7.50 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, $Ar_{Dipp(Rh)}$; 4.24 (s, 6H, N-CH_{3(Rh)}); 2.52 (qq, 4H, ³J_{H-H} = 7.0 Hz, ${}^{3}J_{H-H} = 7.0 \text{ Hz}, {}^{i}\text{Pr}_{C-H}$; 1.21 (d, 12H, ${}^{3}J_{H-H} = 7.0 \text{ Hz}$), 1.26 (d, 12H, ${}^{3}J_{H-H} = 7.0 \text{ Hz}, {}^{i}\text{Pr}_{\text{Me}(\text{Rh})}$; 4.70 (br s, 4H, $\text{COD}_{\text{C-H}(trans)}$); 3.47 (br s, 4H, $\text{COD}_{\text{C-H}(cis)}$); 2.10–1.95 (m, 16H, COD_{alk}). ${}^{13}\text{C}{}^{1}\text{H}$ NMR (100.54 MHz, acetonitrile- d_3 , 26.5 °C): δ 170.7 (d, 2C, ${}^1J_{C-Rh} = 46.5$ Hz, $C_{carbene}$); 144.7 (s, 2C, $Trz_{quat(Rh)}$); 147.0 (s, 4C, $Ar_{quat}-Pr_{(Rh)}$); 135.1 (s, 2C, $Ar_{quat}-N_{Rh}$); 130.5 (s, 2C), 124.2 (s, 4C, $Ar_{C-H(Rh)}$); 131.0 (s, 2C, $linkAr_{quat}$); 134.6 (s, 2C), 131.2 (s, 1C, $linkerAr_{C-H}$); 132.4 (s, 1C, $linkAr_{quat}$ - $linkAr_{C-H}$ - $linkAr_{quat}$); 37.9 (s, 2C, N-CH_{3(Rh})); 28.5 (s, 4C, ⁱPr_{C-H}); 23.6 (s, 4C), 23.2 (s, 4C, ⁱPr_{CH}); 92.6 (br s, 4C, COD_{trans}); 71.2 (br s, 4C, COD_{cis}); 32.2 (br s, 2C), 29.6 (br s, 2C), 25.6 (br s, 2C), 22.1 (br s, 2C, COD_{CH2}). Anal. Calcd for C52H68I2N6Rh2: C, 50.50; H, 5.54; N, 6.80. Found: C, 50.32; H, 5.14; N, 6.62.

(q). 4,4'-(1,3-Phenylene)bis(1-(2,6-diisopropylphenyl)-3-methyl-1H-1,2,3-triazol-5-yl)(η^2 : η^2 -cycloocta-1,5-diene)iodidoiridium(I), [Irl- $(COD)]_{2}(\mu^{-Dipp}Trz_{2})$ (8). The desired product was prepared as described for 7, using 6 (0.543 g, 0.63 mmol), at least a full 1 equiv of $[Ir(\mu -$ OMe)(COD)]₂ (0.452 g, 0.68 mmol), and KI (0.501 g, 3.02 mmol) under an inert $Ar_{(g)}$ atmosphere. The solution was heated at 80 $^{\circ}C$ in a sealed container for 2 h and cooled to room temperature, at which point it turned dark orange. The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of acetonitrile. A 30 mL portion of diethyl ether was added to precipitate a yellow solid, which was washed with 5 \times 25 mL portions of *n*pentane before drying in vacuo, giving a dark orange powder (0.681 g, 76%). ¹H NMR (498.12 MHz, acetonitrile- d_3 , 26.1 °C): δ 8.01 (t, 1H, ${}^{4}J_{H-H} = 1.3 \text{ Hz}$), 7.71 (dd, 2H, ${}^{3}J_{H-H} = 7.7 \text{ Hz}$, ${}^{4}J_{H-H} = 1.3 \text{ Hz}$), 7.43 (t, 1H, ${}^{3}J_{H-H} = 7.7$ Hz, Ar_{link}); 7.58 (t, 2H, ${}^{3}J_{H-H} = 7.8$ Hz), 7.31 (d, 4H, ${}^{3}J_{H-H}$ = 7.8 Hz, Ar_{Dipp(Ir)}); 4.19 (s, 6H, N-CH_{3(Ir)}); 2.35 (qq, 4H, ${}^{3}J_{H-H} = 7.0 \text{ Hz}, {}^{3}J_{H-H} = 7.0 \text{ Hz}, {}^{i}Pr_{C-H}); 1.21 \text{ (d, 12H, } {}^{3}J_{H-H} = 7.1$ Hz), 1.24 (d, 12H, ${}^{3}J_{H-H}$ = 7.1 Hz, ${}^{i}Pr_{Me(Ir)}$); 4.23 (br s, 4H, $COD_{C-H(trans)}$); 3.15 (br s, 4H, $COD_{C-H(cs)}$); 2.15–1.92 (m, 16H, COD_{alk}). ¹³C{¹H} NMR (100.54 MHz, acetonitrile- d_3 , 26.5 °C): δ 169.5 (s, 2C, C_{carbene}); 143.9 (s, 2C, Trz_{quat(Ir)}); 146.1 (s, 4C, $\begin{array}{l} \text{Ar}_{\text{quat}} - \ensuremath{\bar{P}} \mathbf{r}_{(\mathrm{Ir})} \ensuremath{);} 134.9 & (s, 2C, \ensuremath{Ar}_{\text{quat}} - \ensuremath{N}_{\mathrm{Ir}}); 129.0 & (s, 2C), 125.1 & (s, 4C, \ensuremath{Ar}_{\mathrm{C-H}(\mathrm{Ir})}); 130.6 & (s, 2C, \ensuremath{\operatorname{Ar}}_{\text{quat}}); 134.5 & (s, 2C), 131.0 & (s, 1C, \ensuremath{\operatorname{link}} \ensuremath{Ar}_{\mathrm{C-H}}); 132.8 & (s, 1C, \ensuremath{\operatorname{link}} \ensuremath{Ar}_{\mathrm{cut}} - \ensuremath{\operatorname{Im}} \ensuremath{Ar}_{\mathrm{C-H}} - \ensuremath{\operatorname{Im}} \ensuremath{Ar}_{\mathrm{quat}}); 38.2 & (s, 2C, \ensuremath{Ar}_{\mathrm{quat}}); 38.2 & (s, 2C, \ensuremath{Ar}_{\mathrm{cut}} - \ensuremath{\operatorname{Im}} \ensuremath{Ar}_{\mathrm{cut}}); 38.2 & (s, 2C, \ensuremath{Ar}_{\mathrm{quat}}); 38.2 & (s, 2C, \ensuremath{Ar}_{\mathrm{cut}}); 38.2 & (s, 2C, \ensuremath{Ar}_{\mathrm{cut}} - \ensuremath{\mathrm{Im}} \ensuremath{Ar}_{\mathrm{cut}}); 38.2 & (s, 2C, \ensuremath{Ar$ N-CH_{3(Ir)}); 27.9 (s, 4C, ⁱPr_{C-H}); 23.8 (s, 4C), 22.9 (s, 4C, ⁱPr_{CH}); 81.6 (br s, 4C, COD_{trans}); 53.6 (br s, 4C, COD_{cis}); 28.5 (s, 2C), 26.7 (s, 2C), 25.1 (s, 2C), 22.0 (s, 2C, COD_{CH}). Anal. Calcd for C52H68I2Ir2N6: C, 44.13; H, 4.84; N, 5.94. Found: C, 44.26; H, 5.07; N, 6.32.

(h). 4,4'-(1,3-Phenylene)bis(1-(2,6-diisopropylphenyl)-3-methyl-1H-1,2,3-triazol-5-yl)dicarbonyliodidorhodium(I), [Rhl- $(CO)_2]_2(\mu^{-Dipp}Trz_2)$ (9). A 10 mL portion of acetonitrile was added to a flask containing 7 (0.356 g, 0.29 mmol) under an inert $Ar_{(g)}$ atmosphere. A 15 min gentle purge of CO into a stirred solution yielded a pale yellow solution. The conversion to the respective dicarbonyl complex 9 was accompanied by the facile loss of 1,5cyclooctadiene and was monitored to completion using ¹H NMR spectroscopy. The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of CH2Cl2. A 30 mL portion of diethyl ether was quickly added to precipitate a yellow solid, which was washed with 5×25 mL portions of *n*-pentane before drying in vacuo, giving a dark yellow powder (0.253 g, 78%), although all samples showed evidence of decomposition to an unknown, more symmetric product when redissolved in solution (omitted here in spectral data). ¹H NMR (498.12 MHz, acetonitrile- d_3 , 26.1 °C): δ 8.63 (t, 1H, ${}^{4}J_{H-H} = 1.2$ Hz), 8.35 (dd, 2H, ${}^{3}J_{H-H} = 7.4$ Hz, ${}^{4}J_{H-H} = 1.2$ Hz), 7.99 (t, 1H, ${}^{3}J_{H-H} = 7.4$ Hz, Ar_{link}); 7.66 (t, 2H, ${}^{3}J_{H-H} = 7.9$ Hz), 7.45 (d, 4H, ${}^{3}J_{H-H} = 7.9$ Hz, $Ar_{Dipp(Rh)}$); 4.35 (s, 6H, N–CH_{3(Rh)}); 2.50 (qq, 4H, ${}^{3}J_{H-H} = 7.0$ Hz, ${}^{3}J_{H-H} = 7.0$ Hz, ${}^{i}Pr_{C-H}$); 1.23 (d, 12H, ${}^{3}J_{H-H} = 7.0$ Hz), 1.27 (d, 12H, ${}^{3}J_{H-H} = 7.0$ Hz, ${}^{i}Pr_{Me(Rh)}$). ${}^{13}C{}^{1}H$ NMR (100.54 MHz, acetonitrile- d_{3} , 26.5 °C): δ 160.9 (d, 2C, ${}^{1}J_{C-Rh} =$ 40.2 Hz, $C_{carbene}$); 188.7 (d, 2C, ${}^{1}J_{C-Rh} = 53.5$ Hz, CO_{trans}); 182.7 (d, 2C, ${}^{1}J_{C-Rh} = 77.9$ Hz, CO_{cis}); 145.0 (s, 2C, $Trz_{quat(Rh)}$); 148.3 (s, 4C, $Ar_{quat} - {}^{i}Pr_{(Rh)}$); 135.7 (s, 2C, $Ar_{quat} - N_{Rh}$); 131.2 (s, 2C), 124.1 (s, 4C, $Ar_{C-H(Rh)}$); 131.5 (s, 2C, ${}^{link}Ar_{quat}$); 135.9 (s, 2C), 131.9 (s, 1C, ${}^{link}Ar_{C-H}$); 132.7 (s, 1C, ${}^{link}Ar_{quat} - {}^{link}Ar_{C-H} - {}^{link}Ar_{quat}$); 39.9 (s, 2C, $N-CH_{3(Rh)}$); 27.5 (s, 4C, ${}^{i}Pr_{C-H}$); 23.7 (s, 4C), 23.1 (s, 4C, ${}^{i}Pr_{CH_3}$). IR (solution, cm⁻¹): 1988, 2068 (CO). HRMS: m/z calcd for $C_{40}H_{44}IN_{6}O_{4}Rh_{2}$ ($M^{+} - I^{-}$) 1005.0579, found 1005.0575 ($M^{+} - I^{-}$). The ${}^{1}H$ (Figure S2) and ${}^{13}C{}^{1}H$ } (Figure S3) NMR spectra of this compound are given in the Supporting Information.

(i). 4,4'-(1,3-Phenylene)bis(1-(2,6-diisopropylphenyl)-3-methyl-1H-1,2,3-triazol-5-yl)dicarbonyliodidóiridiúm(I), [lŕl- $(CO)_{2l_2}(\mu^{-Dipp}Trz_2)$ (10). The desired product was prepared as described for 9, using 8 (0.645 g, 0.46 mmol). The solution turned pale yellow after 15 min of a CO purge. The crude product was purified as described for 9 and isolated as a yellow powder, giving a dark orange powder (0.401 g, 67%), although all samples showed evidence of decomposition to an unknown, more symmetric product when dissolved in solution (omitted here in spectral data). ¹H NMR (498.12 MHz, acetonitrile- d_{3} , 26.1 °C): δ 8.21 (td, 1H, ${}^{4}J_{H-H} = 1.2$ Hz, ${}^{5}J_{\rm H-H}$ = 0.7 Hz), 8.01 (dd, 2H, ${}^{3}J_{\rm H-H}$ = 7.9 Hz, ${}^{4}J_{\rm H-H}$ = 1.2 Hz), 7.76 (td, 1H, ${}^{3}J_{H-H} = 7.9$ Hz, ${}^{5}J_{H-H} = 0.7$ Hz, Ar_{link}); 7.64 (t, 2H, ${}^{3}J_{H-H} =$ 7.9 Hz), 7.44 (d, 4H, ${}^{3}J_{H-H} = 7.9$ Hz, $Ar_{Dipp(Ir)}$); 4.26 (s, 6H, N-CH_{3(Ir)}); 2.74 (qq, 4H, ${}^{3}J_{H-H} = 7.0 \text{ Hz}, {}^{3}J_{H-H} = 7.0 \text{ Hz}, {}^{i}Pr_{C-H}$); 1.34 (d, 12H, ${}^{3}J_{H-H} = 7.0 \text{ Hz}$), 1.12 (d, 12H, ${}^{3}J_{H-H} = 7.0 \text{ Hz}, {}^{i}Pr_{Me(Ir)}$). ¹³C{¹H} NMR (100.54 MHz, acetonitrile- d_3 , 26.5 °C): δ 160.3 (s, 2C, $C_{carbene}$; 182.1 (s, 2C, CO_{trans}); 173.9 (s, 2C, CO_{cis}); 143.1 (s, 2C, Trz_{quat}); 146.2 (s, 4C, $Ar_{quat}^{-i}Pr$); 136.1 (s, 2C, $Ar_{quat}^{-i}N_{Ir}$); 130.4 (s, 2C), 123.2 (s, 4C, Ar_{C-H}); 131.5 (s, 2C, $linkAr_{quat}$); 134.0 (s, 1C), 129.2 (s, 2C, $linkerAr_{C-H}$); 130.9 (s, 1C, $linkAr_{quat}^{-link}Ar_{C-H}^{-link}Ar_{quat}$); 130.9 (s, 1C), $linkAr_{quat}^{-link}Ar_{C-H}^{-link}Ar_{quat}$); 130.9 (s, 1C), $linkAr_{quat}^{-link}Ar_{C-H}^{-link}Ar_{quat}^{-link}A$ 35.6 (s, 2C, N-CH₃); 28.1 (s, 4C, ${}^{i}Pr_{C-H}$); 23.5 (s, 8C, ${}^{i}Pr_{CH}$). IR (solution, cm⁻¹): 1981, 2053 (CO). Anal. Calcd for $C_{40}H_{44}I_2Ir_2N_6O_4$: C, 36.64; H, 3.38; N, 6.41. Found: C, 36.75; H, 3.55; N, 6.72.

(j). (1-(2,6-Diisopropylphenyl)-4-(3-(1-(2,6-diisopropylphenyl)-3methyl-1H-1,2,3-triazol-3-ium-4-yl)phenyl)-3-methyl-1H-1,2,3-triazol-3-ium-5-yl)(η^2 · η^2 -cycloocta-1,5-diene)iodidorhodium(l) lodide, [Rhl(COD)(κ^1 -^{Dipp}TrzTrz(H))][l] (**11**). The desired product was prepared as described for 7, using 6 (0.114 g, 0.13 mmol), [Rh(μ -OMe)(COD)]₂ (0.042 g, 0.086 mmol), and KI (0.105 g, 0.63 mmol). The solution was heated at 80 °C in a sealed container for 1 h and cooled to room temperature, at which point it turned dark orange. The solvent was removed under reduced pressure, the crude product was redissolved in 3 mL of acetonitrile, and this solution was filtered through Celite. A 45 mL portion of diethyl ether was added to precipitate a yellow solid, and the mother liquor was removed via cannula. The precipitate was washed with 5×20 mL portions of *n*pentane before drying in vacuo, giving a bright yellow powder (0.112 g, 82%). ¹H NMR (399.80 MHz, acetonitrile- d_3 , 26.5 °C): δ 9.06 (s, 1H, H_{Trz}); 8.56 (br dd, 1H, ${}^{4}J_{H-H} = 1.6$ Hz, ${}^{4}J_{H-H} = 1.6$ Hz), 8.42 $(ddd, 1H, {}^{3}J_{H-H} = 7.7 \text{ Hz}, {}^{4}J_{H-H} = 1.6 \text{ Hz}, {}^{4}J_{H-H} = 1.6 \text{ Hz}), 8.01 (ddd, 1H, {}^{3}J_{H-H} = 1.6 \text{ Hz}), 8.01 (ddd, {}^{3}J_{H-H} = 1.6 \text{ Hz}), 8$ 1H, ${}^{3}J_{H-H} = 7.7$ Hz, ${}^{4}J_{H-H} = 1.6$ Hz, ${}^{4}J_{H-H} = 1.6$ Hz), 7.95 (dd, 1H, ${}^{3}J_{H-H} = 7.7$ Hz, ${}^{3}J_{H-H} = 7.7$ Hz, ${}^{3}J_{H-H} = 7.7$ Hz, ${}^{3}J_{H-H} = 7.9$ Hz), 7.45 (d, 2H, ${}^{3}J_{H-H} = 7.9$ Hz, Ar_{Dipp(Rh)}); 7.74 (t, 1H, ${}^{3}J_{H-H} = 7.9$ Hz), 7.54 (d, 2H, ${}^{3}J_{H-H} = 7.9$ Hz, $Ar_{Dipp(H^{+})}$); 4.18 (s, 3H, N-CH_{3(Rh)}); 4.54 (s, 3H, N-CH_{3(H⁺)}); 2.54 (qq, 2H, ${}^{3}J_{H-H} = 6.9$ Hz, ${}^{3}J_{H-H} = 6.9$ Hz), 2.52 (qq, 2H, ${}^{3}J_{H-H} = 6.9$ Hz, ${}^{3}J_{H-H} = 6.9$ Hz, ${}^{i}Pr_{C-H}$); 1.21 (d, 12H, ${}^{3}J_{H-H} = 6.9$ Hz, ${}^{i}Pr_{Me(Rh)}$); 1.27 (d, 12H, ${}^{3}J_{H-H} = 6.9$ Hz, $^{1}Pr_{Me(H^{+})}$; 4.73 (br s, 2H, $COD_{C-H(trans)}$); 3.48 (br s, 2H, $COD_{C-H(cis)}$); 2.01–1.97 (m, 8H, COD_{alk}). $^{13}C{^{1}H}$ NMR (100.54 MHz, acetonitrile- d_3 , 26.5 °C): δ 171.0 (d, 1C, ${}^1J_{C-Rh} = 46.1$ Hz, $C_{carbene}$); 144.5 (s, 1C, $Trz_{quat(Rh)}$); 143.7 (s, 1C, $Trz_{quat(H^{+})}$); 131.3 (s, 1C, Trz_{C-H}); 146.3 (s, 2C, $Ar_{quat} - Pr_{(Rh)}$); 145.7 (s, 2C, $Ar_{quat} - Pr_{(H^*)}$; 135.9 (s, 1C, $Ar_{quat} - N_{Rh}$); 124.0 (br s, 1C, $Ar_{$ N_H⁺); 130.7 (s, 1C), 124.0 (s, 2C, Ar_{C-H(Rh)}); 133.1 (s, 1C), 124.9 (s,

2C, $Ar_{C-H(H^{+})}$; 131.1 (s, 1C), 130.8 (s, 1C, $^{link}Ar_{quat}$); 134.4 (s, 1C), 129.2 (s, 1C), 131.0 (s, 1C, $^{linker}Ar_{C-H}$); 132.2 (s, 1C, $^{link-}Ar_{quat} - ^{link}Ar_{C-H} - ^{link}Ar_{quat}$); 37.9 (s, 1C, N-CH_{3(Rh)}); 40.3 (s, 1C, N-CH_{3(H^{+})}); 28.6 (s, 2C), 28.4 (s, 2C, $^{i}Pr_{C-H}$); 23.9 (s, 4C), 23.1 (s, 4C, $^{i}Pr_{CH_3}$); 92.8 (br s, 2C, COD_{trans}); 71.7 (br s, 2C, COD_{cts}); 32.0 (br s, 1C), 29.8 (br s, 1C), 25.7 (br s, 1C), 22.7 (br s, 1C, COD_{CH_2}). HRMS: *m*/*z* calcd for C₄₄H₅₇IN₆Rh (M⁺ – I⁻) 899.2739, found 899.2739 (M⁺ – I⁻). Anal. Calcd for C₄₄H₅₇I₂N₆Rh: C, 51.47; H, 5.60; N, 8.19. Found: C, 51.32; H, 5.51; N, 8.11. The ¹H (Figure S4) and ¹³C{¹H} (Figure S5) NMR spectra of this compound are given in the Supporting Information.

(k). (1-(2,6-Diisopropylphenyl)-4-(3-(1-(2,6-diisopropylphenyl)-3methyl-1H-1,2,3-triazol-3-ium-4-yl)phenyl)-3-methyl-1H-1,2,3-triazol-3-ium-5-yl)(η^2 : η^2 -cycloocta-1,5-diene)iodidoiridium(l) lodide, [Irl(COD)(κ^1 - Dipp TrzTrz(H))][I] (**12**). The desired product was prepared as described for 7, using 6 (0.115 g, 0.134 mmol), [Ir(μ -OMe)(COD)]₂ (0.056 g, 0.084 mmol), and KI (0.122 g, 0.73 mmol). The solution was heated at 80 °C in a sealed container for 2 h and cooled to room temperature, resulting in a color change from yellow to orange. The crude product was purified as described for 7, giving an orange powder (0.121 g, 81%). ¹H NMR (399.80 MHz, acetonitrile- d_3 , 26.5 °C): δ 8.99 (s, 1H, H_{Trz}); 8.61 (dd, 1H, ${}^4J_{H-H}$ = 1.5 Hz, ${}^{4}J_{H-H} = 1.5$ Hz), 8.19 (ddd, 1H, ${}^{3}J_{H-H} = 7.6$ Hz, ${}^{4}J_{H-H} = 1.5$ Hz, ${}^{4}J_{H-H} = 1.5$ Hz), 7.96 (ddd, 1H, ${}^{3}J_{H-H} = 7.6$ Hz, ${}^{4}J_{H-H} = 1.5$ Hz, ${}^{4}J_{H-H} = 1.5 \text{ Hz}$, 7.81 (dd, 1H, ${}^{3}J_{H-H} = 7.6 \text{ Hz}$, ${}^{3}J_{H-H} = 7.6 \text{ Hz}$, Ar_{link}); 7.63 (t, 1H, ${}^{3}J_{H-H} = 8.0$ Hz), 7.45 (d, 2H, ${}^{3}J_{H-H} = 8.0$ Hz, Ar_{Dipp(Ir)}); 7.55 (t, 1H, ${}^{3}J_{H-H} = 8.0 \text{ Hz}$), 7.37 (d, 2H, ${}^{3}J_{H-H} = 8.0 \text{ Hz}$, Ar_{Dipp(H⁺)}); 4.16 (s, 3H, N-CH_{3(Ir)}); 4.61 (s, 3H, N-CH_{3(H⁺)}); 2.47 (qq, 4H, ${}^{3}J_{H-H} = 6.9 \text{ Hz}, {}^{3}J_{H-H} = 6.9 \text{ Hz}, {}^{i}\text{Pr}_{C-H}$; 1.22 (d, 12H, ${}^{3}J_{H-H} = 6.9 \text{ Hz}$, ${}^{i}Pr_{Me(Ir)}$); 1.29 (d, 12H, ${}^{3}J_{H-H}$ = 6.9 Hz, ${}^{i}Pr_{Me(H^{+})}$); 4.20 (br s, 2H, COD_{C-H(trans)}); 3.24 (br s, 2H, COD_{C-H(cis)}); 1.99-0.97 (m, 8H, COD_{alk}). ¹³C{¹H} NMR (100.54 MHz, acetonitrile- d_3 , 26.5 °C): δ 168.4 (s, 1C, C_{carbene}); 143.4 (s, 1C, Trz_{quat(Ir)}); 143.5 (s, 1C, $Trz_{quat(H^+)}$); 130.9 (s, 1C, Trz_{C-H}); 146.2 (s, 2C, $Ar_{quat}-{}^{i}Pr_{(Ir)}$); 145.1 (s, 2C, Ar_{quat} - $Pr_{(H^{+})}$); 135.8 (s, 1C, Ar_{quat} - N_{Ir}); 124.1 (br s, 1C, Ar_{quat} - $N_{H^{+}}$); 131.0 (s, 1C), 124.6 (s, 2C, $Ar_{C-H(Ir)}$); 133.2 (s, 1C), $N-CH_{3(H^{+})}$; 28.3 (s, 2C), 28.1 (s, 2C, ^{*i*}Pr_{C-H}); 23.8 (s, 4C), 23.1 (s, 4C, ⁱPr_{CH₂}); 80.2 (s, 2C, COD_{trans}); 52.5 (s, 2C, COD_{cis}); 28.1 (s, 1C), 27.2 (s, 1C), 25.2 (s, 1C), 21.7 (s, 1C, COD_{CH}). HRMS: *m/z* calcd for $C_{44}H_{57}IIrN_6$ (M⁺ - I⁻), 989.3313, found 989.3310 (M⁺ - I⁻). Anal. Calcd for C44H57I2N6Ir: C, 47.35; H, 5.15; N, 7.53. Found: C, 47.55; H, 5.32; N, 7.24.

(l). (1-(2,6-Diisopropylphenyl)-4-(3-(1-(2,6-diisopropylphenyl)-3methyl-1H-1,2,3-triazol-3-ium-4-yl)phenyl)-3-methyl-1H-1,2,3-triazol-3-ium-5-yl)dicarbonyliodidorhodium(1) lodide, [Rhl- $(CO)_{2}(\kappa^{1}-DippTrzTrz(H))][I]$ (13). The desired product was prepared as described for 9, except starting with 11 (0.312 g, 0.30 mmol). The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of CH₂Cl₂. A 30 mL portion of diethyl ether was quickly added to precipitate a yellow solid, which was washed with 5 \times 25 mL portions of *n*-pentane before drying in vacuo, giving a yellow powder (0.285 g, 96%) of), although all samples showed evidence of decomposition to an unknown, more symmetric product when dissolved in solution (omitted here in spectral data). ¹H NMR (499.82 MHz, acetonitrile- d_{3} , 27.7 °C): δ 8.87 (s, 1H, H_{Trz}); 8.35 (br dd, 1H, ${}^{4}J_{H-H} = 1.4$ Hz, ${}^{4}J_{H-H} = 1.4$ Hz), 8.13 (ddd, 1H, ${}^{3}J_{H-H} = 7.5$ Hz, ${}^{4}J_{H-H} = 1.4$ Hz, ${}^{4}J_{H-H} = 1.4$ Hz), 7.98 (ddd, 1H, ${}^{3}J_{H-H} = 7.5$ Hz, ${}^{4}J_{H-H} = 1.4 \text{ Hz}, {}^{4}J_{H-H} = 1.4 \text{ Hz}), 7.89 \text{ (dd, 1H, } {}^{3}J_{H-H} = 7.5 \text{ Hz}, {}^{3}J_{H-H} = 1.4 \text{ Hz}$ 7.5 Hz, Ar_{link}); 7.72 (t, 1H, ${}^{3}J_{H-H}$ = 8.0 Hz), 7.43 (d, 2H, ${}^{3}J_{H-H}$ = 8.0 Hz, Ar_{Dipp(Rh)}); 7.63 (t, 1H, ${}^{3}J_{H-H}$ = 7.9 Hz), 7.52 (d, 2H, ${}^{3}J_{H-H}$ = 7.9 Hz, $Ar_{Dipp(H^{+})}$; 4.21 (s, 3H, N-CH_{3(Rh)}); 4.52 (s, 3H, N-CH_{3(H^{+})}); 2.52 (qq, 4H, ${}^{3}J_{H-H} = 6.9$ Hz, ${}^{3}J_{H-H} = 6.9$ Hz, ${}^{i}Pr_{C-H}$); 1.23 (d, 12H, ${}^{3}J_{H-H} = 6.9 \text{ Hz}, {}^{i}Pr_{Me(Rh)}$; 1.19 (d, 12H, ${}^{3}J_{H-H} = 6.9 \text{ Hz}, {}^{i}Pr_{Me(H^{+})}$). $^{13}C{^{1}H}$ NMR (100.54 MHz, acetonitrile- d_3 , 26.5 °C): δ 162.3 (d, 1C, ${}^{1}J_{C-Rh} = 40.1 \text{ Hz}, C_{carbene}$; 187.6 (d, 1C, ${}^{1}J_{C-Rh} = 53.4 \text{ Hz}, CO_{trans}$);

182.1 (d, 1C, ${}^{1}J_{C-Rh} = 77.6$ Hz, CO_{cis}); 143.5 (s, 1C, $Trz_{quat(Rh)}$); 143.2 (s, 1C, $Trz_{quat(H^{-})}$); 133.5 (s, 1C, Trz_{C-H}); 147.2 (s, 2C, $Ar_{quat} - {}^{i}Pr_{(Rh)}$); 145.6 (s, 2C, $Ar_{quat} - {}^{i}Pr_{(H^{-})}$); 135.2 (s, 1C, $Ar_{quat} - N_{Rh}$); 124.1 (s, 1C, $Ar_{quat} - N_{H^{+}}$); 130.5 (s, 1C), 124.1 (s, 2C, $Ar_{C-H(Rh)}$); 133.5 (s, 1C), 125.3 (s, 2C, $Ar_{C-H(H^{+})}$); 130.7 (s, 1C), 131.5 (s, 1C, $IinkAr_{quat}$); 132.1 (s, 1C), 129.3 (s, 1C), 131.2 (s, 1C, $N-CH_{3(Rh)}$); 41.3 (s, 1C, $N-CH_{3(H^{+})}$); 28.5 (s, 2C), 28.2 (s, 2C, ${}^{i}Pr_{C-H}$); 23.8 (s, 4C), 23.1 (s, 4C, ${}^{i}Pr_{CH_3}$). IR (solution, cm⁻¹): 1989, 2065 (CO). HRMS: m/z calcd for $C_{38}H_{45}IN_6O_2Rh$ ($M^{+} - I^{-}$) 847.1698, found 847.1689 ($M^{+} - I^{-}$). The ${}^{1}H$ (Figure S7) NMR spectra of this compound are given in the Supporting Information.

(m). (1-(2,6-Diisopropylphenyl)-4-(3-(1-(2,6-diisopropylphenyl)-3methyl-1H-1,2,3-triazol-3-ium-4-yl)phenyl)-3-methyl-1H-1,2,3-triazol-3-ium-5-yl)dicarbonyliodidoiridium(l) lodide, [Irl- $(CO)_2(\kappa^{1}_DippTrzTrz(H))][I]$ (14). The desired product was prepared as described for 9, except starting with 12 (0.321 g, 0.29 mmol). The solution turned pale yellow after 15 min of a CO purge. The crude product was purified as described for 13 and isolated as a yellow powder (0.210 g, 69%), although all samples showed evidence of decomposition to an unknown, more symmetric product when dissolved in solution (omitted here in spectral data). ¹H NMR (399.80 MHz, acetonitrile-*d*₃, 26.5 °C): δ 8.78 (s, 1H, H_{Trz}); 8.71 (dd, 1H, ${}^{4}J_{H-H} = 1.3$ Hz, ${}^{4}J_{H-H} = 1.3$ Hz), 8.13 (ddd, 1H, ${}^{3}J_{H-H} = 7.7$ Hz, ${}^{4}J_{H-H} = 1.3 \text{ Hz}, {}^{4}J_{H-H} = 1.3 \text{ Hz}), 7.92 \text{ (ddd, 1H, } {}^{3}J_{H-H} = 7.7 \text{ Hz}, {}^{4}J_{H-H}$ = 1.3 Hz, ${}^{4}J_{H-H}$ = 1.3 Hz), 7.81 (dd, 1H, ${}^{3}J_{H-H}$ = 7.7 Hz, ${}^{3}J_{H-H}$ = 7.7 Hz, Ar_{link}); 7.55 (t, 1H, ${}^{3}J_{H-H}$ = 7.8 Hz), 7.45 (d, 2H, ${}^{3}J_{H-H}$ = 7.8 Hz, $\begin{array}{l} \text{Ar}_{\text{Dipp}(\text{Ir})}; \ 7.50 \ (t, \ 1H, \ {}^{3}J_{\text{H}-\text{H}} = 8.0 \ \text{Hz}), \ 7.35 \ (d, \ 2H, \ {}^{3}J_{\text{H}-\text{H}} = 8.0 \ \text{Hz}, \\ \text{Ar}_{\text{Dipp}(\text{I}^{+})}; \ 4.11 \ (s, \ 3H, \ \text{N}-\text{CH}_{3(\text{Ir})}); \ 4.65 \ (s, \ 3H, \ \text{N}-\text{CH}_{3(\text{H}^{+})}); \ 2.47 \end{array}$ $(qq, 4H, {}^{3}J_{H-H} = 6.9 \text{ Hz}, {}^{3}J_{H-H} = 6.9 \text{ Hz}, {}^{P}r_{C-H}); 1.21 \text{ (d, 12H, } {}^{3}J_{H-H})$ = 7.0 Hz, ${}^{i}Pr_{Me(Ir)}$); 1.26 (d, 12H, ${}^{3}J_{H-H}$ = 7.0 Hz, ${}^{i}Pr_{Me(H^{*})}$). ${}^{13}C\{{}^{1}H\}$ NMR (100.54 MHz, acetonitrile- d_{3} , 26.5 °C): δ 160.1 (s, 1C, C_{carbene}); 181.9 (s, 1C, CO_{trans}); 174.2 (s, 1C, CO_{cis}); 142.7 (s, 1C, Trz_{quat}(Ir)); 143.3 (s, 1C, $\operatorname{Trz}_{quat(H^{+})}$); 131.4 (s, 1C, Trz_{C-H}); 145.3 (s, 2C, $Ar_{quat} - {}^{i}Pr_{(Ir)}$; 144.1 (s, 2C, $Ar_{quat} - {}^{i}Pr_{(H^{+})}$); 135.6 (s, 1C, $Ar_{quat} - N_{Ir}$); 122.1 (br s, 1C, $Ar_{quat}-N_{H^{+}}$); 130.6 (s, 1C), 124.5 (s, 2C, $Ar_{C-H(Ir)}$); 133.1 (s, 1C), 124.1 (s, 2C, $Ar_{C-H(H^{\dagger})}$); 130.9 (s, 1C), 129.5 (s, 1C, $^{link}Ar_{quat}$); 134.0 (s, 1C), 129.2 (s, 1C), 130.8 (s, 1C, $^{linker}Ar_{C-H}$); 132.1 (s, 1C, $^{\text{link}}Ar_{\text{quat}} - ^{\text{link}}Ar_{\text{C-H}} - ^{\text{link}}Ar_{\text{quat}}$); 35.5 (s, 1C, N–CH₃(_{Ir})); 40.1 (s, 1C, N–CH₃(_H⁺)); 28.2 (s, 2C), 28.1 (s, 2C, $^{\text{Pr}}C_{\text{-H}}$); 23.7 (s, 4C), 23.0 (s, 4C, ⁱPr_{CH2}). IR (solution, cm⁻¹): 1980, 2054 (CO). Anal. Calcd for C38H45I2IrN6O2: C, 42.90; H, 4.26; N, 7.90. Found: C, 43.15; H, 4.56; N, 7.73.

(n). (1-(2,6-Diisopropylphenyl)-4-(3-(1-(2,6-diisopropylphenyl)-3methyl-1H-1,2,3-triazol-3-ium-5-yl)(($\eta^{2}:\eta^{2}$ -cycloocta-1,5-diene)iodidoiridium(l))phenyl)-3-methyl-1H-1,2,3-triazol-3-ium-5-yl)-($\eta^{2}:\eta^{2}$ -cycloocta-1,5-diene)iodidorhodium(l), [Irl(COD)($\mu^{-Dipp}Trz_{2}$)-Rhl(COD)] (15). Route 1. A 10 mL portion of acetonitrile was added to a solid mixture containing 11 (0.334 g, 0.33 mmol), [Ir(μ -OMe)(COD)]₂ (0.118 g, 0.18 mmol), and KI (0.297 g, 1.79 mmol) under an inert Ar(g) atmosphere. The resulting solution was stirred for 2 h at 80 °C in a sealed container and cooled to room temperature. The solvent was then removed under reduced pressure and the crude product redissolved in 3 mL of acetonitrile and filtered through Celite. A 45 mL portion of *n*-pentane was added to precipitate an orange solid, and the mother liquor was removed via cannula. The product was recrystallized from benzene/*n*-pentane and washed with 5 × 20 mL portions of *n*-pentane before drying in vacuo, giving an orange powder (0.328 g, 76%).

Route 2. The desired product was prepared as described for route 1, using **12** (0.573 g, 0.51 mmol), $[Rh(\mu-OMe)(COD)]_2$ (0.162 g, 0.33 mmol), and KI (0.128 g, 0.77 mmol). The resulting solution was stirred for 1 h at 80 °C in a sealed container and cooled to room temperature. The crude product was purified as described for route 1 and isolated as a bright orange solid (0.544 g, 80%). ¹H NMR (498.12 MHz, acetonitrile- d_3 , 26.1 °C): δ 8.50 (dd, 1H, ${}^4J_{H-H} = 1.3$ Hz, ${}^4J_{H-H} = 1.3$ Hz, ${}^4J_{H-H} = 1.3$ Hz, ${}^4J_{H-H} = 1.3$ Hz), 8.45 (ddd, 1H, ${}^3J_{H-H} = 7.5$ Hz, ${}^4J_{H-H} = 1.3$ Hz, ${}^4J_{H-H} = 1.3$ Hz), 8.21 (ddd, 1H, ${}^3J_{H-H} = 7.5$ Hz, ${}^4J_{H-H} = 1.3$ Hz), H_2 , H_3 , H_2 , H_3

7.95 (dd, 1H, ${}^{3}J_{H-H} = 7.5$ Hz, ${}^{3}J_{H-H} = 7.5$ Hz, Ar_{link}); 7.60 (t, 1H, ${}^{3}J_{H-H} = 8.0 \text{ Hz}$), 7.65 (t, 1H, ${}^{3}J_{H-H} = 7.9 \text{ Hz}$), 7.41 (d, 2H, ${}^{3}J_{H-H} = 7.9 \text{ Hz}$) Hz), 7.45 (d, 2H, ${}^{3}J_{H-H} = 7.9$ Hz, Ar_{Dipp}); 4.18 (s, 3H), 4.13 (s, 3H, N-CH₃); 2.54 (qq, 2H, ${}^{3}J_{H-H} = 6.9$ Hz, ${}^{3}J_{H-H} = 6.9$ Hz), 2.48 (qq, 2H, ${}^{3}J_{H-H} = 6.9$ Hz, ${}^{3}J_{H-H} = 6.9$ Hz, ${}^{1}Pr_{C-H}$); 1.23 (d, 12H, ${}^{3}J_{H-H} = 6.9$ Hz); 1.21 (d, 12H, ${}^{3}J_{H-H} = 6.9$ Hz, ${}^{i}Pr_{Me}$); 4.70 (br s, 2H), 4.10 (br s, 2H, $COD_{C-H(trans)}$; 3.45 (br s, 2H), 3.20 (br s, 2H, $COD_{C-H(cis)}$); 2.03–1.98 (m, 16H, COD_{alk}). ¹³C{¹H} NMR (125.69 MHz, acetonitrile- d_3 , 27.7 °C): δ 171.0 (d, 1C, ¹J_{C-Rh} = 46.7 Hz, C_{carbene(Rh})); 169.5 (s, 1C, C_{carbene(Ir)}); 144.5 (s, 1C), 143.1 (s, 1C, Trz_{quat}); 146.3 (s, 2C), 145.8 (s, 1C, Ar_{quat-iPr}); 135.9 (s, 1C), 135.7 (s, 1C, Ar_{quat-N}); $\begin{array}{l} 131.0 (s, 1C), 130.1 (s, 1C), 124.4 (s, 2C), 124.9 (s, 2C, Ar_{C-H}); 131.2 \\ (s, 1C), 130.8 (s, 1C, linkerAr_{quat}); 134.6 (s, 1C), 133.4 (s, 1C), 131.2 \\ (s, 1C, linkerAr_{C-H}); 132.4 (s, 1C, linkerAr_{quat}-linkerAr_{C-H}-linkAr_{quat}); 38.5 \\ (s, 1C), 37.4 (s, 1C, N-CH_3); 28.8 (s, 2C), 28.7 (s, 2C, Pr_{C-H}); 23.9 \\ \end{array}$ (s, 4C), 23.6 (s, 4C, ⁱPr_{CH₃}); 91.6 (br s, 2C), 80.1 (s, 2C, COD_{trans}); 71.3 (br s, 2C), 51.6 (s, 2C, COD_{cis}); 32.2 (br s, 1C), 30.2 (s, 1C), 29.7 (br s, 1C), 27.2 (s, 1C), 25.6 (s, 1C), 25.4 (br s, 1C), 22.9 (br s, 1C), 20.1 (s, 1C, COD_{CH3}). Anal. Calcd for C₅₂H₆₈I₂IrN₆Rh: C, 47.10; H, 5.17; N, 6.34. Found: C, 46.64; H, 4.85; N, 6.00. The ¹H NMR spectrum (Figure S8) of this compound is given in the Supporting Information.

X-ray Structure Determinations. Crystals were obtained by slow diffusion of diethyl ether into a CH2Cl2 solution of the di-Rh complex 7. Data were collected⁸⁶ using a Bruker APEX II detector/D8 diffractometer equipped with a Cu microfocus source. The data were corrected for absorption through use of Gaussian integration with the indexed faces and measured dimensions of the crystal. The structure was solved using direct methods (SHELXD).⁸⁷ The program SHELXL-97⁸⁸ was used for structure refinements. Hydrogen atoms were assigned positions on the basis of the geometries of their attached carbon atoms and were given thermal parameters 120% of their parent carbons. See Table S1 in the Supporting Information for a listing of crystallographic experimental data. The anisotropic displacement parameters for the carbon atoms of both the cyclooctadiene ligands and the diisopropylphenyl groups indicated significant disorder, which was ultimately modeled as a 50/50 disorder over two positions for each offending group. Within the disordered COD ligands, the C-C distances were restrained to have the same target value (refined to \sim 1.506(6) Å); likewise, the C=C distances were treated similarly (refined to 1.370(9) Å). Further, the phenyl rings for three of the four orientations for disordered diisopropylphenyl groups were constrained to be idealized hexagons with C-C distances of 1.39 Å.

ASSOCIATED CONTENT

S Supporting Information

Figures giving the ¹H NMR spectra of 6, 9, 11, 13, and 15 and the ¹³C{¹H} NMR spectra of 9, 11, and 13, tables of crystallographic experimental details, dihedral angles, and selected bond lengths and angles for compound 7, and a CIF file giving atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for compound 7. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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