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Transition Metal Complexes of a Bis(carbene) Ligand Featuring 1,2,4-Triazolin-5-ylidene Donors: Structural Diversity and Catalytic Applications

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Abstract:

Dialkylation of the 1,3-bis(1,2,4-triazol-1-yl)benzene with ethyl bromide resulted in the formation of [**L**-H_2]Br_2 which upon salt metathesis with NH_4PF_6 readily yielded the bis(triazolium) salt [**L**-H_2]$(PF_6)_2$ with non-coordinating counterions. [**L**-H_2]$(PF_6)_2$ and Ag_2O react in 1:1 ratio to yield a binuclear Ag^I-tetracarbene complex of composition [(**L**)$_2Ag_2$]$(PF_6)_2$ which undergoes facile transmetalation reaction with [Cu(SMe_2)Br] to deliver the corresponding Cu^I-NHC complex [(**L**)$_2Cu_2$]$(PF_6)_2$. In contrast, the [**L**-H_2]Br_2 reacts with [Ir(Cp*)Cl_2]$_2$ to generate a doubly C-H activated Ir^{III}-NHC complex **5**. Similarly, the triazolinylidene donor supported diorthometalated Ru^{II}-complex **6** was also obtained. Complexes **5** and **6** represent the first examples of stable diorthometalated binuclear Ir^{III}/Ru^{II}-complex, respectively supported by 1,2,4-triazolin-5-ylidene donors. The synthesized Ir^{III}-NHC complex **5** was found to be more effective than their Ru^{II}-analogue (**6**) for the reduction of a range of alkenes/alkynes via the transfer hydrogenation strategy. Conversely, the Ru^{II}-complex **6** was identified as an efficient catalyst (0.01 mol% loading) for the β-alkylation of a wide range of secondary alcohols using primary alcohols as alkylating partners via borrowing hydrogen strategy.

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Introduction

During the past few decades, N-heterocyclic carbenes (NHCs) have become very popular in organometallic chemistry especially, in catalysis.[1] The ease of synthesis along with the tuning of their stereoelectronic properties coupled with strong σ-donor ability have made them an elite class of ligands.[1b,2] Although NHC ligands based on the imidazole heterocycles (ImNHCs) are the most extensively studied ones,[1a,3] click-derived triazole containing analogues (tzNHCs), commonly known as mesoionic carbenes (MICs), became popular in the carbene chemistry after their captivating reactivity and applications introduced by Albrecht *et al.*.[4a-e] Among triazole based NHCs, 1,2,3-triazolin-5-ylidenes are the most common ones and have gained the attention of the researchers. On contrary, transition metal chemistry of the 1,2,4-triazolin-5-ylidene donor, introduced to the mainstream research by Enders and coworkers,[4f,g] containing systems are rather unexplored although they might lead to interesting systems because of its weak σ-donating and strong π-accepting properties as compared to the most studied ImNHC moiety.[5]

Cyclometalated, in particular, orthometalated complexes are gaining researchers' attention mostly due to their increased stability as compared to their non-chelated variants.[6] However, the reported orthometalated late transition metal-NHC complexes containing Ir^{III} and Ru^{II} metals mostly are of mononuclear type.[6] Only recently, related multinuclear iridium-NHC complexes[7a-e] have been highlighted for their augmented catalytic efficiency, but, still the multinuclear ruthenium-NHC complexes are rare in the literature.[7f] Multiple azolium units installed at a phenyl ring featuring various substitution patterns are the common structural motifs in this area. In general, 1,4-phenylene-bridged bis(azolium) salts tend to form diorthometalated complexes via double C-H activation (Scheme 1a-b), whereas, 1,3-phenylene-bridged ones are more prevailed to produce mononuclear pincer-type complexes because of the inherent difference in their geometry.[8] In 2014, Sarkar *et al*. have reported the stable diorthometalated, resulting 5-membered iridacycles, Ir^{III}-complexes of 1,4-phenyl-substituted bis(1,2,3-triazole or 1,2,3-triazolin-5-ylidene) containing ligands with a C^N or C^C binding modes (Scheme 1b).[7a] It should be noted that the formation of a mixture of mono- and dinuclear orthometalated Ru^{II}-NHC complexes was observed for the related bis-imidazolium ligand.[7f] Later in 2016, Graiff's group has reported another doubly orthometalated binuclear Ir^{III}-complex of 1,4-phenyl-substituted ImNHC based ligand system, however, featuring six-membered iridium-containing chelate rings (Scheme 1a).[7b]

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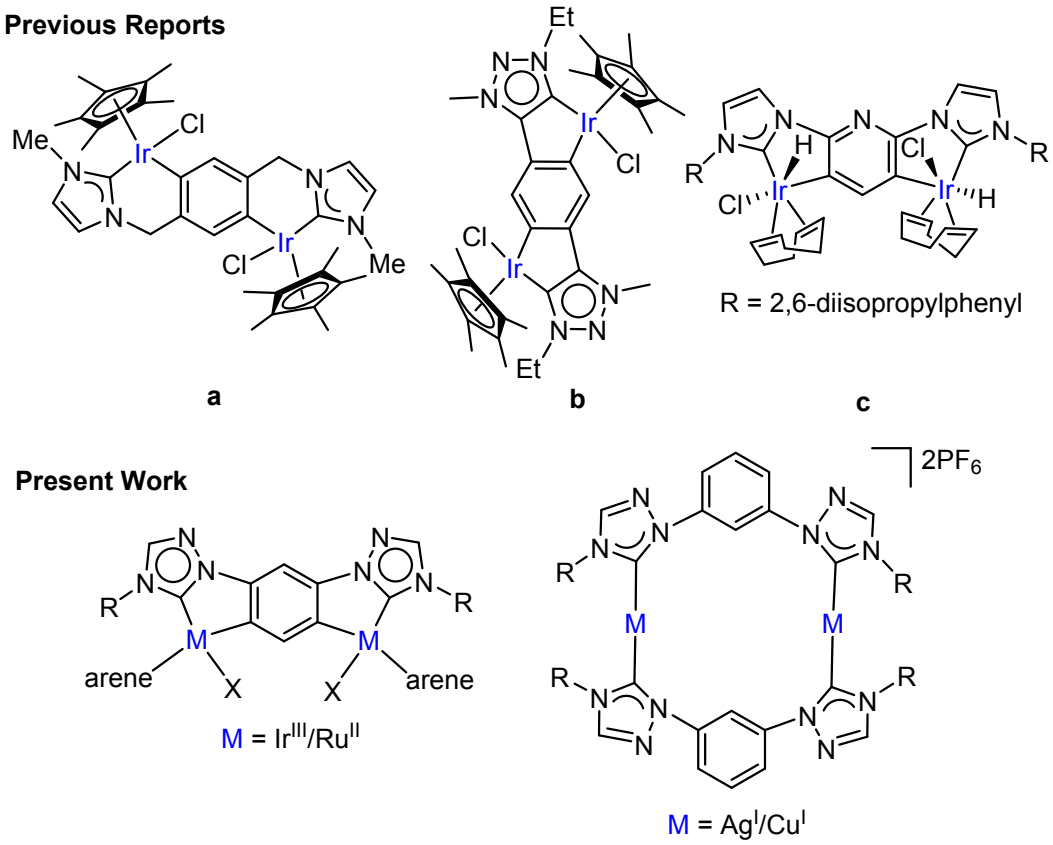
Scheme 1. Overview of the reported orthometalated binuclear bis-NHC complexes and the present work.



Conversely, the only diorthometalated Ir^{III}-NHC metal complex based on a 1,3-diaryl-substitution pattern was reported by Danopoulos *et al*. by employing a ligand precursor where two imidazolium units are installed at a pyridine rather than a phenyl platform (Scheme 1c). However, it should be noted that the relatively reactive Ir^{I}-precursor $[Ir(cod)Cl]_2$ was utilized for this purpose.[9a] It is worth mentioning that the Ru^{II}-based such complexes with double C-H activation are not known in the literature to the extent of our knowledge. Further, the chemistry of poly-NHC ligand possessing 1,2,4-triazolin-5-ylidene donors is rather unexplored.[5e,f] Therefore, we became interested in developing the chemistry of bis(NHC) ligands incorporating 1,2,4-triazolin-5-ylidene donors. Herein, we present the coordination behavior of a 1,3-disubstituted phenylene-based bis(1,2,4-triazolium) salt towards the coinage metals (Ag^{I} and Cu^{I}) as well as the catalytically relevant Ru^{II}- and Ir^{III}-metal centers. Coinage metals resulted in the formation of binuclear tetracarbene complexes of general formula $[(\mathbf{L})_2M_2](PF_6)_2$, whereas, the Ru^{II}- and Ir^{III}-metal centers gave access to the 1,2,4-triazolin-5-ylidene donor supported doubly orthometalated

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binuclear complexes. Iridium-complexes are reported to be effective as catalysts in the reduction of unsaturated functional groups, whereas in recent years, the Ru^{II}-complexes are also securing their position as efficient catalyst systems in various important organic transformations.[5a,6a,b] Keeping this in mind, we also studied the catalytic efficiency of the synthesized binuclear Ir^{III}- and Ru^{II}-NHC complexes which unveiled that the Ir^{III}-NHC complex **5** is more effective than its Ru^{II}-analogue, **6** for the catalytic reduction of alkenes/alkynes via the transfer hydrogenation strategy. Further, the Ru^{II}-complex **6** was identified as an efficient catalyst for the β-alkylation of diverse secondary alcohols using primary alcohols.

Results and Discussion

Synthesis of the Bis(triazolium) Salts 1 and 2. The 1,3-bis(1,2,4-triazol-1-yl)benzene (**A**) was synthesized via coupling of the 1,3-dibromobenzene with 1,2,4-triazole by following a modified literature procedure.[10a] Further alkylation of **A** with ethyl bromide in DMF gave the ethylated compound [**L**-H_2]Br_2 (**1**) in 75% yield as a white solid (Scheme 2a). Presence of the characteristic downfield shifted triazolium proton signals at δ = 11.32/9.64 ppm along with the *N*-ethyl protons at 4.42 ppm (quartet for the CH_2) and 1.60 ppm (triplet for the CH_3) confirms the quaternization of the triazole ring (Fig. S1). Exchange of the bromide counterions in [**L**-H_2]Br_2 with the non-coordinating PF_6 ions via salt metathesis using NH_4PF_6 in methanol provided the [**L**-H_2]$(PF_6)_2$ in an excellent yield of 94% (Scheme 2a). This exchange of counterions is supported by the ^{19}F and ^{31}P NMR studies and the change in chemical shift of the triazolium ^1H NMR signals to δ = 11.12/9.56 ppm. This shift is possibly due to lesser hydrogen bonding interaction of the PF_6 counterions with the triazolium protons as compared to bromide ions.[9b] Formation of the triazolium salts is supported by the ESI mass spectra (positive ions) of [**L**-H_2]Br_2 and [**L**-H_2]$(PF_6)_2$ displaying peaks at *m/z* = 452.9827 for the monopositive fragment $[M+Na]^+$ (calculated *m/z* = 452.9837) and at *m/z* = 415.1573 for the $[M-PF_6]^+$ fragment (calculated *m/z* = 415.1235), respectively. Single crystal X-ray diffraction studies of a crystal of [**L**-H_2]$(PF_6)_2$ (Scheme 2b) confirmed the expected structures of the compounds. Both the triazolium salts were found to be air/moisture stable and are readily soluble in polar organic solvents like DMF/DMSO but insoluble in solvents such as DCM, THF, and diethyl ether.

Scheme 2. (a) Synthesis of the bis(triazolium) salts [**L**-H_2]Br_2/$(PF_6)_2$. (b) Molecular structure of the [**L**-H_2]$(PF_6)_2$ with displacement parameters at 40% probability level. The PF_6 counterions and

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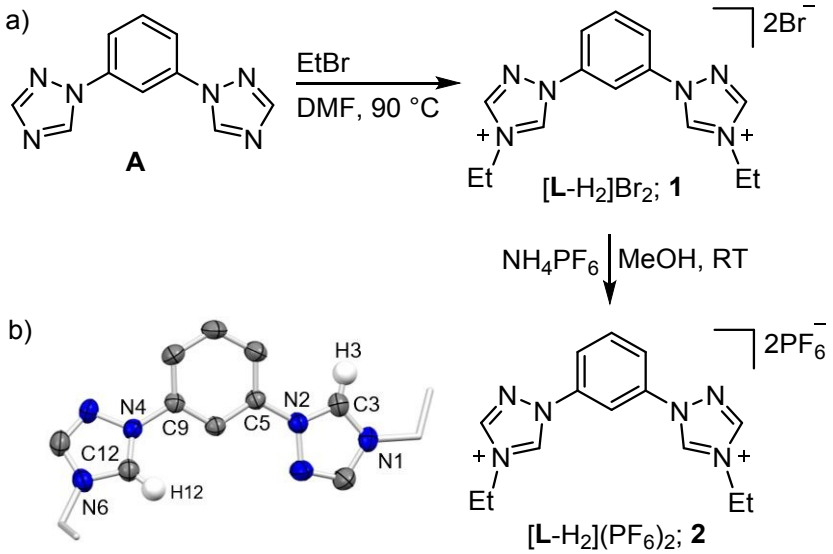
the hydrogen atoms except H3 and H12 are omitted for clarity. *N*-ethyl groups are shown in capped stick.



Synthesis of the Binuclear Ag^{I}- and Cu^{I}-NHC Complexes 3-4. Poly-NHC ligand systems are well known for the generation of supramolecular architectures with coinage metals. Further, Ag^{I}-NHC complexes are known to undergo facile transmetalation reactions to yield various interesting structures containing other transition metal ions.[8a,11] To obtain a new type of Ag^{I}-NHC based architectures, we attempted the metalation of **2** having non-coordinating PF_6 counterions with Ag_2O (which plays the dual role of the base as well as metal source) to give the corresponding Ag^{I}-NHC complex. We chose the triazolium salt with PF_6 rather than a bromide counterion simply because of the fact that (a) presence of a coordinating bromide ion typically leads to complex structures instead of an expected structure based on the ligand architecture employed and (b) absence of coordinating anion leads to the formation of exclusively NHC-based architectures.[12a,b] Accordingly, a binuclear tetracarbene Ag^{I}-complex **3** was isolated from the reaction of **2** with Ag_2O as an air-stable but light-sensitive white solid in an excellent yield of 81% (Scheme 3a). Absence of the most acidic triazolium proton signal at δ = 11.12 ppm and the appearance of the $^{13}C\{^{1}H\}$ NMR signal as two doublets in the range of δ = 183.0–181.4 ppm due to $^{13}C–^{107/109}Ag$ coupling are consistent with the formation of a Ag^{I}-NHC complex (Fig. S8). The appearance of a single ^{1}H NMR resonance at δ = 8.60 ppm for both the triazole backbone protons signifies the formation of a symmetrical complex (Fig. S7). Formation of a binuclear Ag^{I}-tetracarbene complex of composition $[(\mathbf{L})_2Ag_2](PF_6)_2$ is evidenced by the ESI mass spectrometric analysis (positive ions)

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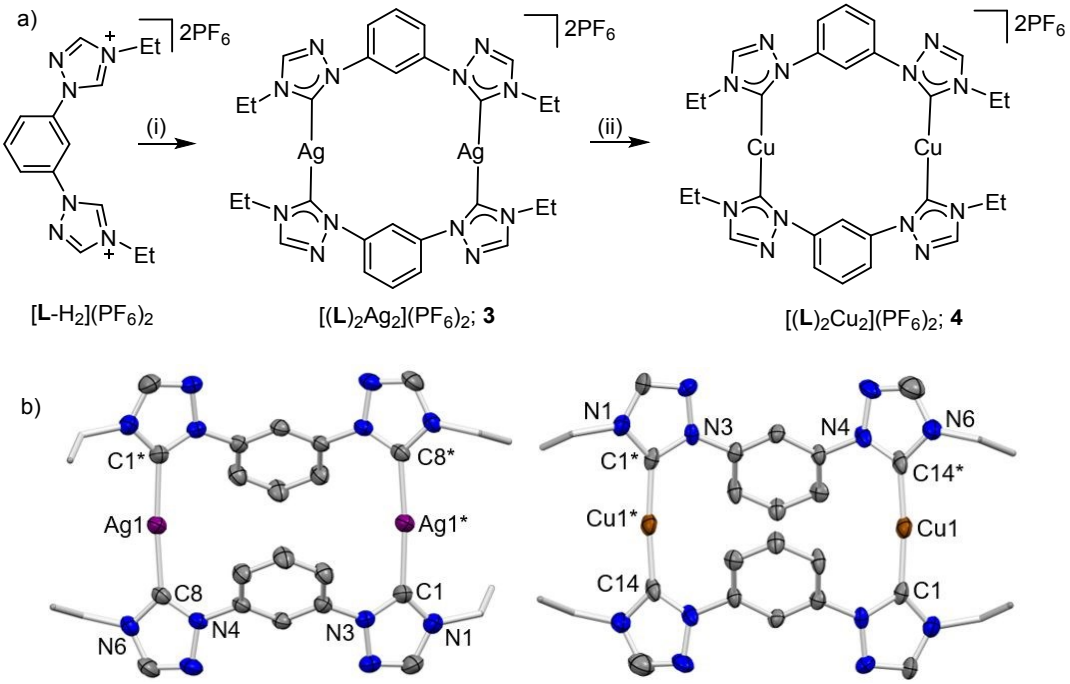
which exhibits the most intense peak at *m/z* = 897.0680 for the corresponding mono-positive fragment $[M-PF_6]^+$ (calculated *m/z* = 897.0619) with isotopic patterns in perfect agreement with the calculated patterns (Fig. S11).

Scheme 3. (a) Synthesis of the binuclear NHC-bridged Ag^I- and Cu^I-complexes **3** and **4**. (i) Ag_2O, CH_3CN, 70 °C, 36 h. (ii) $[Cu(SMe_2)Br]$, CH_3CN, RT, 14 h. (b) Molecular structures of **3** (left) and **4** (right) with displacement parameters at the 40% probability level. Counterions and hydrogen atoms are omitted for clarity. *N*-ethyl groups are shown in capped stick. Some important bond lengths (Å) and bond angles (°): Ag1-C8 2.090(3), Ag1*-C1 2.098(3), C8-Ag1-C1* 174.55(12); Cu1-C1 1.887(11), Cu1*-C14 1.874(12); C1-Cu1-C14* 174.0(4).



The structure of the complex was confirmed by X-ray diffraction studies with a single crystal obtained via slow diffusion of diethyl ether into a saturated solution of the complex **3** in acetonitrile (Scheme 3b). The crystallographic data show that the complex **3** crystallized in monoclinic space group $P2_1/c$. Each silver atom is connected to two triazolinylidene donors from two different ligands in a bridging manner. The geometry around the Ag^I ion slightly deviates from linearity with C8−Ag1−C1* angle of 174.55(12)° and the observed Ag−C_{NHC} bond distances (2.090(3)−2.098(3) Å) fall in the range reported for analogous Ag−NHC complexes.[8a,12c] It is also clear from the crystal structure that the bridging phenyl rings are coplanar to each other with centroid to centroid separation of 4.463 Å and the Ag−Ag distance is found to be 7.218(5) Å.

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Notably the triazolinylidene rings are not oriented perpendicular to the central phenyl ring, but rather inclined towards the phenyl ring (torsion angle of 37.0-44.63°) resulting in a shorter inter-centroid separation of the phenyl rings.

Transmetalation of Ag^{I}-NHC complexes is recognized as a preferred route to obtain various transition metal-NHC complexes than their direct synthesis from the precursor azolium salts.[10b,12b] After getting access to Ag^{I}-NHC complex, we tried the transmetalation strategy to realize other coinage metal complexes and accordingly, treatment of the Ag^{I}-NHC complex **3** with two equivalents of [$Cu(SMe_2)Br$] at room temperature in acetonitrile smoothly afforded a Cu^{I}-NHC complex **4** in good yield of 82%. The complex was isolated as pale yellow air and moisture sensitive solid in contrast to the parent Ag^{I}-NHC complex. Formation of the complex **4** was ascertained by the absence of the characteristic $^{13}C\{^{1}H\}$ NMR resonance of the Ag^{I}-bound carbene carbon at δ= 183.0–181.4 ppm for the complex **3** and the appearance of a new distinct NHC signal at δ= 180.6 ppm corresponding to the Cu^{I}–coordinated carbenic carbon atom. Other ^{1}H (Fig. S12) and ^{13}C-NMR (Fig. S13) resonances for the complex **4** do not show much deviation from the parent Ag-complex. The structure of the complex **4** was established by the X-ray diffraction studies (Scheme 3b) which reveals that the binuclear nature of the parent Ag^{I}–NHC complex **3** is still maintained. Similar transmetalation reactions of polynuclear carbene complexes by retaining the overall structure of the complex have been observed before.[8a,12a] The Cu−Cu separation in **4** was observed to be similar to the corresponding Ag−Ag distance in **3** (7.224(2) vs 7.218(5) Å), whereas, the $Cu-C_{NHC}$ bond lengths are found to be shorter (1.874(12)-1.887(11) Å) than the observed $Ag-C_{NHC}$ bond distances in complex **3** (2.090(3)−2.098(3) Å) as expected from the difference in size between the Cu^{I} and Ag^{I} ions. As observed in the case of Ag^{I}–NHC complex, the phenyl rings are oriented in a co-planar fashion, however, the separation between the centroids of the phenyl rings was found to be 3.980 Å which is ~0.5 Å less than seen in **3**. This can be explained by the shorter bond length of Cu^{I}-NHC than Ag^{I}-NHC and lower torsion angle of the triazolinylidene ring with respect to the phenylene ring in the complex **4** (35.65−43.47°) than in **3** (37.0−44.63°). The geometry around the Cu(I)−center is slightly distorted from the expected linearity with an C1−Cu1−C14* angle of 174.0(5)°.

Synthesis of the Doubly Orthometalated Ir^{III}- and Ru^{II}-NHC Complexes 5-6. After being able to synthesize the binuclear Ag^{I}- and Cu^{I}-NHC complexes which are structurally important and

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thus, no catalytic experiments were performed with them, we then turned our attention towards catalytically relevant Ir^{III}- and Ru^{II}-complexes obtained from [**L**-H_2]Br_2. Taking into consideration that the triazolium salt [**L**-H_2]Br_2 may also provide the corresponding pincer type complexes via activation of the C5-triazolium and one of the central phenyl ring protons, we initially carried out reactions of [**L**-H_2]Br_2 with 0.5 equiv. of [Ir(Cp*)Cl_2]$_2$ under various conditions. However, in all of our attempts, we always observed the formation of a dinuclear Ir^{III}-NHC complex as the main product and mononuclear Ir^{III}-complex was not detected. Finally, the Ir^{III}-complex **5** was obtained in 80% yield as an air stable solid by reacting [**L**-H_2]Br_2 with one equiv. of [Ir(Cp*)Cl_2]$_2$ in presence of Cs_2CO_3 as base in acetonitrile (Scheme 4a). It is to be noted that the related sterically more relaxed 1,4-subtituted bis-imidazolium salt yielded only the mononuclear orthometalated iridium(III)-complex even in the presence of one or more equiv. of [Ir(Cp*)Cl_2]$_2$.[12d] The complex **5** was fully characterized by NMR spectroscopy, mass spectrometry, and elemental analysis as well as by the X-ray crystallographic studies. The ^{1}H NMR spectrum of the complex reveals resonances of the dicarbene ligand at upfield shifted regions as compared to the parent triazolium salt [**L**-H_2]Br_2. Formation of a Ir^{III}-NHC complex is revealed by the absence of the highly downfield shifted ^{1}H NMR signal at δ = 11.32 ppm (the C5-triazolium protons in [**L**-H_2]Br_2) and the appearance of a new signal at δ = 165.9 ppm, characteristics of an Ir^{III}-NHC signal,[6c,12d,13a] in the ^{13}C{^{1}H} NMR of the complex (Fig. S17). Additionally, ^{1}H NMR spectrum (Fig. S16) features three distinct aromatic signals in 1:1:2 ratio corresponding to inequivalent aromatic protons of the phenylene bridge and two equivalent triazole C3-protons, respectively. Further, the presence of only two phenyl ring protons and a single type of triazolinylidene proton suggest the possibility of a symmetrical complex formation via double orthometalation which is backed by the previous observations that an iridium-center activates the aromatic protons in close vicinity.[7a,13] Additionally, diastereotopic nature of the *N*-CH_2 protons of the ethyl moiety as reflected by two sets of quartets in the aliphatic region (δ = 4.25-4.38 ppm) further supports the orthometalation. As per our expectation, orthometalation is also evidenced by the distinct Ir^{III}-coordinated ortho-C_{phenyl} signal at δ = 137.4 ppm (established by 2D correlation NMR spectroscopy). The observed chemical shift for the iridium-C_{Phenyl} carbon atoms is in the range of structurally related diorthometalated complexes,[12d,13a] however, upfield shifted from the monoorthometalated complexes.[6c,12d] Relying on previous literatures, we propose that the doubly orthometalated complex **5** has been formed via triazolinylidene assisted concerted-metalation-deprotonation

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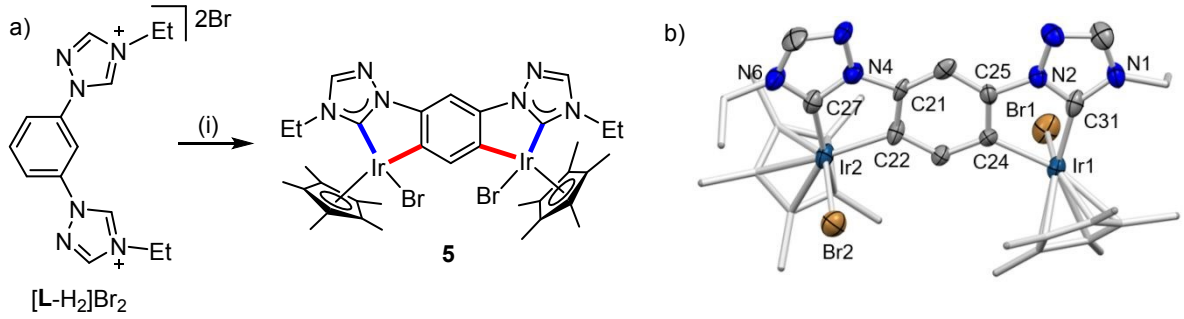
(CMD) pathway.[6b,c,14a-c] Generation of the potential isomers of complex **5** resulting due to the different orientations of the Cp* rings with respect to the central phenylene ring was not observed by NMR spectroscopy.

Scheme 4. (a) Synthesis of the diorthometalated Ir^{III}-complex **5**. (i) $[Ir(Cp^*)Cl_2]_2$, Cs_2CO_3, CH_3CN, reflux, 30 h. (b) Molecular structure of **5** with displacement parameters at 40% probability level. Metric parameters of one out of four molecules in the asymmetric units are shown here and they are within the experimental errors to the parameters observed for other molecules. The *N*-ethyl groups and Cp* are shown in capped stick. Some important bond lengths (Å) and bond angles (°) are mentioned: C22-Ir2 2.056(14), C24-Ir1 2.047(13), C27-Ir2 1.973(17), C31-Ir1 2.001(17), Ir-Br 2.5293(18)-2.5339(18); C27-Ir2-C22 76.9(6), C31-Ir1-C24 77.1(6).



The ESI mass spectrometric analysis (positive ions) provides additional support for the formation of a diorthometalated iridium-NHC complex by showing the most intense peak at *m/z* = 1001.2025 for the fragment $[M\text{-}Br]^+$ (calculated *m/z* = 1001.2052) with isotopic patterns matching properly with the calculated one. To unequivocally confirm the structure of the complex, X-ray crystallographic stuides were performed with a crystal obtained via slow diffusion of diethyl ether into a saturated DCM solution of the complex at ambient temperature. The crystal structure confirmed the formation of a doubly orthometalated binuclear Ir^{III}-NHC metal complex **5** (Scheme 4b**)** as concluded from the NMR and mass spectral analysis. The complex **5** features a typical three-legged piano stool geometry around the metal center and the three legs are represented by the phenylic carbon, bromide ion, and the triazolinylidene carbene carbon. Diorthometalation results in the formation of two 5-membered iridacycles which are bridged by a phenylene spacer and the Ir-Br moieties are observed to be in the thermodynamically more preferred *trans*-orientation with respect to this essentially planar metal-ligand skeleton [torsion angles are 0.60° (C31-N2-C25-C24) and 0.20° (C27-N4-C21-C22)]. The bite angles of the ligands in the iridacycles are noted to be 76.9(6)-77.1(6)° which fall well in the region reported for the Ir^{III}-

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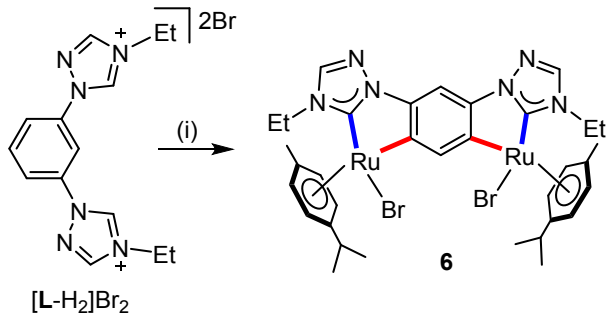
complexes containing 5-membered C_{NHC}^C_{Ph} chelate rings.[6c,7a] The Ir-C_{phenyl} bonds (2.047(13)-2.056(14) Å) are slightly longer than the Ir-C_{NHC} bonds (1.973(17)-2.001(17) Å) and this is probably due to π-back donation from iridium to the reasonably good π-acceptor triazolinylidene moiety.[5a,b] The intramolecular separation between the iridium center is about 6.2 Å and the separation between the iridium center and the Cp* ring centroid measures 1.853-1.857 Å. When compared to the parent triazolium cation, the conversion to a coordinated NHC results in shrinking of the N-C5-N bond angles (~6-7°) and increase of the N-C5 bond distances (Δd ~ 0.049 Å) in line with the previous findings and DFT-calculations.[12d-f]

Scheme 5. Synthesis of the diorthometalated binuclear Ru^{II}-NHC complex **6**. (i) [Ru(*p*-cymene)Cl_2]$_2$, Cs_2CO_3, THF, 70 °C, 24 h.



After the success in accessing the binuclear diorthometalated iridium complex **5**, we turned our attention towards the synthesis of similar doubly orthometalated complex based on the Ru^{II}-center. Accordingly, the triazolium salt [**L**-H_2]Br_2 was reacted with [Ru(*p*-cymene)Cl_2]$_2$ using Cs_2CO_3 as base at 70 °C in THF and to our delight, after the reaction a yellow colored compound was isolated whose spectroscopic data correspond to a diorthometalated Ru^{II}-NHC complex similar to that of the iridium-case described before (Scheme 5). However, contrary to the iridium-complex (**5**), the isolated Ru^{II}-NHC complex was observed to be air and moisture sensitive. This may be due to the presence of two Ru^{II}-C_{aryl} bonds at the same phenylene ring which are prone to hydrolysis especially in presence of a catalytic acidic impurity and similar hydrolytic decomposition of the orthometalated Ru^{II}-NHC has been observed previously.[7f] The most acidic triazolium proton signal observed in [**L**-H_2]Br_2 at δ = 11.32 ppm was, as expected, missing in the ^{1}H NMR of the complex **6** (Fig. S18). The presence of the distinctive metal bound carbene carbon signal at δ = 187.3 ppm, within the usual range for Ru^{II}-complexes containing C_{NHC}^C_{Ph} chelate rings,[6b,7f,12g] in the $^{13}C\{^1H\}$ NMR spectrum (Fig. S19) supports the formation of a Ru^{II}-NHC complex. Furthermore, four

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aromatic protons, two phenylene and the triazolinylidene backbone protons, appear in 1:1:2 ratio as observed for the iridium-complex **5**. These observations along with the presence of a single Ru^{II}-bound phenyl carbon signal at δ = 155.6 ppm (ascertained via 2D correlation NMR spectroscopy) in the expected region[6b,7f,12g] reinforce the formation of a rarely observed symmetrically diorthometalated binuclear Ru^{II}-NHC complex.[7f] Symmetrical diorthometalation is further supported by the single set of diastereotopic *N*-CH_2 protons and the presence of only one set of four (a set of two doublets of each two protons intensity should be observed in the absence of orthometalation) distinct doublets in the region of δ = 5.45-5.81 ppm corresponding to the aromatic protons of *p*-cymene groups. Mass spectrometric analysis (positive ions) of the complex **6** establishes its formation by displaying the most intense peak at *m/z* = 858.1009 corresponding to the mono-positive fragment $[M\text{-}Br+CH_3CN]^+$ (calculated *m/z* = 858.1019) with isotopic patterns matching exactly with the calculated one (Fig. S20). Unfortunately, even after several attempts we could not obtain the single crystals of **6** suitable for X-ray crystallographic analysis due to decomposition of the complex in the chlorinated solvent over time. To the best of our knowledge, **5** and **6** are the first examples of diorthometalated binuclear Ir^{III}/Ru^{II}–complex, respectively with 1,2,4-triazolin-5-ylidene donors.

Ir^{III}-NHC Complex 5 Catalyzed Transfer Hydrogenation Reaction. Hydrogenation of the organic molecules containing unsaturated π-systems is an important and fundamental catalytic process.[15a] Reducing the unsaturated bonds through hydrogen gas is a perilous process whereas transfer hydrogenation which uses inorganic or organic hydrogen source makes it a competent, sustainable, and mild method that is operationally simpler and safer than the direct hydrogenation with dihydrogen.[15b] Possibly because of that, catalytic reduction of the unsaturated bonds via the transfer hydrogenation (TH) strategy is currently one of the most investigated hydrogenation pathways. Transfer hydrogenation of non-polarized substrates such as olefins and alkynes are less studied as compared to the polarized substrates like ketones, imines, and α,β-unsaturated carbonyls. In general, this method involves various hydrogen sources such as formates, amine-borane adducts, and alcohols.[15b-f] Although various transition metal-NHC complexes have shown improved catalytic activities for the reduction of polarized C=O and C=N bonds via transfer hydrogenation strategy,[15b] available reports on the NHC or MIC ligand based catalytic systems for the transfer hydrogenation of more challenging alkenes/alkynes are relatively less[16,17] possibly due

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to inadequate polarization of the C=C and C≡C bonds. Nevertheless, the Peris and Mata *et al.* have described that the iridium complexes of NHC/aNHC based chelating ligands (2.5 mol% loading) may act as catalysts to reduce olefins/phenylacetylene under transfer hydrogenation strategy however, with poor efficiency.[17d] Later on, the Elsevier and Sarkar group have independently shown that related iridium and ruthenium complexes of chelating ligands featuring NHC and/or MIC donors (1 mol% loading) are able to transfer hydrogenate olefins more effectively however, with narrow substrate scope.[17a,c] Very recently, the groups of Diéguez and Wang have separately reported the effective transfer hydrogenation of variety of alkenes using an NCP-iridium pincer complex and triazolinylidene iridium complex, respectively.[17b,18]

After isolating the well characterized air and moisture stable Ir^{III}-NHC complex in decent amount, we moved forward to study its catalytic efficacy. Initially, we tried the transfer hydrogenation of styrene as an exemplary reaction using the complex **5**, under standard transfer hydrogenation conditions (2-propanol as both solvent and hydrogen source with base under reflux condition) using substrate/catalyst/base in the ratio of 1/0.003/0.2. To our delight, quantitative formation of ethylbenzene was achieved in 6 h and among all the different bases tested, NaO^{t}Bu provided the best result. We also studied the catalytic efficiency of the Ru^{II}-NHC complex **6** and observed that it is less effective (only 43% conversion of styrene was observed under the similar conditions employed for Ir^{III}-NHC complex **5**).

With these optimized reaction conditions, we explored the substrate scope of the present catalytic system using a small library of electronically and sterically varied alkenes and the results obtained are summarized in Table 1. The *p*-substituted styrene derivatives were efficiently hydrogenated to the corresponding alkanes (**9b-d**). Among them, styrenes containing electron-donating substituent were reduced faster whereas, the electron withdrawing group (halide) substituted styrenes were comparatively less reactive towards the reduction process (**9b** *vs* **9c-e**). The activity of *ortho*-chlorostyrene was comparable with that of the corresponding *para*-substituted styrene (**9c** *vs* **9e**). 2-Vinylnaphthalene was converted to 2-ethylnaphthalene quantitatively with a slightly higher catalyst loading of 0.5 mol% in 24 h (**9f**). In order to probe the effectivity of our catalytic system towards internal alkenes, cyclooctene was chosen as model substrate and excellent yield was realized in 24 h (**9h**). In line with the previous literature reports,[17b] alkyl substituted olefins undergo slower hydrogenation than that of the aryl substituted olefins (**9g-h** *vs* **9a**). Further, reduction of

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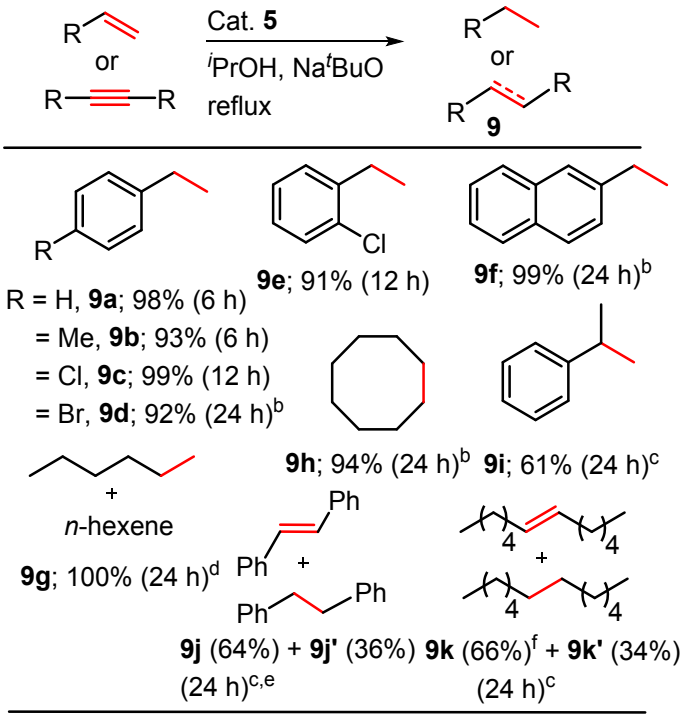
the sterically hindered α-methyl styrene needs longer reaction duration along with higher catalyst loading to obtain the product **9i** in decent yield.

Table 1. Transfer hydrogenation of alkenes and alkynes[a]



[a]**General conditions:** alkenes or alkynes (0.4 mmol), complex **5** (0.3 mol%), Na^{t}BuO (20 mol%), ^{i}PrOH (4 mL), reflux temperature; yields were determined by GC-MS using mesitylene as internal standard. [b]Catalyst (0.5 mol%). [c]Catalyst (1 mol%). [d]Hexene (57%) was observed as mixture of isomers. [e]Calculated based on ^{1}H NMR. [f]And other isomers of dodecene.

To probe the versatility of our present catalytic system, we have also carried out the reduction of selected alkynes using the same strategy. At the outset, diphenylacetylene was transfer hydrogenated under optimized conditions using the complex **5** (1 mol%) and quantitative reduction of diphenylacetylene was observed. However, the ^{1}H NMR analysis of the reaction mixture shows the presence of a mixture of semi-reduced *trans*-stilbene (**9j**, 64%) and completely reduced diphenylethane (**9j'**, rest 36%). Further, the dialkyl-substituted acetylene (6-dodecyne) also undergoes quantitative reaction. In this case, GC-MS analysis of the reaction mixture shows the formation of the completely hydrogenated dodecane (**9k'**) in 34% along with the presence of a mixture of semi hydrogenated isomeric dodecenes (**9k**). This type of isomerization of the obtained alkene product has also been observed previously.[16a,b]

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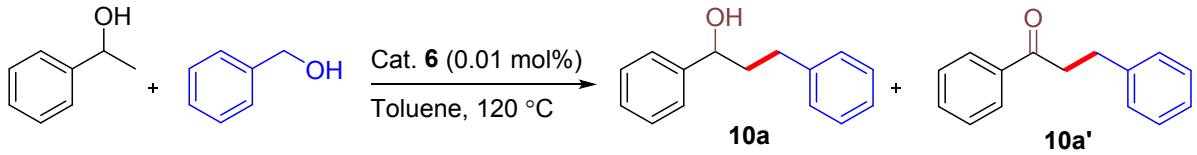
Cross coupling of secondary and primary alcohols via borrowing hydrogen strategy. Development of atom-efficient methods to construct C-C bonds to access long chain/branched alcohols is highly desirable as the produced alcohols are useful as biofuels which are potent alternatives to the conventional fossil fuels.[19a] Notably, borrowing hydrogen (BH) or hydrogen-autotransfer strategy for the alkylation of ketones/alcohols and amines has evolved to be a demanding process because of the atom economy and greener nature as it generates water as sole byproduct.[20] In this context, several transition metal catalysts as well as some metal free systems have been reported for the realization of higher order alcohols via BH strategy.[19d,20a-e,21] β-Alkylation of secondary alcohols using primary alcohols has now become a very important tool and greener alternative to realize long chain alcohols as it avoids the use of expensive alkyl halides or other toxic electrophiles and the use of renewable and non-hazardous alcohols as alkylating agents makes this process versatile with high practical applicability. Despite the significant advancements, most of the reports have their own limitations such as use of high catalyst loading, higher amount of base, and elevated temperatures along with longer reaction duration, which hence reduces the efficiency of the catalytic system.

Table 2. Optimization studies for the β-alkylation reaction[a]



Entry	Catalyst	Base (equiv.)	Time	% Conv.	Product 10a : 10a'
1	**6**	K^{t}BuO (0.1)	12 h	66	79 : 21
2	**6**	K^{t}BuO (0.1)	24 h	100	80 : 20
3	**6**	KOH (0.1)	24 h	100	72 : 28
4	**6**	Cs_2CO_3 (0.1)	24 h	55	64 : 36
5	**6**	K^{t}BuO (0.2)	24 h	99	91 : 9
6	**6**	**K^{t}BuO (0.2)**	**12 h**	**99**	**93 : 7**
7	**5**	K^{t}BuO (0.2)	24 h	100	89 : 11

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[a]**General conditions:** 1-phenylethanol (0.5 mmol), benzyl alcohol (0.55 mmol), catalyst (0.01 mol%), and toluene (1 mL). Base equivalent is w.r.t. 1-phenylethanol. Conversion and product ratio were determined by GC-MS analysis based on 1-phenylethanol using mesitylene as internal standard.

In 2016, Kundu *et al.* has reported 2,2'-bipyridine based effective bifunctional Ru^{II}-catalysts for the β-alkylation of secondary alcohols utilizing primary alcohols using low catalyst (0.1 mol%) but high base (0.5 equiv.) loading.[19b] Same group has recently observed that the introduction of NHC-donor in the supporting ligand leads to a very efficient Ru^{II}-based catalyst system (achieving very high turnover number) for the same process although still demand relatively high base loading (0.4 equiv.).[19c] Inspired by this progress, we focused towards the β-alkylation of secondary alcohols utilizing primary alcohols as alkylating agents using our doubly orthometalated Ru^{II}-NHC complex with lower catalyst and base loadings.

At first, the reaction of 1-phenylethanol with benzyl alcohol was chosen as benchmark alkylation reaction to probe the potential of the present catalytic system. By employing Ru^{II}-precatalyst **6** (0.01 mol%), various bases were screened (Table 2) and observed that K^{t}BuO (20 mol%) at 120 °C for 24 h results in essentially quantitative conversion of 1-phenylethanol with 93% selectivity to the 1,3-diphenylpropan-1-ol (entry 5). Under identical reaction conditions, analogous Ir^{III}-complex **5** showed similar performance (entry 7) and hence we decided to proceed with the reasonably inexpensive Ru^{II}-precatalyst **6**. Further optimizations disclose that the reaction is complete within 12 h maintaining the high selectivity (entry 6) which provide the 1,3-diphenylpropan-1-ol in 88% isolated yield. With these optimized reaction conditions, we explored the scope of the β-alkylation reaction with a diverse range of alcohols using the complex **6** as precatalyst (Table 3). First, 1-phenylethanol was reacted with structurally and electronically different primary alcohols under the optimized reaction conditions. Irrespective of the electronic nature of the substituted (both electron-donating and withdrawing) benzyl alcohols, this catalytic system afforded good to excellent conversions to the corresponding long chain alcohols with high selectivity (entries 2-4). Further, 4-OMe/Cl substituted benzyl alcohols exclusively provided the corresponding β-alkylated alcohols, which could be isolated in good to excellent yields (entries 3-4). The activity of 3-chlorobenzyl alcohol was alike with that of the corresponding 4-chlorobenzyl alcohol (entry 5 *vs* 4).

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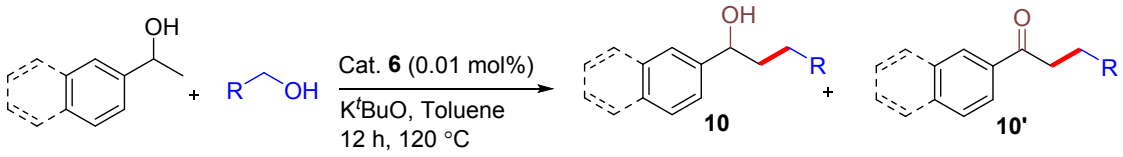
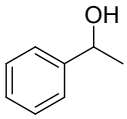
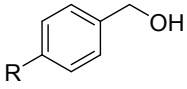
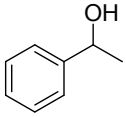
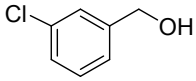
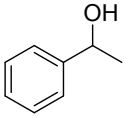
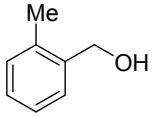
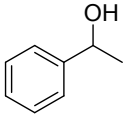
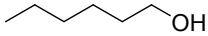
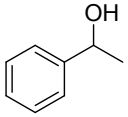
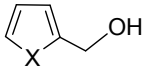
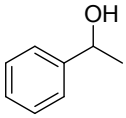
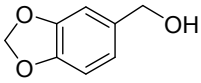
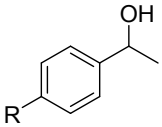
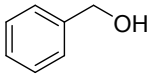
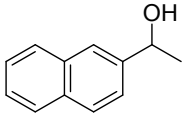
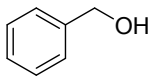
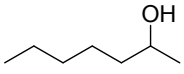
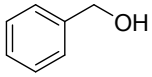
Table 3. Scope for the synthesis of β-alkylated alcohols[a]



Entry	Secondary alcohol	Primary alcohol		Conversion (%)	Product 10 : 10'
1			R = H	99	93:7 (88[c])
2			R = Me	98	96:4
3			R = OMe	92	100:0 (86[c])
4			R = Cl	90	100:0 (74[c])
5				93	93:7 (76[c])
6				90	92:8 (80[c])
7				93[b]	94:6 (84[c])
8			X = O	99[b,d]	90:10
9			X = S	95[b,d]	94:6
10				100	95:5 (91[c])
11			R = Me	95	95:5 (86[c])
12			R = OMe	99	81:19
13			R = Cl	99	91:9
14			R = Br	99	92:5[e] (84[c])
15				98	100:0 (94[c])
16				63[b,f]	95:5

[a]**General conditions:** secondary alcohol (0.5 mmol), primary alcohol (0.55 mmol), catalyst **6** (0.01 mol%), K^{t}BuO (0.1 mmol), and toluene (1 mL). Conversion/product selectivity was determined by GC-MS/^{1}H NMR analysis w.r.t. secondary alcohol (mesitylene/1,3,5-trimethoxybenzene was

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used as internal standard). [b]0.1 mol% catalyst was used. [c]Isolated yields of **10**. [d]16 h. [e]2% debromination of product alcohol was observed. [f]24 h.

The sterically hindered *ortho*-methylbenzyl alcohol can also be utilized to provide the desired product in good yield (entry 6). Next, we targeted the more challenging aliphatic alcohol, 1-hexanol which also afforded the corresponding β-alkylated product in excellent yield when 0.1 mol% catalyst loading was used (entry 7). The heteroaromatic alcohols such as 2-furanmethanol and 2-thiophenemethanol also act as good alkylating agents and provided the corresponding products in excellent yields (entries 8-9). Notably, piperonyl alcohol smoothly coupled with 1-phenylethanol to deliver the corresponding long-chain secondary alcohol in 91% isolated yield (entry 10).

The scope of the reaction was further extended using various secondary alcohols keeping benzyl alcohol same. As seen before for primary alcohols, electron donating (-Me, -OMe) and electron withdrawing groups (-Cl, -Br) containing 1-phenylethanol also efficiently underwent alkylation with benzyl alcohol to afford the corresponding secondary alcohols in excellent yields with high selectivity (entries 11-14). Gratifyingly, this catalyst system offers excellent tolerance towards the aryl-halide bonds (entries 4-5 and 13-14). Further, the (naphthalen-2-yl)ethanol was also successfully coupled to benzyl alcohol and delivered the product in excellent isolated yield of 94% (entry 15). The alkylation of 2-heptanol with benzyl alcohol also provided the desired product with very high selectivity, however in moderate yield (entry 16). Overall, the present system under 0.01 mol% catalyst loading along with lower base loading shows similar activity to the most active Ru(II)-based systems with reasonable substrate scope.[19b,c] However, a direct comparison with the previous reports may not be appropriate due to incompatible catalytic system and reaction conditions. Due to the presence of two ruthenium centers in the precatalyst **6**, it may be tricky to study the reaction mechanism involving metal centers. However, we have studied the time-dependent product distribution of the β-alkylation of 1-phenylethanol with benzyl alcohol under the optimized reaction conditions (Fig. S21). The reaction profile shows that the formation of 1,3-diphenylpropan-1-ol (**10a**) increases steadily over time which reaches maximum towards the end of the reaction. Whereas, the amount of 1,3-diphenylpropan-1-one (**10a'**) remains nominal throughout the course of the reaction. These observations establish that the present catalyst system is highly selective towards the end-alcohol rather than ketone product.

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Conclusion

In summary, we have developed a 1,2,4-triazolin-5-ylidene donor based biscarbene ligand with a phenylene spacer which in presence of coinage metal ions having linear geometry yields the binuclear tetracarbene complexes of general formula $[(\mathbf{L})_2M_2](PF_6)_2$ (M = Ag^I, Cu^I). Whereas, reactions of $[\mathbf{L}\text{-}H_2]Br_2$ with $[Ir(Cp^*)Cl_2]_2$ and $[Ru(p\text{-cymene})Cl_2]_2$ under suitable conditions result in the formation of doubly orthometalated Ir^{III}- and Ru^{II}-NHC complexes **5** and **6**, respectively. Complexes **5** and **6** represent the first examples of 1,2,4-triazolin-5-ylidene donor supported stable diorthometalated binuclear Ir^{III}/Ru^{II}-complexes. When applied as catalyst, the Ir^{III}-NHC complex **5** was detected to be more active than **6** for the transfer hydrogenation of a variety of alkenes and alkynes. Further, the Ru^{II}-NHC complex **6** was identified as an efficient catalyst for the β-alkylation of diverse secondary alcohols via cross coupling with primary alcohols under low catalyst (0.01 mol%) loading.

Experimental Section

General considerations. All manipulations were performed under argon atmosphere using either standard Schlenk line or Glove box techniques. Glassware were dried at 130 °C in an oven overnight before use. The solvents used for the synthesis were dried, distilled, and degassed by standard methods and stored over 4 Å molecular sieves. NMR measurements were performed using Bruker 400 and 500 MHz FT-NMR spectrometers. The chemical shifts in the ^1H NMR spectra were referenced to the residual proton signals of the deuterated solvents (DMSO-d_6, ^1H 2.50 ppm and $^{13}C\{^1H\}$ 39.52 ppm; CD_3CN, ^1H 1.94 ppm and $^{13}C\{^1H\}$ 1.32 and 118.26 ppm; $CDCl_3$, ^1H 7.26 ppm and $^{13}C\{^1H\}$ 77.16 ppm) and reported relative to tetramethylsilane. Coupling constants are expressed in Hz. ESI-MS spectra were recorded with a Micromass Q-TOF Mass spectrometer or an Agilent 6545A Q-TOF Mass spectrometer and the elemental analysis were performed using PerkinElmer 24000 instrument. The starting materials $[Ru(p\text{-cymene})Cl_2]_2$, $[Ir(Cp^*)Cl_2]_2$, and $[Cu(SMe_2)Br]$ were prepared according to the literature procedures.[22a-c] All other chemicals were purchased from commercial sources and used as received without further purification. Secondary and primary alcohols were synthesized following reported procedure.[22d]

1,3-bis(1,2,4-triazol-1-yl)benzene (A). The compound **A** was prepared by following a modified reported procedure.[10a] 1,3-dibromobenzene (4.0 g, 16.96 mmol), 1,2,4-triazole (2.908 g, 42.10 mmol), K_2CO_3 (5.88 g, 42.59 mmol), CuO (0.162 g, 2.06 mmol), and DMSO (25 mL) were taken in a predried schlenk tube under inert atmosphere and heated at 150 °C for 48 h. After that, the reaction mixture was cooled to room temperature and extracted with DCM several times. The combined DCM layer was washed with brine solution and dried over $MgSO_4$. Finally, the pure compound was obtained as off-white solid via column chromatographic separation using

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CH_2Cl_2/MeOH as eluent in 81% yield (2.93 g, 13.80 mmol). Formation of the product is confirmed by correlating the spectral data with previous literature data.

1,3-Bis(1-ethyl-triazolium-3-yl)benzene bromide [L-H$_2$](Br)$_2$ (1). An oven dried schlenk tube was charged with compound **A** (2.0 g, 9.424 mmol) and ethyl bromide (13.97 mL, 188.48 mmol) followed by DMF (20 mL). The resulting mixture was stirred at reflux temperature for 24 h. After the completion of the reaction, mother liquor was decanted off and the precipitate obtained was washed with diethyl ether (3 x 10 mL). Finally, after drying in high vacuum, the compound was obtained as white air stable powder. Yield: 3.042 g (7.072 mmol, 75%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.32 (s, N-C*H*-N$_{Trz}$, 2H), 9.63 (s, N-C*H*-N$_{Trz}$, 2H), 8.59 (s, 1H), 8.24 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 2H), 8.06 (t, $^3J_{H\text{-}H}$ = 8.2 Hz, 1H), 4.42 (q, $^3J_{H\text{-}H}$ = 7.3 Hz, 4H, N-*CH$_2$*), 1.60 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 6H, N-*CH$_3$*) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 145.1, 142.4, 136.1, 132.2, 122.0, 112.8, 43.7, 14.2 ppm. MS (ESI, positive ions): *m/z* 452.9827 (calculated for [M + Na]$^+$ 452.9837).

1,3-Bis(1-ethyl-triazolium-3-yl)benzene hexafluorophosphate [L-H$_2$](PF$_6$)$_2$ (2). The bis-triazolium dibromide salt, **1** (2.0 g, 4.64 mmol) was dissolved in a minimum amount of MeOH in a schlenk tube. A solution of NH_4PF_6 (1.51 g, 9.29 mmol) in methanol was then added to it. The resulting solution was stirred for 2 h at ambient tempearture. After the reaction, the precipitate obtained was washed with diethyl ether (3 × 10 mL) and dried in high vacuum to provide the pure compound as creamy white air stable solid. Yield: 2.44 g (4.36 mmol, 94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.12 (s, N-C*H*-N$_{Trz}$, 2H), 9.56 (s, N-C*H*-N$_{Trz}$, 2H), 8.53 (s, 1H), 8.20 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 2H), 8.06 (t, $^3J_{H\text{-}H}$ = 8.2 Hz, 1H), 4.39 (q, $^3J_{H\text{-}H}$ = 7.3 Hz, 4H, N-*CH$_2$*), 1.59 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 6H, N-*CH$_3$*) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 145.1, 142.4, 136.2, 132.3, 122.0, 112.8, 43.8, 14.2 ppm. ^{19}F NMR (471 MHz, DMSO-d_6) δ -70.18 ppm. ^{31}P NMR (202 MHz, DMSO-d_6) δ -144.22 ppm. MS (ESI, positive ions): *m/z* 415.1573 (calculated for [M-PF$_6$]$^+$ 415.1235).

Synthesis of the silver complex [(L)$_2$Ag$_2$](PF$_6$)$_2$ (3). Compound **2** (0.2 g, 0.357 mmol) and Ag_2O (0.1075 g, 0.464 mmol) were added to a predried schlenk tube under inert condition with the exclusion of light. Dry acetonitrile (8 mL) was then added to the schlenk tube and heated for 36 h in a preheated oil bath at 70 °C. After the specific time, the reaction mixture was cooled to room temperature and the suspension obtained was filtered through a small pad of celite to obtain a clear solution. The filtrate was then concentrated and precipitated out using diethyl ether to get the compound as a light sensitive white solid. Yield: 0.15 g, (0.144 mmol, 81%). ^{1}H NMR (400 MHz, CD_3CN) δ 8.60 (s, N-*CH*-N$_{Trz}$, 2H), 7.98 (s, 1H), 7.80 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 1H), 7.78 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 1H), 7.27 (t, $^3J_{H\text{-}H}$ = 8.1 Hz, 1H), 4.40 (q, $^3J_{H\text{-}H}$ = 7.2 Hz, 4H, N-*CH$_2$*), 1.57 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 6H, N-*CH$_3$*) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_3CN) δ 183.0 (Ag-C$_{NHC}$), 181.4 (Ag-C$_{NHC}$), 144.8, 140.9, 131.1, 124.0, 118.7, 45.2, 16.5 ppm. ^{19}F NMR (471 MHz, CD_3CN) δ -70.11 ppm. ^{31}P NMR (202 MHz, CD_3CN) δ -144.20 ppm. MS (ESI, positive ions): *m/z* 897.0680 (calculated for [M-PF$_6$]$^+$ 897.0619). Anal. Calcd. (%) for $C_{28}H_{32}N_{12}Ag_2P_2F_{12}$: C 32.26%, H 3.09%, N 16.13%; Found: C 32.83%, H 2.48%, N 15.5%.

Synthesis of the copper complex [(L)$_2$Cu$_2$](PF$_6$)$_2$ (4). Complex **3** (0.120 g, 0.115 mmol), [Cu(SMe$_2$)Br] (0.071 g, 0.345 mmol) were added in predried schlenk tube under inert condition. Then dry acetonitrile (8 mL) was added to the schlenk tube and stirred overnight at room

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temperature under the exclusion of light. The obtained light yellow color solution was filtered over celite under argon atmosphere. The filtrate was concentrated and precipitated using dry diethyl ether to get the compound as air and moisture sensitive yellow powder. Yield: 0.09 g, (0.094 mmol, 82%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.41 (s, N-*CH*-N$_{Trz}$, 2H), 9.18 (s, 1H), 8.44 (d, $^{3}J_{H-H}$ = 7.5 Hz, 2H), 8.10 (t, $^{3}J_{H-H}$ = 7.5 Hz, 1H), 4.70 (q, $^{3}J_{H-H}$ = 6.8 Hz, 4H, N-*CH*$_2$), 1.86 (t, $^{3}J_{H-H}$ = 6.8 Hz, 6H, N-*CH*$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_3CN) δ 180.6 (Cu-C$_{NHC}$), 143.8, 140.7, 131.4, 130.8, 122.8, 44.6, 16.4 ppm. ^{19}F NMR (471 MHz, CD_3CN) δ -72.84 ppm. ^{31}P NMR (202 MHz, CD_3CN) δ -144.64 ppm. Consistent CHN data could not be obtained due to the sensitive nature of the compound.

Synthesis of the iridium triazolinylidene complex [(L)Ir$_2$(Cp*)$_2$Br$_2$] (5). Compound **1** (0.054 g, 0.125 mmol), [Ir(Cp*)Cl$_2$]$_2$ (0.1 g, 0.125 mmol) and Cs_2CO_3 (0.188 g, 0.577 mmol) were added in a predried schlenk tube under inert condition. Then dry acetonitrile (10 mL) was added to the schlenk tube and stirred at 80 °C for 30 h. After the specific reaction time, the reaction mixture was allowed to cool to ambient temperature and all the volatiles were removed in high vacuum. Then the resulting residue was extracted with DCM and filtered through a small pad of celite. The clear yellow solution obtained was concentrated and precipitated using dry diethyl ether. The compound was obtained as bright yellow-orange air and moisture stable powder. Yield: 0.108 g, (0.1 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, Ar-*CH*, 1H), 7.98 (s, N-*CH*-N$_{Trz}$, 2H), 7.71 (s, Ar-*CH*, 1H), 4.38 (q, $^{3}J_{H-H}$ = 7.1 Hz, 2H), 4.25 (q, $^{3}J_{H-H}$ = 7.1 Hz, 2H), 1.86 (s, 30H), 1.60 (t, J = 7.1 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.9 (Ir-C$_{NHC}$), 145.2, 140.3, 139.7, 137.4 (Ir-C$_{Phenyl}$), 97.7, 91.6, 42.8, 16.6, 10.2 ppm. MS (ESI, positive ions): *m/z* 1001.2025 (calculated for [M-Br]$^+$ 1001.2052). Anal. Calcd. (%) for $C_{34}H_{44}N_6Ir_2Br_2$: C 37.77%, H 4.10%, N 7.78%; Found: C 37.51%, H 3.41%, N 7.97%.

Synthesis of ruthenium complex [(L)Ru$_2$(*p*-cymene)$_2$Br$_2$], 6. Compound **1** (0.05 g, 0.116 mmol), [Ru(*p*-cymene)Cl$_2$]$_2$ (0.71 g, 0.116 mmol) and Cs_2CO_3 (0.189 g, 0.58 mmol) were added to a predried schlenk tube under inert condition. Then dry THF (10 mL) was added to the schlenk tube and the reaction mixture was stirred at 70 °C for 24 h. After specific time, reaction mixture was allowed to cool to room temperature and all the volatiles were removed in high vacuum. The residue obtained was extracted with DCM and filtered through a small pad of neutral alumina to obtain a clear brownish yellow solution. The filtrate was then concentrated and precipitated using dry hexane to get a pale yellow powder. Yield: 0.036 g, (0.041 mmol, 35%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, Ar-*CH*, 1H), 8.00 (s, N-*CH*-N$_{Trz}$, 2H), 7.63 (s, Ar-*CH*, 1H), 5.81 (d, $^{3}J_{H-H}$ = 6.0 Hz, 2H), 5.59 (d, $^{3}J_{H-H}$ = 5.8 Hz, 2H), 5.40 (d, $^{3}J_{H-H}$ = 6.0 Hz, 2H), 5.35 (d, $^{3}J_{H-H}$ = 5.8 Hz, 2H), 4.63 (q $^{3}J_{H-H}$ = 13.7, 7.3 Hz, 2H), 4.48 (q, $^{3}J_{H-H}$ = 13.7, 7.3 Hz, 2H), 2.46 (m, 2H), 2.05 (s, 6H), 1.67 (t, J = 7.3 Hz, 6H), 1.00 (d, J = 6.8 Hz, 6H), 0.87 (d, J = 6.8 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 187.3 (Ru-C$_{NHC}$), 155.6 (Ru-C$_{Phenyl}$), 152.8, 139.3, 138.7, 102.5, 99.6, 97.7, 91.9, 88.5, 86.2, 83.0, 42.4, 30.0, 22.1, 20.7, 18.5, 15.5 ppm. MS (ESI, positive ions): *m/z* 858.1009 (calculated for [M–Br+CH_3CN]$^+$ 858.1019).

General procedure for the transfer hydrogenation of alkenes/alkynes. An oven dried pressure tube was charged with NaO^{t}Bu (0.08 mmol, 20 mol%) inside an argon filled glove box. To this,

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catalyst (0.0012 mmol, 0.3 mol%), alkene/alkyne (0.4 mmol), and isopropanol (4 mL) were added using standard schlenk technique. The resulting mixture was refluxed for the specified time and cooled to room temperature. Then a small portion of the reaction mixture was diluted with methanol and an aliquot was analyzed by GC-MS (mesitylene was used as internal standard) to obtain product ratio.

General procedure for the C-alkylation reaction. An ovendried Schlenk tube was charged with the required amount of catalyst **6** stock solution in acetonitrile (0.01 mol%) and acetonitrile was evaporated in vacuo. To this, KO^{t}Bu (0.1 mmol, 20 mol%), secondary alcohol (0.5 mmol), and primary alcohol (0.55 mmol) followed by toluene (1 mL) were added using standard schlenk technique. The resulting mixture was refluxed for the specified time and cooled to room temperature. Then a small portion of the reaction mixture was diluted with methanol and an aliquot was analyzed by GC-MS (mesitylene was used as internal standard) to obtain the product ratio. For the isolation of the product, all the volatiles were removed after the completion of the reaction and the obtained residue was purified via column chromatography using ethyl acetate and hexane as eluent.

Details of Crystallographic data. X-ray data were collected on a Bruker AXS Kappa APEX-II CCD diffractometer or a Bruker APEX-II CCD equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).[23a] Crystal was fixed at the tip of a glass fiber loop and after mounting on the goniometer head, it was optically centered. The APEX2 and APEX2-SAINT/Bruker SAINT programme were used for the data collection and unit cell determination, respectively. Processing of the raw frame data was performed using SAINT/XPREP or Bruker SAINT.[23b-c] The structures were solved by SHELXT-2014/4 or SHELXS-97 methods[23d] and refined against F^2 using all reflections with the SHELXL-2014/7 and SHELXL-2018/3 (WinGX) program.[23e-f] Non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were placed in calculated positions. The crystal data (CCDC Nos. 1972778-1972781) and refinement details are summarized in table S1 and S2 of the supporting information. The graphical representations were performed using the program Mercury.[23g]

Conflicts of interest

There are no conflicts to declare.

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Supporting Information. Electronic supplementary information (ESI) available: Full characterization data for the compounds **1-6** and the ^{1}H NMR data of in situ experiments and the isolated compounds from catalytic runs. CCDC 1972778-1972781.

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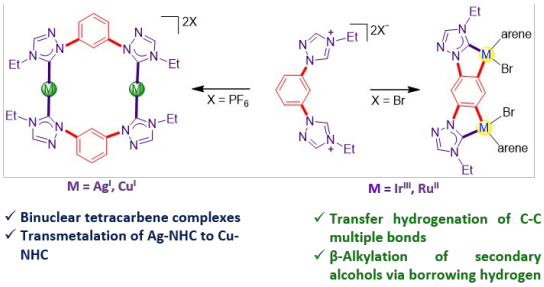

The 1,2,4-triazolin-5-ylidene donor based bis(carbene) ligand provides binuclear tetracarbene complexes of general formula $[(\mathbf{L})_2M_2](PF_6)_2$ with coinage metal ions ($M = Ag^I$, Cu^I), whereas, formation of doubly orthometalated NHC complexes were observed in case of Ir^{III}- and Ru^{II}-metal ions. Further, the Ir^{III}- and Ru^{II}-NHC complexes were detected to be efficient catalysts for the transfer hydrogenation of alkenes/alkynes and β-alkylation of diverse secondary alcohols using various primary alcohols (under low catalyst loading 0.01 mol%), respectively.

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