# **ORGANOMETALLICS**

# Synthesis of Multinuclear Rh(I) Complexes Bearing Triazolylidenes and Their Application in C–C and C–Si Bond Forming Reactions

David Rendón-Nava, Jose M. Vásquez-Pérez, Cesar I. Sandoval-Chávez, Alejandro Alvarez-Hernández, and Daniel Mendoza-Espinosa\*

Cite This: htt	:ps://dx.doi.org/10.1021/acs.organ	omet.0c00517	Read Online		
ACCESS	ull Metrics & More	E Art	icle Recommendations	s Suppo	orting Information
ABSTRACT: Mu	ultidentate carbene ligands	are valuable fram	neworks for the	Mes	5

**ADSTRACT:** Multidentate carbene fights are valuable frameworks for the preparation of carbene complexes displaying higher nuclearity. In the present work, we report the synthesis of a series of mono- to tetra-[Rh(COD)I] complexes (**3a**-**d**) supported by mesoionic triazol-5-ylidenes. The general synthetic procedure involves the one step reaction of the appropriate triazolium (**2a**-**d**) salt in the presence of KHMDS and stoiquiometric amounts of the rhodium(I) precursor. Treatment of complexes **3a**-**d** with an excess of carbon monoxide allows for the quantitative preparation of complexes **4a**-**d** featuring a [Rh(CO)<sub>2</sub>I] fragment used for the determination of the donor properties of the new triazolylidene ligands. All complexes have been fully characterized by means of <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, melting point, elemental analysis, and in the case of complex **3a**, by X-ray crystallography. Comparison of the catalytic activity of the new rhodium complexes in C-C and C-Si bond forming processes demonstrate the enhanced performance of the tetranuclear species suggesting the possibility of strong cooperative effects in these multinuclear complexes.



# INTRODUCTION

Ever since the isolation of the first stable crystalline 1,2,3triazol-5-ylidene,<sup>1</sup> and later the  $bis(1,2,3-triazol-5-ylidene)^2$ reported by Bertrand, the studies of the chemistry related to mesoionic carbenes (MICs) has growth exponentially. Mesoionic 1,2,3-triazolylidene ligands have received considerable attention owing to their intrinsic mesoionic character and to the fact that they have been postulated as better sigma donors compared to their classical N-heterocyclic carbene (NHC) counterparts.<sup>3</sup> It is well-known that the copper(I)catalyzed 1,3-dipolar cycloaddition reaction of an azide to an alkyne, known as the "click" reaction, typically leads to the formation of 1,2,3-triazoles.<sup>4</sup> This procedure is highly flexible and allows numerous functionalities to be introduced in the ligand backbone.<sup>5</sup> Further N-alkylation results in the formation of the substituted 1,2,3-triazolium salts, which can act as precursors for the preparation of MICs.<sup>6</sup>

Owing to this synthetic versatility, a vast family of metal complexes bearing 1,2,3-triazol-5-ylidenes has been reported in the literature with the main target of testing the performance of these complexes in various homogeneous catalytic processes.<sup>7</sup> Recently, we have reported on such types of complexes as catalysts for various organic transformations including Suzuki–Miyaura cross coupling reactions, alpha arylations of ketones, alkyne cyclizations, C–N bond forming processes, and hydroaminations.<sup>8</sup> Surprisingly, despite the easy access to various triazolium frameworks, to date most of the reported

complexes possessing 1,2,3-triazol-5-ylidene ligands are of mononuclear type. In fact, only a few dinuclear and trinuclear complexes possessing a MIC donor at each metal center have been reported in the literature,<sup>9</sup> and the presence of tetra-triazolylidene ligands has only recently been described.<sup>8d,10</sup>

The increasing interest in developing cleaner chemical processes has risen particular attention in multifunctional complexes owing to its superiority in terms of enhanced reactivity and selectivity over their monometallic counterparts.<sup>11</sup> A number of these multinuclear complexes have demonstrated to be highly efficient as catalysts for a variety of chemical reactions including C–C and C–N bond forming processes, hydroaminations, and olefin polymerizations, among others.<sup>12</sup> The improvement in the catalytic activity and selectivity achieved by these catalysts is attributed mainly to cooperative interactions between proximal metal centers where features such as intermetallic distances, three-dimensional structures, and the enhanced probability of interaction with the substrates play a key role.<sup>13</sup>

Received: July 31, 2020



In line with our interest in multimetallic complexes for catalytic applications, we report herein the preparation and full characterization of a series of mono- to tetra-triazolylidene-[Rh(COD)I] complexes (3a-3d) which are obtained by the one-step treatment of triazolium precursors (2a-d) with KHMDS in the presence of the [Rh(COD)Cl]dimer. Reaction of 3a-d with an excess of carbon monoxide permitted the preparation of complexes 4a-d displaying a  $[Rh(CO)_2I]$ fragment that allowed the quantification of the sigma-donor properties of the new ligands. Complexes 3a-d were tested in the cross-coupling of 2-cyclohexenone with boronic acid and in the hydrosilylation of terminal alkynes. In both catalytic processes, the tetranuclear complex 3d displayed the best performance and selectivity of the series, suggesting cooperative effects in the multinuclear complexes. Details of the full characterization of the new complexes and their catalytic comparison will be discussed.

# RESULTS AND DISCUSSION

Mono- to tris-triazolium salts 2a-c were prepared according to the procedure described in Scheme 1. The triazole precursors

Scheme 1. Synthesis of Triazoliums 2a-d



(1a-d) are readily obtained in moderate to good yields (65– 98%) by the reaction of mesityl azide with the proper alkyne through the click process. Further *N*-alkylation with methyl iodide affords the corresponding triazolium salts, 2a-c, in good yields (70–98%) after column chromatography purification. The synthesis of triazolium salt 2d was carried out in a similar procedure starting from tetrakis(2-propynyloxymethyl)methane and mesityl azide following the literature procedure (Scheme 1).<sup>8d</sup>

Formation of triazolium salts 2a-c was easily confirmed in <sup>1</sup>H NMR spectroscopy by the presence of the characteristic chemical shift values of the triazolyl hydrogens (singlets) located between 9.03 and 9.38 ppm, and the N-bound methyl

groups displayed single peaks in the range of 4.55 and 4.72 ppm. In solution, the <sup>1</sup>H and <sup>13</sup>C NMR patterns of triazolium salts **2b** and **2c** display  $C_2$  and  $C_3$  fold axis owing to the high symmetry in the molecules. All the NMR characterization data for prepared triazolium **2d** is consistent with the reported literature.<sup>8d</sup>

In order to get access to the desired rhodium triazolylidene complexes, we initially tested the reaction of triazolium salt **2a** with equimolar amounts of hexamethyldisilazane (KHMDS) and a half equivalent of the [Rh(COD)Cl] dimer in THF at -78 °C. After work up and purification by column chromatography, complex **3a** was isolated in 63% yield as an air-stable yellow solid (Scheme 2).

#### Scheme 2. Synthesis of Complex 3a



NMR spectroscopy studies confirmed the formation of complex 3a by the disappearance of the acidic CH<sup>+</sup> proton in the <sup>1</sup>H NMR spectra, and the observation of a low field signal at 172.8 ppm (doublet, J = 45.7 Hz) in <sup>13</sup>C NMR which corresponds to the carbenic carbon bound to rhodium. With respect to the ligands, the hydrogens of the methylene bridge in the MIC are observed now as a pair of doublets (geminal coupling due to nonequivalent methylene protons), while fully asymmetric patterns for the olefinic cyclooctadiene protons are observed. The full set of NMR patterns are consistent with neutral square planar NHC-Rh(COD)X type complexes where the cyclooctadiene ligand occupies two coordination sites and the carbene and iodine centers complete the metal coordination sphere.<sup>14</sup> To gain further insight into the structural features of complexes 2a and 3a, single crystals were grown from a mixture of acetonitrile and hexanes at room temperature (Figure 1).



Figure 1. Molecular structures of triazolium 2a (top) and rhodium complex 3a (bottom). Ellipsoids are shown at 40% of probability. Coordinated solvents are omitted for clarity.

Complex 3a crystallizes in the monoclinic system with the P21/c space group (Table 1), and the monomeric structure

# Table 1. Crystallographic Data and Summary of Data Collection and Structure Refinement

	2a	3a
formula	$C_{38}H_{46}I_2N_6O_4$	C <sub>27</sub> H <sub>33</sub> IN <sub>3</sub> ORh
fw	904.61	645.37
cryst syst	monoclinic	monoclinic
space group	P21/c	P21/c
Т, К	293(2)	293(2)
a, Å	15.4985(4)	14.4357(4)
b, Å	14.8445(3)	12.2861(3)
c, Å	18.7010(4)	16.4385(4)
$\alpha$ , deg	90	90
$\beta$ , deg	112.096(3)	109.202(3)
γ, deg	90	90
<i>V</i> , Å <sup>3</sup>	3986.50(18)	2753.30(14)
Ζ	4	4
$d_{\rm calc}~({\rm g}\cdot{\rm cm}^{-3})$	1.507	1.557
$\mu$ , mm <sup>-1</sup>	12.753	1.764
refl collected	41616	193149
$T_{\rm min}/T_{\rm max}$	0.922	0.898
$N_{ m measd}$	8421	7645
$[R_{\rm int}]$	0.1004	0.0441
$R[I > 2\sigma(I)]$	0.0595	0.0380
R (all data)	0.0678	0.0654
$R_{\rm w}[I > 2\sigma(I)]$	0.1632	0.0861
R <sub>w</sub> (all data)	0.1735	0.1059
GOF	1.057	1.098

displays a carbene–rhodium bond distance of 2.048(3) Å and a Rh–I bond distance of 2.646(10) Å, which are in the range of recently reported MIC–Rh analogues.<sup>15</sup>

The rhodium center is bound to the triazolylidene ligand, the cyclooctadiene fragment ( $\eta^2$ ), and the iodine atom in a slightly distorted square planar geometry, and no short contact with the phenoxy moiety is observed. The carbene bond angle in complex **3a** [101.8(3)°] is slightly more acute than the corresponding angle of triazolium salt **2a** [105.5(3)°]. This feature is consistent with the increased  $\sigma$ -character of the  $\sigma$ lone pair orbital on the carbene atom in **3a** as compared with the C-H<sup>+</sup> bond orbital in cationic precursor **2a** (Figure 1).

With the successful metalation of monotriazolium salt 2a, we followed a similar strategy for the preparation of the bis-, tris-, and tetra-rhodium triazolylidene complexes. Thus, as depicted in Scheme 3, the one-pot reaction of triazolium salts 2b-d with excess of KHMDS and the required amounts of the [Rh(COD)Cl] dimer (according to the MIC centers available) produces complexes 3b-d in adequate yields (65–72%). Purification of the complexes was achieved by chromatography column using a mixture of hexanes/ethyl acetate as eluent and interestingly, despite of the high degree of metalation in complexes 3b-d, all of them display excellent solubility in benzene, toluene, and a variety of chlorinated solvents.

Characterization of complexes was achieved by NMR spectroscopy, melting point, and elemental analysis. In the case of multinuclear complexes **3b** and **3c**, asymmetric <sup>1</sup>H NMR patterns for *N*-methyl, methylene, and cyclooctadiene protons are observed. Interestingly, two (172.3 and 172.2 ppm, J = 45.7 Hz) and three (173.5, 173.4, and 173.3 ppm, J = 45.5 Hz) set of doublets for the carbonic carbon bond to rhodium

# Scheme 3. Synthesis of Complexes 3b-d



in the <sup>13</sup>C NMR spectra are displayed for 2 and 3, respectively. In the case of complex 3d, along with the asymmetry observed for the *N*-methyl hydrogens and the two core OCH<sub>2</sub>- protons, four overlapping (171.7, 171.7, 171.5, and 171.5 ppm, J = 46.0 Hz) set of doublets for the carbenic carbon bound to rhodium are observed. The asymmetric NMR patterns observed in complexes 3b-d are similar to previously reported multinuclear analogues<sup>8a</sup> and is related to the bulkiness associated with the cyclooctadiene ligands and the mesityl moieties which deter the N-methyl and methylene free rotation in these complexes. Surprisingly, we observed that in complex 3d by simply changing the NMR solvent from CDCl<sub>3</sub> to CD<sub>3</sub>CN at 25 °C the N-methyl group protons were resolved as a single peak (4.20 ppm), while the peaks for the COD hydrogens broaden considerably. The symmetrical patterns are also observed in the <sup>13</sup>C NMR spectra, as only one doublet for the carbenic carbon bound to rhodium is observed (171.73 ppm, I = 46.8 Hz). This solution behavior could be explained by the rapid exchange of the COD ligands with CD<sub>3</sub>CN, which allows for the Rh-carbene free rotation in complexes 3b-d.

In order to assess the donor properties of the new triazolylidene ligands, corresponding rhodium(I) carbonyl complexes 4a–d were prepared from the reaction of precursors 3a–d with excess of carbon monoxide in dichloromethane (Scheme 4). Each of rhodium complexes 4a–d present only two Rh–CO bands in agreement with the symmetric patterns observed in NMR spectroscopy. The average CO vibration frequency for complexes 4a ( $\nu_{av} = 2018 \text{ cm}^{-1}$ ), 4b ( $\nu_{av} = 2029 \text{ cm}^{-1}$ ), 4c ( $\nu_{av} = 2031 \text{ cm}^{-1}$ ), and 4d ( $\nu_{av} = 2028 \text{ cm}^{-1}$ ) and the calculated TEP values<sup>15a</sup> for 4a (2034 cm<sup>-1</sup>), 4b (2043 cm<sup>-1</sup>), 4c (2045 cm<sup>-1</sup>), and 4d (2034 cm<sup>-1</sup>) indicate that the new triazolylidenes are stronger donors compared to conventional NHCs ( $\nu_{av} = 2039-2041 \text{ cm}^{-1}$ )<sup>16</sup> and cyclic(alkyl)-(amino) carbenes ( $\nu_{av} = 2036 \text{ cm}^{-1}$ )<sup>17</sup> but slightly lower than other imidazol- and triazole-based mesoionic carbenes ( $\nu_{av} = 2016-2025 \text{ cm}^{-1}$ ).

Additional to the electron-donor properties of the new ligands, the NMR data after the carbonylation process indicates that complexes 4a-d recover symmetry in solution.

#### Scheme 4. Synthesis of Complexes 4a-d



For instance, all the *N*-methyl groups and the methylene fragments are resolved as single sharp peaks in the <sup>1</sup>H NMR spectra. In <sup>13</sup>C NMR, the removal of the cyclooctadiene fragment is confirmed by the appearance of two new doublets between 187.2 and 182.1 ppm, which are consistent with the cis-arrangement of the carbonyl groups around the metal center. Owing to the equivalence in solution, complexes 4a–d display only one doublet for the MIC–Rh bonds (165.8–164.2 ppm) which shift upfield when compared to the precursors 3a-d (173.5–171.5 ppm) due to the more electron-poor nature of the carbonylated rhodium center.

Despite our numerous efforts to crystallize the multimetallic rhodium complexes, we were unsuccessful in obtaining X-ray quality samples. Thus, in order to get more insight into the structural features of the new rhodium complexes, we carried out density functional theory (DFT) calculations, at the B3LYP/6-31G(d,p)/LANL2DZ level of theory with Grimme's D3 correction and using the LANL2DZ pseudopotentials only for transition metal atoms. As illustrated in Figure 2, the rhodium centers in the tri- and tetranuclear complexes are close to the expected square planar geometries which is common for Rh(CO)<sub>2</sub>X and Rh(COD)X fragments coordinated to a triazolylidene ligand. The calculated bond distances for the Rh–MIC (2.036-2.80 Å) and Rh–I (2.767-2.838 Å)



Figure 2. Calculated geometries of complexes 3c (top right), 3d (top left), 4c (bottom right), and 4d (bottom left) optimized at the B3LYP/6-31G(d,p)/LANL2DZ level of theory. Mesityl groups and hydrogen atoms omitted for clarity.

moieties also fall in the normal parameters for monodentate MIC-rhodium complexes reported in the literature<sup>15</sup> and close to the values reported in the crystal structure of complex 1 (Figure 2).

Some interesting trends are discovered by the calculated structures of 3c, 3d, 4c, and 4d. In the case of the carbonyl complexes (3c and 3d), rhodium atoms were coordinated in a square-planar geometry with the two carbonyls always occupying adjacent positions in the vertices of the square. Moreover, these complexes showed an overall extended conformation where iodine atoms are separated from nearby atoms by distances larger than the sum of their van der Waals radii. In contrast, complexes 4c and 4d resulted in compact geometries with the cyclooctadiene and mesitylene groups arranged as close as possible around the iodine atoms. The higher proximity between the COD ligands with the vicinal mesityl fragments in complexes 3c and 3d result in fully asymmetric structures that are consistent with the asymmetric patterns observed in <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

Rhodium catalysts have shown great impact across a broad range of organic transformations.<sup>19</sup> Their versatility is related to their high reactivity for both polar and nonpolar chemical bonds such as dihydrogen, Si-H, B-H, and C-H bonds. Additionally, in situ generated organometallic rhodium species are highly prone to transmetalations, migratory insertions, and reductive eliminations which increase their catalytic activity. Owing to the high cost of rhodium(I) precursors, its use in small amounts in catalytic processes is imperative, and a great deal of research is focused on improving this important task. In this context, the use of multinuclear complexes as catalysts to enhance the rate and selectivity of catalyzed reactions is of significant interest. A multimetallic catalyst is often substantially more efficient than a monometallic catalyst of similar structure owing to cooperative interactions among the several metal centers and the reaction substrate.<sup>20</sup> Motivated by the hitherto documented enhanced performance of carbene-based multinuclear precatalysts,<sup>12</sup> and to evaluate the possible cooperative effects of the multinuclear species, we decided to test the efficiency of complexes (3a-d) in the 1,4-conjugated addition of phenyl boronic acid to 2-cyclohexenone which has been successfully achieved with NHC-Rh based precatalysts.<sup>2</sup> Initial reaction conditions employed mononuclear complex 3a in 3 mol % loading at 110 °C for 24 h of reaction in toluene. As observed in Table 2, the conversion under these conditions is quantitative (entry 1) and challenging the catalyst performance by decreasing the loading to 0.1 mol % presents no change in the conversions (entries 2-5). Changing the reaction temperature to 80 °C affects the catalytic performance with a decrease in the conversion to 82% (entry 6). The best conditions regarding the temperature are observed with catalyst loadings of 0.5 mol % and using benzene as solvent (entries 8-11).

With the optimized reaction conditions, we then compared the efficiency of complexes 3a-d in the cross-coupling process using the conditions described in the entry 10 of Table 2. Monitoring of the conversions was carried out via <sup>1</sup>H NMR spectroscopy analyzing the product formation every 15 min for a period of 2 h. We observed that conversions after the first 15 min increases gradually as the number of metal centers increases (Table S1). Remarkably, the performance of the tetranuclear complex (3d) is by far the most effective with conversions of 93% after 15 min and presenting full conversions after 45 min. After 2 h, complex 3a reaches 84%

Table 2. Optimization of the 1,4-Addition of Boronic	Acid
to 2-Cyclohexenone Using Complex 3a <sup>a</sup>	

• —		1.1 Ph—B(O Complex 3 KOH 0.75 eq	9H) <sub>2</sub> 3a uiv.			
	•		C <sub>6</sub> D <sub>6</sub> , N <sub>2</sub>			
en	ntry 3	<b>Ba</b> (mol %)	temp (°C)	time	solvent	yield (%)
1	L	3	110	24 h	toluene	99
2	2	1	110	24 h	toluene	99
3	3	0.1	110	24 h	toluene	99
4	1	0.1	110	5 h	toluene	99
5	5	0.1	110	2 h	toluene	99
e	5	0.1	80	2 h	toluene	82
7	7	0.1	80	1 h	toluene	74
8	3	0.5	80	8 h	benzene	99
9	)	0.5	80	4 h	benzene	99
1	10	0.5	80	2 h	benzene	98
1	1	0.5	80	1 h	benzene	90
<sup>a</sup> Re hex	eaction enone	conditions: (0.10 mmol)	Phenylboron , solvent (0.6	ic acid mL).	(0.11 mmol)	, 2-cyclo-

yield, while the conversions for the dinuclear (3b) and trinuclear (3c) complexes are 91 and 93%, respectively.

With complex 3d as the best of the series, we then examined the scope of the conjugated addition of a variety of boronic acids to cyclohexenone. As depicted in Table 3, complex 3d produces the respective addition products in high yields (91–

Table 3. Scope of the 1,4-Addition of a Variety of Boronic Acids to 2-Cyclohexenone Catalyzed by  $3d^a$ 

) L	1. ا	1 Ar—B(OH) <sub>2</sub> <b>3d</b> ] 0.5 %mol	° –
		→ → ₀D <sub>6</sub> 80 °C, N <sub>2</sub>	Ar
Entry	Ar	Product	Yield <sup>b</sup>
1	$C_6H_5$		97
2	$(4-Br)C_6H_4$	O Br	92
3	(4-Me)C <sub>6</sub> H <sub>4</sub>	OMe	94
4	(4-OMe)C <sub>6</sub> H <sub>4</sub>	о — — — — — — — — — — — — — — — — — — —	99
5	(4-CF <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>		83°
6	(4-acetyl)C <sub>6</sub> H <sub>4</sub>		96
7	(4-0Me)C <sub>6</sub> H <sub>4</sub>	O OMe	91

<sup>*a*</sup>Reaction conditions: Phenylboronic acid (0.11 mmol), 2-cyclohexenone (0.10 mmol), complex **3d** (0.5 mol %, based in the metal),  $C_6D_6$  (0.6 mL), 2 h. <sup>*b*</sup>Isolated yields as the average of two runs. <sup>*c*</sup>Reaction carried out at 110 °C.

99%) using boronic acids bearing electron-donor and -withdrawing groups. The more challenging trifluoromethylated boronic acid (entry 6) needs heating at 110  $^{\circ}$ C to reach a maximum conversion of 83%.

Vinyl silanes are highly important reactants in organic synthesis that can be successfully produced by means of the metal-catalyzed hydrosilylation of alkynes.<sup>22</sup> Despite the relevance of this process, the quest for active and selective catalyst still represents an important challenge as the hydrosilylation of alkynes usually produces up to three isomers namely, b-(Z), b-(E). and a isomers.<sup>23</sup> With the positive results observed in the cross-coupling reaction, we decided to further test the activities of complexes 3a-d in the hydrosilylation of alkynes to produce vinylsilanes. As initial screening test for the hydrosilylation process, we carried out the reaction of phenylacetylene with triethylsilane at 80 °C, in benzene- $d_6$ and catalyst loadings of 0.5 mol % (based in the metal). Monitoring of the conversions was performed by <sup>1</sup>H NMR spectroscopy analyzing the products formation at different times over 1 h.

The performance of tetranuclear complex 3d is once again the best of the series, reaching conversions of 97% after only 20 min of reaction (Table S2). The overall yields after 1 h of reaction reach completion for complexes 3b-d, while mononuclear complex 3a achieves a maximum of 73% yield. Regarding the selectivity, all four complexes are highly *E*selective with the tetranuclear complex displaying the highest selectivity value (93%). Monitoring of the reaction using complex 3d by <sup>1</sup>H NMR spectroscopy in C<sub>6</sub>D<sub>6</sub> (Supporting Information) demonstrated that the  $E/\alpha$  ratio remained constant during the reaction course, suggesting that the *Z*vinylsilane is not an intermediate in the formation of the *E*isomer or that there is not an appreciable accumulation of this isomer.

Once tetranuclear complex 3d was established as the best catalyst of the series, we then explored the scope of the hydrosylation of a variety of alkynes with triethylsilane. As observed in Table 4, the catalytic system is compatible with a variety of substituted phenylacetylenes featuring electrondonor and -withdrawing groups (entries 1-10), reaching conversions over 98% and displaying a good selectivity for the *E*-isomer in all examples. The presence of potential oxygen coordination atoms did not interfere in the hydrosilylation although the selectivity is highly affected (entry 11). Finally, the challenging hydrosilane addition to propargyl alcohol and ethynyltrimethylsilane present good conversions with a high preference to the *E*-isomer.

Owing to the high temperature used in the hydrosilylation process and in order to rule out the formation of colloidal rhodium particles as the active catalyst, the reaction of phenylacetylene and triethylsilane using complex 3d was disturbed by the addition of elemental mercury at different reaction times (t = 0, 15, 30, and 60 min). We observed that regardless of the mercury addition time the conversions are not affected significantly. For instance, addition of mercury at t = 0and 30 min decreases the conversions by only 7 and 3%, respectively (Scheme S1). The small change in conversions strongly suggest that at 80 °C the catalytic conversions of tetranuclear complex 3d are essentially performed by molecular species.

Among the various catalysts employed for alkyne hydrosilulation, those based in NHC-rhodium architectures have attracted great attention owing to their high performance

10

11

12

13

Table 4	4. Scope of	the Hydros	silylation o	of Various	Alkynes
with T	riethylsiland	e Catalyzed	by Comp	lex 3d <sup>a</sup>	

with Themyishane Catalyzed by Complex 3d							
R	Et <sub>3</sub> SiH 1.2 equiv. <b>3d</b> 0.5%	R SiEt <sub>3</sub>	+ R	SiEt <sub>3</sub>			
	C <sub>6</sub> D <sub>6</sub> , 80 °C, N <sub>2</sub>	E/Z		α			
Entry	Alkyne	Product	Conv(%)	$E/Z/\alpha$			
1	Me <sub>2</sub> N	Me <sub>2</sub> N	96(1h)	62/34/4			
2	MeO	MeO SiEt <sub>3</sub>	95(1h)	84/13/3			
3	O <sub>2</sub> N	O <sub>2</sub> N	99(1h)	76/22/2			
4	NC	NC SiEt <sub>3</sub>	99(1h)	100/0/0			
5		SiEt <sub>3</sub>	99(4 h)	77/18/5			
6		SiEt <sub>3</sub>	99(6 h)	82/5/13			
7	OMe	OMe	94(8 h)	74/10/16			
8	CI	CI	99(9 h)	81/13/6			
9	MeO	MeO	99(4 h)	74/10/16			
	11						

<sup>*a*</sup>Reaction conditions: Alkyne (0.10 mmol), triethylsilane (0.12 mmol), catalyst (0.5 mol %, based in the metal),  $C_6D_6$  (0.6 mL). Yield and  $E/Z/\alpha$  ratios were determined by <sup>1</sup>H NMR spectroscopy using mesitylene as internal standard.

98(8h)

85(15h)

99(6h)

77(15h)

87/10/3

47/44/9

70/30/0

87/0/13

under mild reaction conditions. Table 5 show a comparison of the catalytic performance of complex 3d with recently reported NHC-rhodium-based catalysts. In general, complex 3d compares well with the few reported multinuclear NHC-rhodium catalysts in terms of catalyst loading, conversions, time, and reaction temperatures.<sup>24</sup> Interestingly, complex 3d displays a better selectivity toward the (*b*)-*E* vinylsilane isomer compared to these dinuclear complexes; however, its selectivity is still behind the pyridyl functionalized NHC-Rh complex reported by Suarez and co-workers.<sup>25</sup> Even though complex 3d is not as active as the known Crabtree (Triso)Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>

complex,<sup>26</sup> it performs better than the other catalysts presented in Table 5.

To gain deeper insight into the catalytic performance of new complexes 3a-d, we sought on investigating the reaction order with respect to the catalyst. Thus, we have performed a comparative study on the hydrosilylation of phenylacetylene with triethylsilane using different concentrations (1.0 mol %, 0.5 mol % and 0.25 mol %) of catalysts 3a-d and with a starting concentration of phenylacetylene of 1.63 mmol. Following the normalized time scale method  $t[\operatorname{cat}]_T^n$  reported by Bures and co-workers,<sup>27</sup> we found that mononuclear complex 3a fit for a first-order reaction, while the order in dinuclear complex 3b is not very clear under the conditions used (Figures S62 and S63). In contrast, a second-order reaction with respect to the catalyst is easily observed in complexes 3c and 3d (Figures S64 and S65). Although catalytic cooperativity in multinuclear complexes is very difficult to prove and more formal mechanistic studies are necessary, the results of catalyst order in 3a-d suggest that the presence of various metals in the same ligand exert a positive effect in the catalytic performance, suggesting an increased local concentration of active catalytic sites under homogeneous conditions.

### CONCLUSIONS

In summary, we have reported the synthesis of a series of mono- to tetra-[Rh(COD)I] complexes (3a-d) supported by mesoionic triazol-5-ylidenes. The treatment of complexes 3ad with an excess of carbon monoxide allows for the quantitative preparation of complexes 4a-d featuring a  $[Rh(CO)_{2}I]$  fragment which were used for the determination of the donor properties of the new triazolylidene ligands. All complexes have been fully characterized by means of <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, melting point, elemental analysis, and in the case of complex 3a, by X-ray crystallography. Comparison of the catalytic activity of the new rhodium complexes in C-C and C-Si bond forming processes demonstrate the enhanced performance of the tetranuclear species suggesting the possibility of cooperative effects in these multinuclear species. Interestingly, the hydrosilylation process is highly selective toward the E-isomer in a variety of alkyne substrates. Mercury poisoning tests indicate that at 80 °C the hydrosilylation process catalyzed by complex 3d is essentially performed by molecular species. Further exploration of the catalytic potential of complexes of type 3a-d is currently being explored in our laboratory.

# EXPERIMENTAL SECTION

Synthesis of Triazolium Salts 2a–c. *Triazolium Salt 2a*. Methyl iodide (2.04 mL, 32.8 mmol) was added to 15 mL of an acetonitrile solution of triazole 1a (640 mg, 2.18 mmol), and the resulting clear solution was refluxed for 18 h. After reaching room temperature, the solvent was reduced to 2/3 of the original volume, and diethyl ether was added until a precipitate was formed. The solid was collected by filtration and washed thoroughly with cold diethyl ether. Pure product is obtained as yellow solid in 79% yield (749 mg, 1.72 mmol) after removing the solvent under reduced pressure. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 9.03 (s, 1H, CH<sub>12</sub>), 7.22 (dd, *J* = 8.6, 7.8 Hz, 2H, CH<sub>ar</sub>), 7.04 (d, *J* = 7.9 Hz, 2H, CH<sub>ar</sub>), 6.98–6.93 (m, 3H, CH<sub>3</sub>), 2.02 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 156.7 (C<sub>ar</sub>), 142.7 (C<sub>tz</sub>), 141.1 (C<sub>mes</sub>), 134.4 (C<sub>mes</sub>), 132.7 (C<sub>mes</sub>), 131.0 (CH<sub>tz</sub>), 129.9 (CH<sub>ar</sub>), 129.9 (CH<sub>mes</sub>), 122.7 (CH<sub>ar</sub>), 115.3 (CH<sub>ar</sub>),

Catalyst	mol(%)	Substrate (mmol)	Silane	Conv.(%)	Temp (°C)	Time (h)	E/Z/a
(COD) Rh Bu-N N N N N-Bu	2-3.5ª	Ph—=== (0.46)	PhMe <sub>2</sub> SiH	100	80	2	2/8/92
(COD) Rh CI CI Rh-(COD) Bu-N N N-Bu	2.4 <sup>b</sup>	Ph	PhMe2SiH	100	75	1.5	49/0/51
(COD) Rh Rh (COD) Bu-N N N-Bu	0.78 <sup>b</sup>	Ph—=== (0.77)	PhMe2SiH	83	Rt	2	8/92/0
3d	0.5°	Ph	Et₃SiH	100	80	1	93/5/2
N Rh COD	2.0 <sup>d</sup>	Ph—=== (0.28)	<sup>n</sup> Pr₃SiH	97	60	2	99/0/1
(Triso)Ir(C2H4)2	0.001°	Ph-=== (17.4)	Et₃SiH	80	Rt	2.5	1/99/0

Table 5.	Comparison of	Compl	lex 4 wit	h Recently	Reported	NHC-Rh-Based	Hydros	ylation	Catal	yst
----------	---------------	-------	-----------	------------	----------	--------------	--------	---------	-------	-----

<sup>a</sup>Ref 24a. <sup>b</sup>Ref 24b. <sup>c</sup>This work. <sup>d</sup>Ref 25. <sup>e</sup>Ref 26.

59.6 (CH<sub>2</sub>), 40.9 (NCH<sub>3</sub>), 21.2 (CH<sub>3</sub>), 18.1 (CH<sub>3</sub>). Found: C, 52.51; H, 5.33; N, 9.28. Calcd for  $C_{19}H_{22}IN_3O$ : C, 52.42; H, 5.09; N, 9.65.

Triazolium Salt 2b. Methyl iodide (1.3 mL, 20.7 mmol) was added to 7 mL of an acetonitrile solution of bistriazole 1b (350 mg, 0.68 mmol), and the resulting clear solution was refluxed for 18 h. After reaching room temperature, the solvent was reduced to 2/3 of the original volume and diethyl ether was added until a precipitate was formed. The solid was collected by filtration and washed thoroughly with cold diethyl ether. Pure product is obtained as white solid in 68% yield (367 mg, 0.462 mmol) after column chromatography purification using a mixture of dichloromethane/petroleum ether (1:1) as eluent. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 9.15 (s, 2H, CH<sub>tz</sub>), 7.22 (t, J = 2.3 Hz, 1H, CH<sub>ar</sub>), 7.11 (t, J = 8.2 Hz, 1H, CH<sub>ar</sub>), 6.96 (s, 4H,  $CH_{mes}$ ), 6.73 (dd, J = 8.2, 2.3 Hz, 2H,  $CH_{ar}$ ), 5.93 (s, 4H,  $CH_2$ ), 4.64 (s, 6H, NCH<sub>3</sub>), 2.30 (s, 6H, CH<sub>3</sub>), 2.03 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 158.0 (C<sub>ar</sub>), 142.5 (C<sub>tz</sub>), 141.1 (C<sub>mes</sub>), 134.3 ( $C_{mes}$ ), 132.3 ( $C_{mes}$ ), 131.0 ( $CH_{ar}$ ), 130.6 ( $CH_{tz}$ ), 129.8 (CH<sub>mes</sub>), 110.2 (CH<sub>ar</sub>), 102.8 (CH<sub>ar</sub>), 60.3 (CH<sub>2</sub>), 41.5 (NCH<sub>3</sub>), 21.2 (CH<sub>3</sub>), 18.0 (CH<sub>3</sub>). Found: C, 48.21; H, 5.01; N, 10.77. Calcd for C<sub>32</sub>H<sub>38</sub>I<sub>2</sub>N<sub>6</sub>O<sub>2</sub>: C, 48.50; H, 4.83; N, 10.60.

*Triazolium Salt* **2c**. Methyl iodide (1.6 mL, 24.8 mmol) was added to 10 mL of an acetonitrile solution of tristriazole **1c** (400 mg, 0.55 mmol), and the resulting clear solution was refluxed for 18 h. After reaching room temperature, the solvent was reduced to 2/3 of the original volume, and diethyl ether was added until a precipitate was formed. The solid was collected by filtration and washed thoroughly with cold diethyl ether. Pure product is obtained as yellow solid in 98% yield (620 mg, 0.54 mmol) after removing the solvent under reduced pressure. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 9.38 (s, 3H, CH<sub>1z</sub>), 7.09 (s, 3H, CH<sub>a</sub>), 6.93 (s, 6H, CH<sub>mes</sub>), 5.97 (s, 6H, CH<sub>2</sub>), 4.72 (s, 9H, NCH<sub>3</sub>), 2.29 (s, 9H, CH<sub>3</sub>), 2.06 (s, 18H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 158.8 (C<sub>a</sub>), 142.2 (C<sub>mes</sub> + C<sub>tz</sub>), 134.5 (C<sub>mes</sub>), 132.1 (CH<sub>tz</sub>), 131.3 (C<sub>mes</sub>), 129.9 (CH<sub>mes</sub>), 98.1 (CH<sub>a</sub>), 62.0 (CH<sub>2</sub>), 42.4 (NCH<sub>3</sub>), 21.2 (CH<sub>3</sub>), 18.4 (CH<sub>3</sub>). Found: C, 47.33; H, 4.52; N, 11.12. Calcd for C<sub>45</sub>H<sub>54</sub>I<sub>3</sub>N<sub>9</sub>O<sub>3</sub>: C, 47.01; H, 4.73; N, 10.96.

Synthesis of Complexes 3a-c. Complex 3a. Rhodium(I) cyclooctadiene chloride dimer (28.0 mg, 0.057 mmol), potassium hexamethyl disilazide (30.0 mg, 0.149 mmol), and triazolium salt 2a (50.0 mg, 0.115 mmol) were combined in a Schlenk flask and dissolved in THF (9 mL) at -78 °C. The resulting mixture was stirred for 16 h while reaching room temperature. The final clear suspension was dried under vacuum, and the residue was extracted with dichloromethane (10 mL). After cannula filtration and removal of the solvent, the crude product is purified by column chromatography using a mixture of hexanes/ethyl acetate (8:2) as eluent providing the title product as yellow solid in 63% yield (63 mg, 0.073 mmol). Single crystals were obtained by the slow evaporation of a concentrated THF/acetronitrile (1:1) solution. Mp = 198-202 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta = 7.41 - 7.34$  (m, 2H, CH<sub>ar</sub>), 7.21-7.16 (m, 2H, CH<sub>ar</sub>), 7.10–7.02 (m, 2H, CH<sub>mes</sub> + CH<sub>ar</sub>), 6.93 (s, 1H,  $CH_{mes}$ ), 6.30 (d, J = 12.8 Hz, 1H,  $CH_2$ ), 5.21 (d, J = 12.8 Hz, 1H, CH<sub>2</sub>), 5.15–5.08 (m, 1H, CH<sub>COD</sub>), 5.02–4.95 (m, 1H, CH<sub>COD</sub>), 4.17 (s, 3H, NCH<sub>3</sub>), 3.69–3.63 (m, 1H, CH<sub>COD</sub>), 3.15–3.07 (m, 1H, CH<sub>COD</sub>), 2.46 (s, 3H, CH<sub>3</sub>), 2.38 (s, 3H, CH<sub>3</sub>), 2.16-1.95 (m, 3H, CH<sub>2-COD</sub>), 1.82-1.74 (m, 4H, CH<sub>3</sub> + CH<sub>COD</sub>), 1.72-1.58 (m, 2H, CH<sub>2-COD</sub>), 1.54–1.46 (m, 1H, CH<sub>2-COD</sub>), 1.44–1.34 (m, 1H, CH<sub>2-COD</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  = 172.8 (d, J = 45.7 Hz, C=Rh), 157.9 ( $C_{ar}$ ), 141.3 ( $C_{tz}$ ), 140.0 ( $C_{mes}$ ), 136.2 ( $C_{mes}$ ), 135.8 (C<sub>mes</sub>), 134.5 (C<sub>mes</sub>), 129.7 (CH<sub>mes</sub>), 129.7 (CH<sub>ar</sub>), 128.2  $(CH_{mes})$ , 122.0  $(CH_{ar})$ , 115.3  $(CH_{ar})$ , 94.4  $(d, J = 7.2 \text{ Hz}, CH_{COD})$ , 93.8 (d, J = 6.9 Hz, CH<sub>COD</sub>), 72.8 (d, J = 13.9 Hz, CH<sub>COD</sub>), 71.0 (d, J = 13.8 Hz,  $CH_{COD}$ ), 63.3 ( $CH_2$ ), 37.2 ( $NCH_3$ ), 33.5 ( $CH_{2-COD}$ ),

31.1 (CH<sub>2-COD</sub>), 30.1 (CH<sub>2-COD</sub>), 28.7 (CH<sub>2-COD</sub>), 21.2 (CH<sub>3</sub>), 21.2 (CH<sub>3</sub>), 17.6 (CH<sub>3</sub>). FT-IR in KBr (cm<sup>-1</sup>): 3432, 2926, 2873, 2830, 2348, 1601, 1495, 1453, 1236, 1177, 1152, 1074, 1032, 856, 753. Found: C, 50.13; H, 5.25; N, 6.77. Calcd for  $C_{27}H_{32}IN_3ORh$ : C, 50.33; H, 5.01; N, 6.52.

Complex 3b. Following the procedure for the synthesis of complex 3a and using rhodium(I) cyclooctadiene chloride dimer (31.0 mg, 0.063 mmol), potassium hexamethyl disilazide (32.0 mg, 0.164 mmol), and bistriazolium salt 2b (50.0 mg, 0.063 mmol), the title product is purified by column chromatography using a mixture of hexanes/ethyl acetate (8:2) as eluent. Yellow solid, 72% yield (55 mg, 0.045 mmol). Mp = 163–166 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 7.39 (t, J = 8.16, 1H, CH<sub>ar</sub>), 7.08 (s, 2H, CH<sub>mes</sub>), 6.94 (s, 2H, CH<sub>mes</sub>), 6.93-6.88 (m, 3H, CH<sub>ar</sub>), 6.34-6.28 (m, 2H, CH<sub>2</sub>), 5.25-5.17 (m, 2H, CH<sub>2</sub>), 5.13–5.05 (m, 2H, CH<sub>COD</sub>), 5.02–4.95 (m, 2H, CH<sub>COD</sub>), 4.22-4.17 (m, 6H, NCH<sub>3</sub>), 4.76-4.68 (m, 2H, CH<sub>COD</sub>), 3.18-3.10 (m, 2H, CH<sub>COD</sub>), 2.46 (s, 6H, 2CH<sub>3</sub>), 2.39 (s, 6H, 2CH<sub>3</sub>), 2.19–2.09 (m, 2H, CH<sub>2-COD</sub>), 2.07–1.95 (m, 4H, CH<sub>2-COD</sub>), 1.88–1.74 (m, 8H, CH<sub>3</sub> + CH<sub>2-COD</sub>), 1.69–1.55 (m, 4H, CH<sub>2-COD</sub>), 1.54–1.45 (m, 2H, CH<sub>2-COD</sub>), 1.43–1.33 (m, 2H, CH<sub>2-COD</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  = 172.3 (d, J = 45.7 Hz, C=Rh), 172.2 (d, J = 45.7 Hz, C=Rh), 158.3 (C<sub>ar</sub>), 139.9 (C<sub>trz</sub>), 130.0 (C<sub>mes</sub>), 135.2 (C<sub>mes</sub>), 134.8 (C<sub>mes</sub>), 133.5 (C<sub>mes</sub>), 129.5 (CH<sub>ar</sub>), 128.7 (CH<sub>mes</sub>), 127.2 (CH<sub>mes</sub>), 107.1 (CH<sub>ar</sub>), 101.9 (CH<sub>ar</sub>), 101.8 (CH<sub>ar</sub>), 93.3 (CH<sub>COD</sub>),93.3 (CH<sub>COD</sub>), 93.2 (CH<sub>COD</sub>), 93.2 (CH<sub>COD</sub>), 93.0 (CH<sub>COD</sub>), 93.0 (CH<sub>COD</sub>), 92.9 (CH<sub>COD</sub>), 92.9 (CH<sub>COD</sub>), 71.9 (CH<sub>COD</sub>), 71.8 (CH<sub>COD</sub>), 69.9 (CH<sub>COD</sub>), 69.8 (CH<sub>COD</sub>), 62.1 (s, CH<sub>2</sub>), 36.1 (NCH<sub>3</sub>), 32.6 (CH<sub>2-COD</sub>), 29.9 (CH<sub>2-COD</sub>), 29.2 (CH<sub>2-COD</sub>), 27.6 (CH<sub>2-COD</sub>), 20.1 (CH<sub>3</sub>), 16.7 (CH<sub>3</sub>). FT-IR in KBr (cm<sup>-1</sup>): 3446, 2923, 2364, 2059, 1606, 1446, 1382, 1330, 1283, 1236, 1156, 1132, 1035, 908, 850, 760. Found: C, 47.41; H, 4.66; N, 6.69. Calcd for C48H59I2N6O2Rh2: C, 47.58; H, 4.91; N, 6.94.

Complex 3c. Following the procedure for the synthesis of complex 3a and using rhodium(I) cyclooctadiene chloride dimer (32.0 mg, 0.065 mmol), potassium hexamethyl disilazide (34.0 mg, 0.169 mmol), and tristriazolium salt 2c (50.0 mg, 0.043 mmol), the title product is purified by column chromatography using a mixture of dichloromethane/ethanol (95:5) as eluent. Yellow solid, 65% yield (50 mg, 0.028 mmol). Mp = 250-252 °C. <sup>1</sup>H NMR (CDCl<sub>2</sub>, 400 MHz)  $\delta = 7.02$  (s, 3H, CH<sub>mes</sub>), 6.89 (s, 3H, CH<sub>mes</sub>), 6.62–6.55 (m, 3H, CH<sub>ar</sub>) 6.32–6.22 (m, 3H, CH<sub>2</sub>), 5.15–5.08 (m, 3H, CH<sub>2</sub>), 5.03– 4.96 (m, 3H, CH<sub>COD</sub>), 4.95-4.89 (m, 3H, CH<sub>COD</sub>), 4.16 (s, 9H, NCH<sub>3</sub>), 3.75-3.68 (m, 3H, CH<sub>2-COD</sub>), 3.13-3.05 (m, 3H, CH<sub>2-COD</sub>), 2.40 (s, 9H, CH<sub>3</sub>), 2.33 (s, 9H, CH<sub>3</sub>), 2.15-2.05 (m, 3H, CH<sub>2-COD</sub>), 1.98–1.88 (m, 6H0, CH<sub>2-COD</sub>), 1.83–1.68 (m, 12H,  $\begin{array}{l} CH_{3}+CH_{2-COD}),\,1.60-1.50\,\,(m,\,6H,\,CH_{2-COD}),\,1.47-1.38\,\,(m,\,3H,\,CH_{2-COD}),\,1.37-1.28\,\,(m,\,3H,\,CH_{2-COD}),\,^{13}C\,\,NMR\,\,(CDCl_{3},\,100\,\,CDCl_{3}),\,100\,\,CDCl_{3},\,100\,\,CDC$ MHz)  $\delta$  = 173.5 (d, J = 45.5 Hz, C=Rh), 173.4 (d, J = 45.6 Hz, C= Rh), 173.3 (d, J = 45.5 Hz, C=Rh), 160.4 (C<sub>ar</sub>), 140.8 (C<sub>tz</sub>), 140.1 (C<sub>mes</sub>), 136.2 (C<sub>mes</sub>), 135.9 (C<sub>mes</sub>), 134.7 (C<sub>mes</sub>), 129.8 (CH<sub>mes</sub>), 128.4 (CH<sub>mes</sub>), 95.4 (CH<sub>ar</sub>), 95.3 (CH<sub>ar</sub>), 94.3 (CH<sub>COD</sub>), 94.2 (CH<sub>COD</sub>), 73.3 (CH<sub>COD</sub>), 73.2 (CH<sub>COD</sub>), 63.0 (CH<sub>2</sub>), 37.3 (NCH<sub>3</sub>), 33.9 (CH<sub>2-COD</sub>), 30.9 (CH<sub>2-COD</sub>), 30.4 (CH<sub>2-COD</sub>), 28.6 (CH<sub>2-COD</sub>), 21.3 (CH<sub>3</sub>), 18.1 (CH<sub>3</sub>), 18.0 (CH<sub>3</sub>). Found: C, 46.51; H, 5.12; N, 7.24. Calcd for C70H90I3N9O3Rh3: C, 46.84; H, 5.05; N, 7.02. FT-IR in KBr (cm<sup>-1</sup>): 3433, 2916, 2372, 2172, 1605, 1439, 1377, 1329, 1245, 1159, 1042, 854. [ESI-MS, positive mode]:  $M^+ = 1794.9 \ m/z; \ [M^+ - I]^+ \ 1669.9 \ m/z.$ 

*Complex* **3d**. Following the procedure for the synthesis of complex **3a** and using rhodium(I) cyclooctadiene chloride dimer (33.0 mg, 0.066 mmol), potassium hexamethyl disilazide (34.0 mg, 0.173 mmol), and tetratriazolium salt **2d** (50.0 mg, 0.033 mmol), the title product is purified by precipitation with petroleum ether. Yellow solid, 69% yield (54 mg, 0.023 mmol). Mp = 260–261 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 6.99 (s, 4H, CH<sub>mes</sub>), 6.86 (s, 4H, CH<sub>mes</sub>), 5.08–5.37 (m, 8H, CH<sub>2</sub>), 4.92 (s, 8H, CH<sub>COD</sub>), 4.25–4.10 (m, 12H, NCH<sub>3</sub>), 3.95–3.80 (m, 8H, CH<sub>2</sub>), 3.54 (s, 4H, CH<sub>COD</sub>), 3.02 (s, 4H, CH<sub>COD</sub>), 2.37 (s, 12H, CH<sub>3</sub>), 2.31 (s, 12H, CH<sub>3</sub>), 2.27–2.15 (m, 4H, CH<sub>2–COD</sub>), 2.05–1.90 (m, 8H, CH<sub>2–COD</sub>), 1.77–1–67 (m, 16H, CH<sub>3</sub> + CH<sub>2–COD</sub>), 1.66–1.57 (m, 4H, CH<sub>2–COD</sub>), 1.42–1.25 (m, 8H,

CH<sub>2−COD</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  = 171.7 (d, *J* = 44.1 Hz, C=Rh), 171.7 (d, *J* = 45.4 Hz, C=Rh), 171.5 (d, *J* = 45.9 Hz, C= Rh), 171.5 (d, *J* = 46.0 Hz, C=Rh), 141.9 (C<sub>tz</sub>), 141.9 (C<sub>tz</sub>), 139.9 (C<sub>mes</sub>), 136.2 (C<sub>mes</sub>), 136.0 (C<sub>mes</sub>), 134.6 (C<sub>mes</sub>), 134.5 (C<sub>mes</sub>), 129.8 (CH<sub>mes</sub>), 128.8 (C<sub>mes</sub>), 128.4 (CH<sub>mes</sub>), 94.2 (CH<sub>COD</sub>), 93.5 (CH<sub>COD</sub>), 93.4 (CH<sub>COD</sub>), 72.6 (CH<sub>COD</sub>), 72.5 (CH<sub>COD</sub>), 70.8 (CH<sub>2−C<sub>pent</sub>), 70.6 (CH<sub>2−Cpent</sub>), 66.1 (CH<sub>2</sub>), 66.0 (CH<sub>2</sub>), 46.9 (C<sub>pent</sub>), 38.2 (NCH<sub>3</sub>), 38.1 (NCH<sub>3</sub>), 34.3 (CH<sub>2−COD</sub>), 30.7 (CH<sub>2−COD</sub>), 21.3 (CH<sub>3</sub>), 21.2 (CH<sub>3</sub>), 18.0 (CH<sub>3</sub>), 18.0 (CH<sub>3</sub>). Found: C, 45.32; H, 5.37; N, 7.02. Calcd for C<sub>89</sub>H<sub>120</sub>I<sub>4</sub>N<sub>12</sub>O<sub>4</sub>Rh<sub>4</sub>: C, 45.70; H, 5.08; N, 7.19. FT-IR in KBr (cm<sup>-1</sup>): 3446, 2916, 2872, 2823, 1614, 1447, 1326, 1262, 1153, 1072, 1030, 956, 853, 799. [ESI-MS, positive mode]: M<sup>+</sup> = 2340.6 m/z; [M<sup>+</sup> − I]<sup>+</sup> 2213.6 m/z.</sub>

General Synthesis of Carbonylated Complexes 4a–c. Carbon monoxide was bubbled for 15 min to a solution of the appropriate [Rh(COD)Cl]-triazolylidene (0.05 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. The light-orange solution turned slightly yellow. The solvent was removed under vacuum, and the residue was washed thrice with 5 mL of petroleum ether to produce the pure carbonylated complex.

*Complex 4a.* Yellow solid, 89% yield (0.0445 mmol). Mp = 238–240 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 7.36–7.31 (m, 2H, CH<sub>ar</sub>), 7.14–7.10 (m, 2H, CH<sub>ar</sub>), 7.05–7.01 (m, 1H, CH<sub>ar</sub>), 6.99 (s, 2H, CH<sub>mes</sub>), 5.54 (s, 2H, CH<sub>2</sub>), 4.27 (s, 3H, NCH<sub>3</sub>), 2.37 (s, 3H, CH<sub>3</sub>), 2.03 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  = 187.1 (d, *J* = 52.7 Hz, Rh–CO), 182.2 (d, *J* = 77.3 Hz, Rh–CO), 165.8 (d, *J* = 38.8 Hz, C=Rh), 157.0 (C<sub>ar</sub>), 143.2 (C<sub>tz</sub>), 143.2 (C<sub>tz</sub>), 140.8 (C<sub>mes</sub>), 135.7 (C<sub>mes</sub>), 134.7 (C<sub>mes</sub>), 129.8 (CH<sub>ar</sub>), 129.4 (CH<sub>mes</sub>), 122.2 (CH<sub>ar</sub>), 115.3 (CH<sub>ar</sub>), 62.0 (CH<sub>2</sub>), 37.8 (NCH<sub>3</sub>), 21.3 (CH<sub>3</sub>), 18.6 (CH<sub>3</sub>). FT-IR in KBr (cm<sup>-1</sup>): 3444,2919, 2850, 2052 (C=O), 1983 (C=O), 1598, 1586, 1487, 1462, 1231, 1169, 1078, 1034, 1016, 1014, 861, 845. Found: C, 42.77; H, 3.89; N, 7.51. Calcd for C<sub>21</sub>H<sub>21</sub>IN<sub>3</sub>O<sub>3</sub>Rh: C, 42.52; H, 3.57; N, 7.08.

Complex **4b**. Yellow solid, 99% yield (0.0498 mmol). Mp = 236– 238 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 7.27 (t, *J* = 8.3 Hz, 1H, CH<sub>ar</sub>), 6.99 (s, 4H, CH<sub>mes</sub>), 6.88 (t, *J* = 2.3 Hz, 1H, CH<sub>ar</sub>), 6.80 (dd, *J* = 8.3, 2.4 Hz, 2H, CH<sub>ar</sub>), 5.51 (s, 4H, CH<sub>2</sub>), 4.29 (s, 6H, NCH<sub>3</sub>), 2.37 (s, 6H, CH<sub>3</sub>), 2.03 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  = 187.1 (d, *J* = 52.7 Hz, Rh–CO), 182.2 (d, *J* = 77.4 Hz, Rh–CO), 165.8 (d, *J* = 38.9 Hz, C=Rh), 158.5 (C<sub>ar</sub>), 143.0 (C<sub>tz</sub>), 143.0 (C<sub>tz</sub>), 140.9 (C<sub>mes</sub>), 135.7 (C<sub>mes</sub>), 134.8 (C<sub>mes</sub>), 130.6 (CH<sub>ar</sub>), 129.5 (CH<sub>mes</sub>), 108.5 (CH<sub>a</sub>), 103.2 (CH<sub>a</sub>), 62.1 (CH<sub>2</sub>), 37.8 (NCH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 18.7 (CH<sub>3</sub>). FT-IR in KBr (cm<sup>-1</sup>): 3450, 2924, 2850, 2066 (C=O), 1992 (C=O), 1599, 1489, 1450,1328, 1248, 1180, 1147, 1031, 850. Found: C, 39.31; H, 3.52; N, 7.30. Calcd for C<sub>36</sub>H<sub>36</sub>L<sub>2</sub>N<sub>6</sub>O<sub>6</sub>Rh<sub>2</sub>: C, 39.01; H, 3.27; N, 7.58.

Complex 4c. Yellow solid, 80% yield (0.040 mmol). Mp = 233– 234 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 6.99 (s, 6H, CH<sub>mes</sub>), 6.57 (s, 3H, CH<sub>ar</sub>), 5.49 (s, 6H, CH<sub>2</sub>), 4.30 (s, 9H, NCH<sub>3</sub>), 2.37 (s, 9H, CH<sub>3</sub>), 2.04 (s, 18H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  = 187.2 (d, J = 52.6 Hz, Rh–CO), 182.1 (d, J = 77.2 Hz, Rh–CO), 165.6 (d, J = 38.9 Hz, C=Rh), 159.4 (C<sub>ar</sub>), 142.8 (C<sub>tz</sub>), 142.8 (C<sub>tz</sub>), 140.9 (C<sub>mes</sub>), 135.7 (C<sub>mes</sub>), 134.7 (C<sub>mes</sub>), 129.4 (CH<sub>mes</sub>), 96.2 (CH<sub>ar</sub>), 62.1 (CH<sub>2</sub>), 37.9 (NCH<sub>3</sub>), 21.3 (CH<sub>3</sub>), 18.7 (CH<sub>3</sub>). Found: C, 38.56; H, 3.42; N, 7.88. Calcd for C<sub>52</sub>H<sub>54</sub>I<sub>3</sub>N<sub>9</sub>O<sub>9</sub>Rh<sub>3</sub>: C, 38.12; H, 3.32; N, 7.69. FT-IR in KBr (cm<sup>-1</sup>): 3450, 2924, 2855, 2176, 2067 (C=O), 1995 (C=O), 1951, 1605, 1453, 1378, 1330, 1252, 1155, 1036, 851. [MALDI-TOF MS, positive mode], M<sup>+</sup> = 1623.4529 m/z; [M<sup>+</sup> – 5CO]<sup>+</sup> = 1479.977 m/z.

Complex 4d. Yellow solid, 99% yield (0.0498 mmol). Mp = 218– 220 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 6.98 (s, 8H, CH<sub>mes</sub>), 5.58 (s, 8H, CH<sub>2</sub>), 4.31 (s, 12H, NCH<sub>3</sub>), 3.76 (s, 8H, CH<sub>2</sub>), 2.36 (s, 12H, CH<sub>3</sub>), 2.07 (s, 24H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  = 187.1 (d, J = 52.5 Hz, Rh–CO), 182.3 (d, J = 77.4 Hz, Rh–CO), 164.2 (d, J = 38.7 Hz, C=Rh), 143.6 (d, J = 2.0 Hz, C<sub>tz</sub>), 140.8 (C<sub>mes</sub>), 135.7 (C<sub>mes</sub>), 134.7 (C<sub>mes</sub>), 129.5 (CH<sub>mes</sub>), 70.3 (CH<sub>2</sub>), 64.6 (CH<sub>2</sub>), 38.3 (NCH<sub>3</sub>), 21.3 (CH<sub>3</sub>), 18.8 (CH<sub>3</sub>). Found: C, 36.05; H, 3.64; N, 8.02. Calcd for C<sub>65</sub>H<sub>72</sub>I<sub>4</sub>N<sub>12</sub>O<sub>12</sub>Rh<sub>4</sub>: C, 36.61; H, 3.41; N, 7.88. FT-IR in KBr (cm<sup>-1</sup>): 3453, 2922, 2855, 2064 (C=O), 1992 (C=O), 1607, 1449, 1327, 1259, 1166, 1075, 1030, 853, 802. [MALDI-TOF MS, positive mode]  $M^+ = 2132.6029 \ m/z \ [M^+ + H - I^+] \ 2003.964 \ m/z.$ 

**Catalytic 1,4-Addition of Boronic Acids to 2-Cyclohexe-none.** A scintillation vial was charged with the proper phenyl boronic acid (0.11 mmol), KOH (42 mg, 0.75 mmol), 2-cyclohexenone (10 mg, 0.10 mmol), and catalyst **3d** (0.5 mol %, based in the metal). Benzene (5 mL) was added, and the mixture heated at 80 °C. Product formation was monitored by TLC. The solvent was removed under vacuum, and the products were purified by column chromatography using proper hexanes/ethyl acetate mixtures as eluent.

General Procedure for the Catalytic Hydrosilylation Reactions. An NMR tube was charged with the tiethylsylane (1.2 equiv), the proper alkyne (1.0 equiv), and the catalyst (0.5 mol %, based in the metal). Deuterated benzene was added (0.7 mL), and the mixture heated at 80 °C. Product formation and selectivity were determined by <sup>1</sup>H NMR spectroscopy using mesitylene as internal standard.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00517.

Experimental procedures. Sample <sup>1</sup>H and <sup>13</sup>C NMR for new compounds and catalytic products (PDF)

Cartesian coordinates (XYZ)

#### Accession Codes

CCDC 1977420 and 1977421 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

#### AUTHOR INFORMATION

# **Corresponding Author**

Daniel Mendoza-Espinosa – Área Académica de Química, Universidad Autónoma del Estado de Hidalgo, Mineral de la Reforma, Hidalgo 42090, México; o orcid.org/0000-0001-9170-588X; Email: daniel mendoza@uaeh.edu.mx

#### Authors

- David Rendón-Nava Área Académica de Química, Universidad Autónoma del Estado de Hidalgo, Mineral de la Reforma, Hidalgo 42090, México
- Jose M. Vásquez-Pérez Conacyt Research Fellow, Área Académica de Química, Universidad Autónoma del Estado de Hidalgo, Mineral de la Reforma, Hidalgo 42090, México; orcid.org/0000-0002-2389-2646
- **Cesar I. Sandoval-Chávez** Conacyt Research Fellow, Área Académica de Química, Universidad Autónoma del Estado de Hidalgo, Mineral de la Reforma, Hidalgo 42090, México
- Alejandro Alvarez-Hernández Área Académica de Química, Universidad Autónoma del Estado de Hidalgo, Mineral de la Reforma, Hidalgo 42090, México; orcid.org/0000-0002-4937-6944

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00517

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

D.M.-E. is grateful to CONACYT for financial support (project A1-S-8892). C.I.S–C is grateful to Grant Cátedra-CONACYT-2016-222.

### REFERENCES

(1) Guisado-Barrios, G.; Bouffard, J.; Donnadieu, B.; Bertrand, G. Crystalline 1H-1,2,3-triazol-5-ylidenes: New Stable Mesoionic Carbenes. *Angew. Chem., Int. Ed.* **2010**, *49*, 4759–4762.

(2) Guisado-Barrios, G.; Bouffard, J.; Donnadieu, B.; Bertrand, G. Bis(1,2,3-triazol-5-ylidenes) (i-bitz) as Stable 1,4-Bidentate Ligands Based on Mesoionic Carbenes (MICs). *Organometallics* **2011**, *30*, 6017–6021.

(3) (a) Albrecht, M. C4-bound imidazolylidenes: from curiosities to high-impact carbene ligands. Chem. Commun. 2008, 3601-3610. (b) Schuster, O.; Yang, L.; Raubenheimer, H. G.; Albrecht, M. Beyond Conventional N-Heterocyclic Carbenes: Abnormal, Remote, and Other Classes of NHC Ligands with Reduced Heteroatom Stabilization. Chem. Rev. 2009, 109, 3445-3478. (c) Schweinfurth, D.; Hettmanczyk, L.; Suntrup, L.; Sarkar, B. Metal Complexes of Click Derived Triazoles and Mesoionic Carbenes: Electron Transfer, Photochemistry, Magnetic Bistability, and Catalysis. Z. Anorg. Allg. Chem. 2017, 643, 554-584. (d) Guisado-Barrios, G.; Soleilhavoup, M.; Bertrand, G. 1H-1,2,3-Triazol-5-ylidenes: Readily Available Mesoionic Carbenes. Acc. Chem. Res. 2018, 51, 3236-3244. (e) Vivancos, A.; Segarra, C.; Albrecht, M. Mesoionic and Related Less Heteroatom-Stabilized N-Heterocyclic Carbene Complexes: Synthesis, Catalysis, and Other Applications. Chem. Rev. 2018, 118, 9493-9586. (f) Crabtree, R. H. Abnormal, Mesoionic and Remote N-Heterocyclic Carbenes. Coord. Chem. Rev. 2013, 257, 755-766.

(4) (a) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Click Chemistry: Diverse Chemical Function from a Few Good Reactions. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021. (b) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. A Stepwise Huisgen Cycloaddition Process: Copper(I)-catalyzed Regioselective "Ligation" of Azides and Terminal Alkynes. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599. (c) Tornøe, C. W.; Christensen, C.; Meldal, M. Peptidotriazoles on Solid Phase: [1,2,3]-Triazoles by Regiospecific Copper(I)-Catalyzed 1,3-Dipolar Cycloadditions of Terminal Alkynes to Azides. *J. Org. Chem.* **2002**, *67*, 3057–3064.

(5) For selected reviews, see (a) Liang, L.; Astruc, D. The copper(I)catalyzed alkyne-azide cycloaddition (CuAAC) "click" reaction and its applications. An overview. *Coord. Chem. Rev.* **2011**, *255*, 2933–2945. (b) Diez-Gonzalez, S. Well-defined copper(I) complexes for Click azide-alkyne cycloaddition reactions: one Click beyond. *Catal. Sci. Technol.* **2011**, *1*, 166–178. (c) Hein, J. E.; Fokin, V. V. Coppercatalyzed azide-alkynecycloaddition (CuAAC) and beyond: new reactivity of copper(I) acetylides. *Chem. Soc. Rev.* **2010**, *39*, 1302– 1315. (d) Meldal, M.; Tornøe, C. W. Cu-Catalyzed Azide-Alkyne Cycloaddition. *Chem. Rev.* **2008**, *108*, 2952–3015. (e) Bock, V. D.; Hiemstra, H.; van Maarseveen, J. H. Cu<sup>I</sup>-Catalyzed Alkyne-Azide "Click" Cycloadditions from a Mechanistic and Synthetic Perspective. *Eur. J. Org. Chem.* **2006**, *2006*, 51–68.

(6) See, for example, (a) Mathew, P.; Neels, A.; Albrecht, M. 1,2,3-Triazolylidenes as Versatile Abnormal Carbene Ligands for Late Transition Metals. J. Am. Chem. Soc. 2008, 130, 13534–13535. (b) Karthikeyan, T.; Sankararaman, S. Palladium complexes with abnormal N-heterocyclic carbene ligands derived from 1,2,3triazolium ions and their application in Suzuki coupling. Tetrahedron Lett. 2009, 50, 5834–5837. (c) Poulain, A.; Canseco-Gonzalez, D.; Hynes-Roche, R.; Muller-Bunz, H.; Schuster, O.; Stoeckli-Evans, H.; Neels, A.; Albrecht, M. Synthesis and Tunability of Abnormal 1,2,3-Triazolylidene Palladium and Rhodium Complexes. Organometallics 2011, 30, 1021–1029.

(7) For recent reports on the coordination chemistry of MICs, see (a) Saravanakumar, R.; Ramkumar, V.; Sankararaman, S. Synthesis and Structure of 1,4-Diphenyl-3-methyl-1,2,3-triazol-5-ylidene Palladium Complexes and Application in Catalytic Hydroarylation of

Alkynes. Organometallics 2011, 30, 1689-1694. (b) Schulze, B.; Escudero, D.; Friebe, C.; Siebert, R.; Görls, H.; Köhn, U.; Altuntas, E.; Baumgaertel, A.; Hager, M. D.; Winter, A.; et al. A Heteroleptic Bis(tridentate) Ruthenium(II) Complex of a Click-Derived Abnormal Carbene Pincer Ligand with Potential for Photosensitzer Application. Chem. - Eur. J. 2011, 17, 5494-5498. (c) Bezuidenhout, D. I.; Kleinhans, G.; Guisado- Barrios, G.; Liles, D. C.; Ung, G.; Bertrand, G. Isolation of a potassium bis(1,2,3-triazol-5-ylidene)carbazolide: a stabilizing pincer ligand for reactive late transition metal complexes. Chem. Commun. 2014, 50, 2431-2433. (d) Hohloch, S.; Kaiser, S.; Duecker, F. L.; Bolje, A.; Maity, R.; Kosmrlj, J.; Sarkar, B. Catalytic oxygenation of sp<sup>3</sup> "C-H" bonds with Ir(III) complexes of chelating triazoles and mesoionic carbenes. Dalton Trans. 2015, 44, 686-693. (e) Mendoza-Espinosa, D.; Alvarez-Hernandez, A.; Angeles- Beltran, D.; Negron-Silva, G. E.; Suarez-Castillo, O. R.; Vasquez- Perez, J. M. Bridged N-Heterocyclic/Mesoionic (NHC/MIC) Heterodicarbenes as Ligands for Transition Metal Complexes. Inorg. Chem. 2017, 56, 2092-2099. (f) Ruiz-Mendoza, F. J.; Mendoza-Espinosa, D.; Gonzalez-Montiel, S. Synthesis and Catalytic Activity of Coumarinand Chrysin-Tethered Triazolylidene Gold(I) Complexes. Eur. J. Inorg. Chem. 2018, 2018, 4622-4629. (g) Schweinfurth, D.; Hettmanczyk, L.; Suntrup, L.; Sarkar, B. Metal Complexes of Click-Derived Triazoles and Mesoionic Carbenes: Electron Transfer, Photochemistry, Magnetic Bistability, and Catalysis. Z. Anorg. Allg. Chem. 2017, 643, 554-584. (h) Priante-Flores, A.; Salazar-Pereda, V.; Rheingold, A. L.; Mendoza-Espinosa, D. Synthesis and characterization of a gold(I) bis(triazolylidene) complex featuring a large [(Tp<sup>Me2</sup>)<sub>2</sub>K] anion. New J. Chem. 2018, 42, 15533-15537. (i) Mejuto, C.; Royo, B.; Guisado-Barrios, G.; Peris, E. Rhodium, Iridium and Nickel Complexes with a 1,3,5-triphenylbenzene tris-MIC ligand. Study of the Electronic Properties and Catalytic Activities. Beilstein J. Org. Chem. 2015, 11, 2584-2590.

(8) (a) Mendoza-Espinosa, D.; González-Olvera, R.; Negrón-Silva, G. E.; Angeles-Beltrán, D.; Suárez-Castillo, O. R.; Álvarez-Hernández, A.; Santillan, R. Phenoxy-Linked Mesoionic Triazol-5-ylidenes as Platforms for Multinuclear Transition Metal Complexes. Organometallics 2015, 34, 4529-4542. (b) Mendoza-Espinosa, D.; González-Olvera, R.; Osornio, C.; Negrón-Silva, G. E.; Álvarez-Hernández, A.; Bautista-Hernández, C. I.; Suarez-Castillo, O. R. Structural diversity of phenoxy functionalized triazol-5-ylidene palladium(II) complexes and their application in C-N bond formation. J. Organomet. Chem. 2016, 803, 142-149. (c) Mendoza-Espinosa, D.; Rendon-Nava, D.; Alvarez-Hernandez, A.; Angeles-Beltran, D.; Negrón-Silva, G. E.; Suarez-Castillo, O. R. Visible-Light-Promoted Au<sup>II</sup> to Au<sup>III</sup> Oxidation in Triazol-5-ylidene Complexes. Chem. - Asian J. 2017, 12, 203-207. (d) Flores-Jarillo, M.; Mendoza-Espinosa, D.; Salazar-Pereda, V.; Gonzalez-Montiel, S. Synthesis and Catalytic Benefits of Tetranuclear Gold(I) Complexes with a  $C_4$ -Symmetric Tetratriazol-5-ylidene. Organometallics 2017, 36, 4305-4312. (e) Flores-Jarillo, M.; Salazar-Pereda, V.; Ruiz-Mendoza, F. J.; Alvarez-Hernández, A.; Suarez-Castillo, O. R.; Mendoza-Espinosa, D. Expedient Synthesis of Highly Functionalized Abnormal Carbenegold(I) Complexes. Inorg. Chem. 2018, 57, 28-31. (f) Rendón-Nava, D.; Alvarez-Hernandez, A.; Rheingold, A. L.; Suarez-Castillo, O. R.; Mendoza-Espinosa, D. Hydroxyl-functionalized triazolylidene-based PEPPSI complexes: metallacycle formation effect on the Suzuki coupling reaction. Dalton Trans 2019, 48, 3214-3222.

(9) (a) Maity, R.; Mekic, A.; van Der Meer, M.; Verma, A.; Sarkar, B. Triply cyclometalated trinuclear iridium(III) and trinuclear palladium(II) complexes with a tri-mesoionic carbene ligand. *Chem. Commun.* 2015, *51*, 15106–15109. (b) Maity, R.; van der Meer, M.; Hohloch, S.; Sarkar, B. Di- and Trinuclear Iridium(III) Complexes with Poly-Mesoionic Carbenes Synthesized through Selective Base-Dependent Metalation. *Organometallics* 2015, *34*, 3090–3096. (c) Vivancos, A.; Albrecht, M. Influence of the Linker Length and Coordination Mode of (Di)Triazolylidene Ligands on the Structure and Catalytic Transfer Hydrogenation Activity of Iridium(III) Centers. *Organometallics* 2017, *36*, 1580–1590. (d) Zamora, M. T.; Ferguson, M. J.; Cowie, M. Di-Mesoionic Carbene-Bridged

Complexes of Rh<sub>2</sub>, Ir<sub>2</sub>, and RhIr: A Stepwise Metalation Strategy for the Synthesis of di-MIC-Bridged Mixed-Metal Systems. Organometallics 2012, 31, 5384-5395. (e) Keske, E. C.; Zenkina, O. V.; Wang, R.; Crudden, C. M. Synthesis and Structure of Silver and Rhodium 1,2,3-Triazol-5-ylidene Mesoionic Carbene Complexes. Organometallics 2012, 31, 456-461. (f) Mejuto, C.; Guisado-Barrios, G.; Gusev, D.; Peris, E. First homoleptic MIC and heteroleptic NHC-MIC coordination cages from 1,3,5-triphenylbenzene-bridged tris-MIC and tris-NHC ligands. Chem. Commun. 2015, 51, 13914-13917. (g) Sinha, N.; Tan, T. T. Y.; Peris, E.; Hahn, E. High-Fidelity, Narcissistic Self-Sorting in the Synthesis of Organometallic Assemblies from Poly-NHC Ligands. Angew. Chem., Int. Ed. 2017, 56, 7393-7397. (h) Al-Shnani, F.; Guisado-Barrios, G.; Sainz, D.; Peris, E. Tris-triazolium Salts as Anion Receptors and as Precursors for the Preparation of Cylinder-like Coordination Cages. Organometallics 2019, 38, 697-701.

(10) Frutos, M.; de la Torre, M. C.; Sierra, M. A. Steroid Derived Mesoionic Gold and Silver Mono- and Polymetallic Carbenes. *Inorg. Chem.* **2015**, *54*, 11174–11185.

(11) (a) Shibasaki, M.; Yamamoto, Y. *Multimetallic Catalysts in Organic Synthesis*; Wiley-VHC: Weinheim, Germany, 2005. (b) Haak, R. M.; Wezenberg, S. J.; Kleij, A. W. Cooperative multimetallic catalysis using metallosalens. *Chem. Commun.* **2010**, *46*, 2713–2723. (c) Sammis, G. M.; Danjo, H.; Jacobsen, E. N. Cooperative Dual Catalysis: Application to the Highly Enantioselective Conjugate Cyanation of Unsaturated Imides. *J. Am. Chem. Soc.* **2004**, *126*, 9928–9929. (d) Yamagiwa, N.; Qin, H.; Matsunaga, S.; Shibasaki, M. Lewis Acid-Lewis Acid Heterobimetallic Cooperative Catalysis: Mechanistic Studies and Application in Enantioselective Aza-Michael Reaction. *J. Am. Chem. Soc.* **2005**, *127*, 13419–13427.

(12) (a) Rajabi, F.; Thiel, W. R. An Efficient Palladium N-Heterocyclic Carbene Catalyst Allowing the Suzuki-Miyaura Cross-Coupling of Aryl Chlorides and Arylboronic Acids at Room Temperature in Aqueous Solution. Adv. Synth. Catal. 2014, 356, 1873-1877. (b) Magano, J.; Dunetz, J. R. Large-Scale Applications of Transition Metal-Catalyzed Couplings for the Synthesis of Pharmaceuticals. Chem. Rev. 2011, 111, 2177-2250. (c) Maity, A.; Sulicz, A. N.; Deligonul, N.; Zeller, M.; Hunter, A. D.; Gray, T. G. Suzuki-Miyaura coupling of arylboronic acids to gold(III). Chem. Sci. 2015, 6, 981-986. (d) Broussard, M. E.; Juma, B.; Train, S. G.; Peng, W. J.; Laneman, S. A.; Stanley, G. G. A bimetallic hydroformylation catalyst: high regioselectivity and reactivity through homobimetallic cooperativity. Science 1993, 260, 1784-1788. (e) Gonell, S.; Poyatos, M.; Peris, E. Triphenylene-Based Tris(N-Heterocyclic Carbene) Ligand: Unexpected Catalytic Benefits. Angew. Chem., Int. Ed. 2013, 52, 7009-7013. (f) Poyatos, M.; Mata, J. A.; Peris, E. Complexes with Poly(N-heterocyclic carbene) Ligands: Structural Features and Catalytic Applications. Chem. Rev. 2009, 109, 3677-3707.

(13) See, for example, (a) Bratko, I.; Gomez, M. Polymetallic complexes linked to a single-frame ligand: cooperative effects in catalysis. *Dalton Trans.* **2013**, *42*, 10664–10681. (b) Park, J.; Hong, S. Cooperative bimetallic catalysis in asymmetric transformations. *Chem. Soc. Rev.* **2012**, *41*, 6931–6943. (c) Allen, A. E.; MacMillan, D. W. C. Synergistic catalysis: A powerful synthetic strategy for new reaction development. *Chem. Sci.* **2012**, *3*, 633–658. (d) van der Vlugt, I. J. Cooperative Catalysis with First-Row Late Transition Metals. *Eur. J. Inorg. Chem.* **2012**, *2012*, 363–375. (e) van den Beuken, E. K.; Feringa, L. B. Bimetallic Catalysis by the Late Transition Metal Complexes. *Tetrahedron* **1998**, *54*, 12985–13011. (f) Mata, J. A.; Hahn, F. E.; Peris, E. Heterometallic Complexes, Tandem Catalysis and Catalytic Cooperativity. *Chem. Sci.* **2014**, *5*, 1723–1732.

(14) (a) Jimenez, M. V.; Perez-Torrente, J. J.; Bartolome, M. I.;
Gierz, V.; Lahoz, F. J.; Oro, L. A. Rhodium(I) Complexes with Hemilabile N-Heterocyclic Carbenes: Efficient Alkyne Hydrosilylation Catalysts. Organometallics 2008, 27, 224–234. (b) Praetorius, J. M.; Crudden, C. M. N-Heterocyclic carbene complexes of rhodium: structure, stability and reactivity. Dalton Trans. 2008, 31, 4079–4094.
(c) Jansen, E.; Lutz, M.; de Bruin, B.; Elsevier, C. J. ChargeDelocalized  $\kappa^2 C_1 N$ -NHC-Amine Complexes of Rhodium, Iridium, and Ruthenium. *Organometallics* **2014**, 33, 2853–2861.

(15) See, for example, (a) Tolley, L. C.; Strydom, I.; Louw, W. J.; Fernandes, M. A.; Bezuidenhout, D. I.; Guisado-Barrios, G. Diverse Coordination Modes of Bidentate COC and Tridentate CNC Ligands Comprising 1,2,3-Triazol-5-ylidenes. ACS Omega 2019, 4, 6360-6374. (b) Sluijter, S. N.; Elsevier, C. J. Synthesis and Reactivity of Heteroditopic Dicarbene Rhodium(I) and Iridium(I) Complexes Bearing Chelating 1,2,3-Triazolylidene-Imidazolylidene Ligands. Organometallics 2014, 33, 6389-6397. (c) Makhloufi, A.; Frank, W.; Ganter, C. Diamino- and Mixed Amino-Amido-N-Heterocyclic Carbenes Based on Triazine Backbones. Organometallics 2012, 31, 2001-2008. (d) Lazaro, G.; Iglesias, M.; Fernandez-Alvarez, F. J.; Sanz Miguel, P. J.; Perez-Torrente, J. J.; Oro, L. A. Synthesis of Poly(silyl ether)s by Rhodium(I)-NHC Catalyzed Hydrosilylation: Homogeneous versus Heterogeneous Catalysis. ChemCatChem 2013, 5, 1133-1141. (e) Steinbeck, M.; Frey, G. D.; Schoeller, W. W.; Herrmann, W. A. Synthesis and characterization of chiral mono Nheterocyclic carbene-substituted rhodium complexes and their catalytic properties in hydrosilylation reactions. J. Organomet. Chem. 2011, 696, 3945-3954.

(16) Furstner, A.; Alcarazo, M.; Krause, H.; Lehmann, C. W. Effective Modulation of the Donor Properties of N-Heterocyclic Carbene Ligands by "Through-Space" Communication within a Planar Chiral Scaffold. *J. Am. Chem. Soc.* **2007**, *129*, 12676–12677.

(17) Lavallo, V.; Canac, Y.; Dehope, A.; Donnadieu, B.; Bertrand, G. A rigid cyclic (alkyl)(amino)carbene ligand leads to isolation of low-coordinate transition-metal complexes. *Angew. Chem., Int. Ed.* **2005**, 44, 7236–7239.

(18) (a) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. Stable cyclic carbenes and related species beyond diaminocarbenes. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810–8849. (b) Donnelly, K. F.; Petronilho, A.; Albrecht, M. Application of 1,2,3-triazolylidenes as versatile NHC-type ligands: synthesis, properties, and application in catalysis and beyond. *Chem. Commun.* **2013**, *49*, 1145–1159.

(19) (a) Beller, M.; Bolm, C. Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals; Wiley-VCH, 2004. (b) Evans, P. A. Modern Rhodium-Catalyzed Organic Reactions; Wiley-VCH, 2005.
(20) (a) Gavrilova, A. L.; Bosnich, B. Principles of Mononucleating and Binucleating Ligand Design. Chem. Rev. 2004, 104, 349–384.
(b) Shibasaki, M.; Matsunaga, S. Design and application of linked-BINOL chiral ligands in bifunctional asymmetric catalysis. Chem. Soc. Rev. 2006, 35, 269–279. (c) Delferro, M.; Marks, T. J. Multinuclear Olefin Polymerization Catalysts. Chem. Rev. 2011, 111, 2450–2485.
(d) Park, J.; Hong, S. Cooperative bimetallic catalysis in asymmetric transformations. Chem. Soc. Rev. 2012, 41, 6931–6943.

(21) (a) Ramasamy, B.; Prakasham, A. P.; Gangwar, M. K.; Ghosh, P. 1,4-Conjugate Addition of Aryl boronic Acids on Cyclohexenone as Catalyzed by Rhodium(I) Complexes of C2-Symmetric Bioxazoline Fused N-heterocyclic Carbenes. Chem. Select 2019, 4, 8526-8533. (b) Mejuto, C.; Escobar, L.; Guisado-Barrios, G.; Gusev, D.; Ballester, P.; Peris, E. Self-Assembly of Di-N-Heterocyclic Carbene-Gold-Adorned Corannulenes on C60. Chem. - Eur. J. 2017, 23, 10644-10651. (c) Bratko, I.; Guisado-Barrios, G.; Favier, I.; Mallet-Ladeira, S.; Teuma, E.; Peris, E.; Gomez, M. Triazolium Salts as Appropriate Catalytic Scaffolds for 1,4-Additions to a, b-Unsaturated Carbonyls. Eur. J. Org. Chem. 2014, 2014, 2160-2167. (d) Mejuto, C.; Guisado-Barrios, G.; Peris, E. Novel Rhodium and Iridium Complexes Coordinated to C3-symmetric Tris-NHC ligands Based on a 1,3,5-Triphenylbenzene Core. Electronic and Catalytic Properties. Organometallics 2014, 33, 3205-3211. (e) Peñafiel, I.; Pastor, I. M.; Yus, M.; Esteruelas, M. A.; Olivan, M. Preparation, Hydrogen Bonds, and Catalytic Activity in Metal Promoted Addition of Arylboronic Acids to Enones of a Rhodium Complex Containing an NHC Ligand with an Alcohol Funtion. Organometallics 2012, 31, 6154-6161.

(22) (a) Langkopf, E.; Schinzer, D. Uses of Silicon-Containing Compounds in the Synthesis of Natural Products. *Chem. Rev.* **1995**, 95, 1375–1408. (b) Fleming, I.; Barbero, A.; Walter, D. Stereochemical Control in Organic Synthesis Using Silicon-Containing Compounds. Chem. Rev. **1997**, 97, 2063–2192. (c) Denmark, S. E.; Sweis, R. F. Design and Implementation of New, Silicon-Based, Cross-Coupling Reactions: Importance of Silicon-Oxygen Bonds. Acc. Chem. Res. **2002**, 35, 835–846. (d) Komiyama, T.; Minami, Y.; Hiyama, T. Recent Advances in Transition-Metal-Catalyzed Synthetic Transformations of Organosilicon Reagents. ACS Catal. **2017**, 7, 631–651.

(23) (a) Marciniec, B.; Maciejewski, H.; Pietraszuk, C.; Pawluc, P. Hydrosilylation of Alkynes and their derivatives. In *Hydrosilylation. A Comprehensive Review of Recent Advances*; Marciniec, B., Ed.; Springer: Berlin, 2009. (b) Lim, D. S. W.; Anderson, E. A. Synthesis of Vinylsilanes. *Synthesis* **2012**, *44*, 983–1010. (c) Trost, B. M.; Ball, Z. T. Addition of Metalloid Hydrides to Alkynes: Hydrometallation with Boron, Silicon, and Tin. *Synthesis* **2005**, *2005*, 853–887.

(24) (a) Diachenko, V.; Page, M. J.; Gatus, M. R. D.; Bhadbhade, M.; Messerle, B. A. Bimetallic N-Heterocyclic Carbene Rh(I) Complexes: Probing the Cooperative Effect for the Catalyzed Hydroelementation of Alkynes. *Organometallics* **2015**, *34*, 4543– 4552. (b) Huckaba, A. J.; Hollis, T. K.; Howell, T. O.; Valle, H. U.; Wu, Y. Synthesis and Characterization of a 1,3-Phenylene-Bridged N-Alkyl Bis(benzimidazole) CCC-NHC Pincer Ligand Precursor: Homobimetallic Silver and Rhodium Complexes and the Catalytic Hydrosilylation of Phenylacetylene. *Organometallics* **2013**, *32*, 63–69.

(25) Morales-Ceron, J. P.; Lara, P.; Lopez-Serrano, J.; Santos, L. L.; Salazar, V.; Alvarez, E.; Suarez, A. Rhodium(I) Complexes with Ligands Based on N-Heterocyclic Carbene and Hemilabile Pyridine Donors as Highly E Stereoselective Alkyne Hydrosilylation Catalysts. *Organometallics* **2017**, *36*, 2460–2469.

(26) Tanke, R. S.; Crabtree, R. H. Unusual activity and selectivity in alkyne hydrosilylation with an iridium catalyst stabilized by an oxygen-donor ligand. *J. Am. Chem. Soc.* **1990**, *112*, 7984–7989.

(27) Burés, J. A Simple Graphical Method to Determine the Order in Catalyst. *Angew. Chem., Int. Ed.* **2016**, *55*, 2028–2031.