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FULL PAPER

Rhodium(I)-NHC Complexes Bearing Bidentate Bis-Heteroatomic Acidato Ligands as *gem*-Selective Catalysts for Alkyne Dimerization

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Abstract: A series of Rh(κ^2-BHetA)(η^2-coe)(IPr) complexes bearing 1,3-bis-hetereoatomic acidato ligands (BHetA) including carboxylato (O,O), thioacetato (O,S), amidato (O,N), thioamidato (N,S), and amidinato (N,N), have been prepared by reaction of the dinuclear precursor [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ with the corresponding anionic BHetA species. The Rh^{I}-NHC-BHetA compounds catalyze the dimerization of aryl alkynes, showing excellent selectivity for the head-to-tail enynes. Among them, the acetanilidato-based catalyst has shown an outstanding catalytic performance reaching unprecedented TOF levels of 2500 h^{-1} with complete selectivity for the *gem* isomer. Investigation of the reaction mechanism supports a non-oxidative pathway in which the BHetA ligand behaves as proton shuttle through intermediate κ^1-HBHetA species. However, in the presence of pyridine as additive, the identification of the common Rh^{III}H(C≡CPh)$_2$(IPr)(py)$_2$ intermediate gives support for an alternative oxidative route.

Introduction

Transition-metal complexes bearing 1,3-bis-heteroatomic LX-type ligands such as carboxylato,[1] amidato,[2] amidinato,[3] or the corresponding thio-substituted derivatives,[4] are versatile compounds that have found relevant applications in a variety of areas ranging from functional materials,[5] medicinal chemistry[6] or catalysis.[7] These anionic derivatives can be termed as "BHetA" (Bis-Hetereoatomic Acidato) species since they formally arise from a hydrogen atom abstraction within the bis-heteroatomic neutral precursors, even for the sparingly acidic derivatives (Chart 1). However, synthetic methods are not limited to deprotonation procedures as it can also be accessed via X=C=Y insertion into M-R bonds or nucleophilic attack over C≡X functionalities.[2b] The reactivity of 1,3-BHetA complexes is mainly governed by the coordination mode and basicity of the ligand. In this context, although bridging di- or polynuclear paddlewheel or lantern derivatives are by far the most common,[8] a wide array of monodentate or bidentate chelating complexes have also been described. Flexibility of coordination modes spans from tight bridging, which is a key feature in the structural stabilization of M-M multiple bonds,[9] to a hemilabile behavior as a practical attribute for catalytic applications.[10] Regarding basicity there is also great variability, from the highly basic amidinato species to the lower pK_a value of the thioacetic acid. The versatility of these metal-ligand frameworks enables a cooperative effect essential in C-H functionalization processes proceeding via a CMD/AMLA (Concerted Metalation-Deprotonation/Ambiphilic Metal-Ligand Activation) mechanism.[11] Therefore, highly basic BHetA ligands would promote the initial C-H activation, whereas the final protonolysis occurring after the coupling event should be favored by strong acidic derivatives. Thus, a balance between the strength of the conjugated acid-base pair is required for efficient proton shuttle.

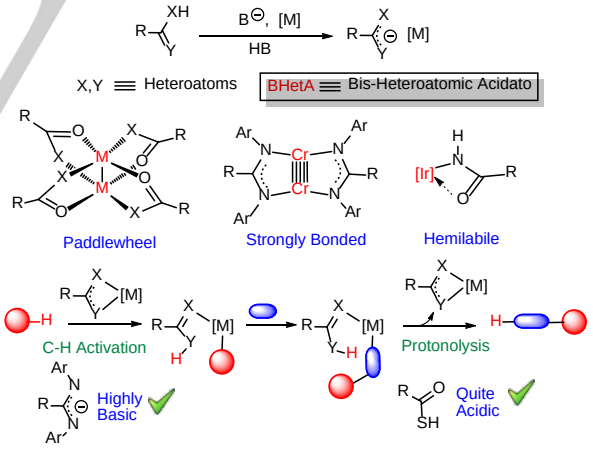

Chart 1. Typical BHetA complexes and potential application in C-H functionalization.

Within catalytic coupling reactions via C-H activation, alkyne dimerization constitutes an efficient atom economical method for the preparation of conjugated 1,3-enynes, which are important subunits in a variety of functional organic materials and biologically active molecules.[12] The relevance of this transformation is reflected in the myriad of efficient catalysts available in the

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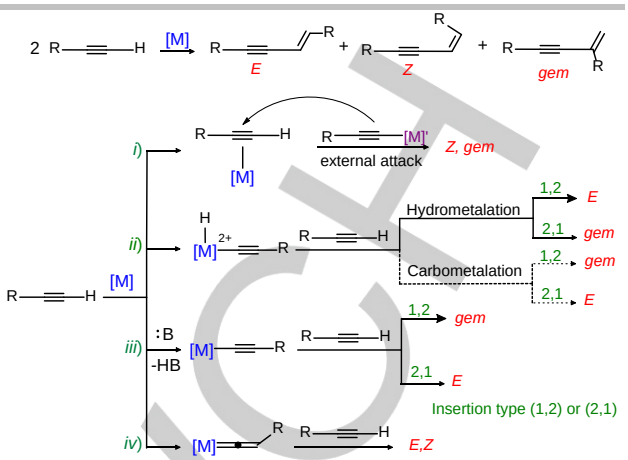
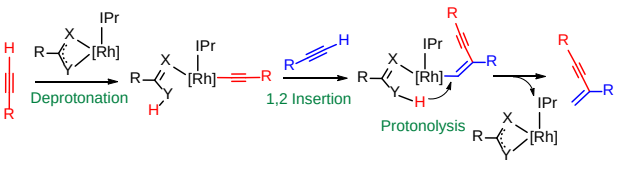
literature, including f-block,[13] early[14] or late transition metals,[15] main group,[16] and more recently first-row earth-abundant transition metals[17] or organocatalysts.[18] The formation of head-to-head (*E*/*Z*) or head-to-tail (*gem*) dimers usually competes with that of oligomers,[13e] polymers,[19] butatrienes,[20] cyclotrimers,[21] or azulenes,[22] among others. Although a few highly selective catalysts have been described for *E*-,[15g,v,17b] *Z*-,[13c,14d,17c,f] or *gem*-enynes,[15l,17d,g,18b] the precise elucidation of the factors that control the catalytic process for a defined combination of metal-ligands-additives is far to be resolved and still represents a passionate challenge. Further, the operative mechanism is made unpredictable due to the diverse reactivity of alkynes toward transition metals. In fact, a diversity of π-alkyne, hydride-alkynyl, or vinylidene species have been proposed as key intermediates. Moreover, small energy differences are typically found for the selectivity-determining step, therefore, fine tuning of the ancillary ligands arise as a key factor for an efficient catalytic outcome.[15q,w,17e]

The operative mechanisms for transition-metal-mediated alkyne dimerization can be classified into four main pathways, each one leading to different regioisomers: *i*) external attack on coordinated π-alkyne; *ii*) oxidative addition of terminal alkyne; *iii*) non-oxidative base-mediated formation of metal-alkynyl species, and *iv*) dimerization via a vinylidene intermediate (Scheme 1). Given our interest in the selective preparation of *gem*-enynes as useful molecules and valuable synthetic intermediates,[15l,r,t,16,23] pathways *i* and *iv* can be excluded as practical approaches. Vinylidene intermediates via pathway *iv* yield exclusively head-to-head isomers, whereas external attack promoted by bimetallic catalytic systems (route *i*) gives preferentially *Z*-regioisomers,[13c,d,14d] although *gem*-enyne formation has also been occasionally observed.[15m] Within the remaining alternatives, the most common pathway for metal precursors in low oxidation states is oxidative addition of alkyne to yield metal-hydride-alkynyl intermediates via route *ii*. Then, alkyne insertion into metal-hydride bond prevails over carbometalation with subsequent preferential 1,2- versus 2,1-insertion, therefore leading to the *E*-isomer after reductive elimination. However, remarkable research efforts have been made in order to reverse this trend by ligand design in order to obtain preferentially *gem*-enynes.[15n,p,r,w,24] An alternative approach directed to improve *gem*-selectivity is the non-oxidative pathway *iii*. The presence of a base prevents the formation of a hydride species, thus only the carbometalation route would be operative. Indeed, the generally preferred 1,2-insertion pave the way to *gem*-enynes after a protonolysis step. However, as it can rationally be deduced from Scheme 1, although the non-oxidative pathway *iii* seems to be the best option for high head-to-tail selectivity, many other possibilities remain open. Therefore, an in depth understanding of the particular mechanistic issues is crucial in order to fine tune the catalytic system to direct the selectivity outcome of this intricate catalytic process.



Scheme 1. Main mechanistic pathways for transition-metal mediated alkyne dimerization.

The advent of N-heterocyclic carbenes (NHCs) in the last two decades has revolutionized organometallic catalysis.[25] The effect of this new wave has also been perceived in the alkyne dimerization field.[15f,h,m,q,r,v,w,17d,g] In this context, we have disclosed new Rh^{I}-NHC complexes as *gem*-selective catalyst for alkyne dimerization in the presence of pyridine as additive.[15n] Moreover, the challenging cross-dimerization coupling was also feasible.[26] In order to rationalize the head-to-tail selectivity, an oxidative mechanism of type *ii* following a hydrometalation route with an unconventional 2,1-insertion was proposed. In spite of the high level of regioselectivity attained under mild conditions (up to 92 % for phenylacetylene at 40 °C), addition of pyridine was mandatory and therefore there is still room for improvement. We anticipate that new strategies that enforce the catalytic system to proceed via the non-oxidative pathway *iii* would led to much higher levels of efficiency. In this context, BHetA ligands can play a key role (Scheme 2). Initially, they can behave as an internal base to deprotonate the terminal alkyne leading to metal-alkynyl species. After subsequent insertion of a second molecule of alkyne, the coordinated acidic ligand should be able to release the proton to close the catalytic cycle. Herein, we report on the synthesis of a variated set of Rh^{I}-NHC 1,3-BHetA-based complexes and their study as catalysts for *gem*-selective alkyne dimerization. It has been revealed that the nature of the heteroatoms in the BHetA moiety is crucial for an efficient catalytic outcome.



Scheme 2. Rh-NHC-BHetA approach for efficient alkyne dimerization.

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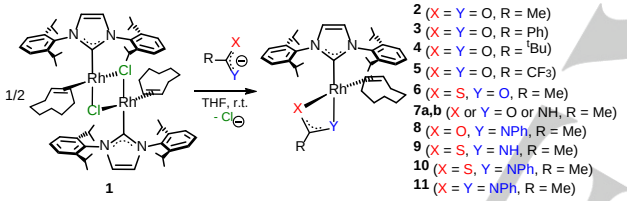
Results and Discussion

Synthesis of Rh-NHC-BHetA Complexes

The dinuclear complex [Rh(μ-Cl)(η^2-coe)(IPr)]$_2$[27] (**1**) {IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-carbene; coe = cyclooctene} has been revealed as a very useful synthetic precursor to a variety of Rh^I complexes through reactions either involving metathesis of the chlorido ligand or η^2-olefin replacement.[28] Thus, reaction of **1** with the corresponding BHetA ligands in THF at room temperature cleanly afforded complexes of type Rh(κ^2-BHetA)(η^2-coe)(IPr) **2**-**11**, which were isolated as yellow solids in good yield (Scheme 3). Potassium salts were used for the synthesis of **2**-**4** and **6**, whereas *in-situ* deprotonation of the corresponding neutral precursors with ^{t}BuOK was followed for the other complexes. Rh-IPr-BHetA derivatives are slightly soluble in hexane, thus, compounds **2**-**6** can be washed with cold hexane, whereas the nitrogen-containing counterparts **7**-**11** can be purified by extraction from this solvent and subsequent slow evaporation to yield microcrystalline yellow solids. Rh^I-NHC-carboxylato complexes are scarce,[29] whereas, as far as we are aware, 1,3-BHetA complexes having O,S; O,N; N,S; or N,N as donor atoms has not yet been reported.



Scheme 3. Preparation of BHetA complexes **2**-**11**.

The structure of Rh-NHC-BHetA complexes was confirmed by X-ray structural analysis. Figure 1 contains the ORTEP views of **2**, **6**, **7a** and **8** along with selected bond lengths and angles (see Figure S1 in Supporting Information, for the ORTEP view of **3** and **10**). Mononuclear species were observed in all the cases. The bidentate coordination of the BHetA ligand brings about a distorted square planar geometry at the metal center with a *cis* arrangement of the NHC and coe ligands {C(1)–Rh–ct, 94º av.; ct = centroid of C(30) and C(31) olefinic atoms}. Notably, the NHC-imidazolin ring and the plane containing the metal center, the carbene atom C(1) and the centroid of the coordinated olefin intersect at angles smaller than 90º (**2**, 63.7º; **3**, 64.8º; **6**, 66.9º; **7a**, 63.7º; **8**, 80.1º; **10**, 66.2º), thus rendering a chiral complex. Figure S2 in Supporting Information shows a view of the *Δ* and *Λ* enantiomers based on the skew line convention.[30] In this connection, it is worth a mention that the space groups of **2** ($P2_1$), **7a** ($P2_1$) and **8** ($P2_12_12_1$) are non-centrosymmetric and the measured crystal contains either the *Δ* (**8**) or the *Λ* (**2**, **7a**) enantiomer. On the other hand, the space groups of **3** ($P2_1/n$), **6** ($P2_1/c$) and **10** ($P2_1/c$) are centrosymmetric, thus the crystals contain both enantiomers in a 1:1 ratio. The pitch and yaw angles[28c,f] calculated for the NHC-imidazolin ring indicate that its coordination deviates from the ideal arrangement with respect to the metal-carbon bond in all the cases, except for the sulfur containing heteroacidato derivatives **6** and **10** (see Figures 1 and S1). Nonetheless, the observed metal–carbon bond lengths Rh–C(1) fall within those commonly observed for the Rh^I–IPr metal–carbon bond.[28]

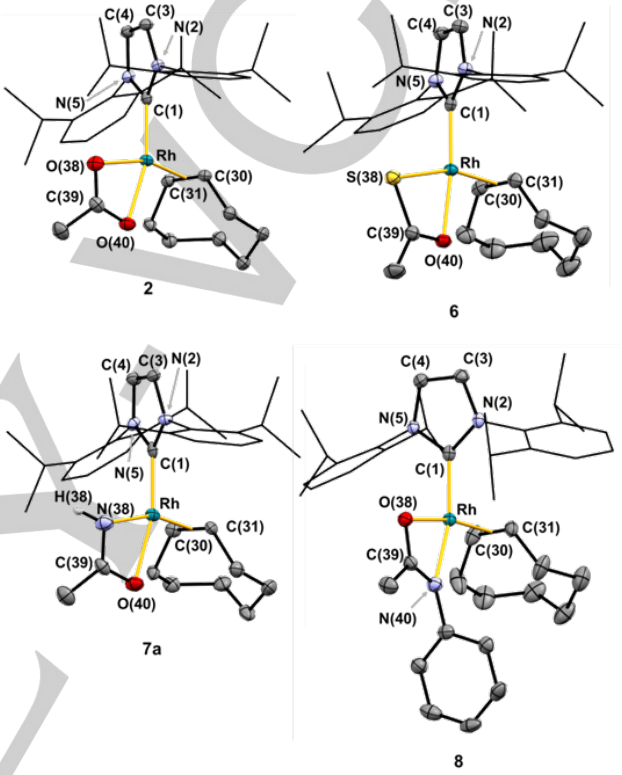


Figure 1. ORTEP view of **2**, **6**, **7a** and **8** with ellipsoids at 50 % probability. For clarity most hydrogen atoms have been omitted and the 2,5–(^{i}Pr)C$_6$H$_3$ substituents are shown in wireframe style. Selected bond lengths (Å) and angles (º) are: **2**, Rh–C(1) 1.949(2), Rh–ct 1.9601(14), Rh–O(38) 2.1564(14), Rh–O(40) 2.1921(14), C(39)–O(38) 1.267(2), C(39)–O(40) 1.270(2), O(38)–C(39)–O(40) 120.23(18), C(1)–Rh–ct 96.25(7), NHC pitch *θ* 10.0º, yaw *ψ* 2.4º. **6**, Rh–C(1) 1.957(2), Rh–ct 1.9940(2), Rh–S(38) 2.3963(6), Rh–O(40) 2.2006(16), C(39)–S(38) 1.715(2), C(39)–O(40) 1.255(3), O(38)–C(39)–O(40) 117.36(18), C(1)–Rh–ct 93.86(6), NHC pitch *θ* 0.6º, yaw *ψ* 1.6º. **7a**, Rh–C(1) 1.950(5), Rh–ct 1.969(3), Rh–N(38) 2.087(4), Rh–O(40) 2.215(3), C(39)–N(38) 1.309(5), N(38)–H(38) 0.91(6), C(39)–O(40) 1.279(5), N(38)–C(39)–O(40) 116.4(4), C(1)–Rh–ct 96.96(15), NHC pitch *θ* 8.9º, yaw *ψ* 2.2º. **8**, Rh–C(1) 1.938(3), Rh–ct 1.9747(3), Rh–O(38) 2.143(2), Rh–N(40) 2.159(3), C(39)–O(38) 1.287(4), C(39)–N(40) 1.309(4), O(38)–C(39)–N(40) 115.9(3), C(1)–Rh–ct 93.74(9), NHC pitch *θ* 10.7º, yaw *ψ* 0.5º. ct: centroid of C(30) and C(31).

The NMR spectroscopic data confirm that the solid state structure of complexes is maintained in solution. The presence of IPr, BHetA, and coe, ligands in **2**-**11** is corroborated in the ^{13}C{^{1}H}-APT NMR spectra by the presence of three carbon-

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rhodium coupling doublets. The most noticeable feature of the ^{1}H-NMR spectra is the appearance of only one septuplet around δ 3 ppm corresponding to the four isopropyl protons of the IPr ligand, which is in agreement with the presence of a symmetry plane containing the BHetA ligand and bisecting coe and IPr, as well as a rotational process of the carbene ligand around the Rh-C(carbene) axis.[28a] This septuplet splits into two broad signals at low temperature as a result of slowing down the rotational process (See Figure S3 in Supporting Information for **8**). Accordingly, two signals for the CH-isopropyl protons were observed in the ^{1}H NMR spectrum of **11** at room temperature, as a result of hindered rotation of the carbene hampered by the bulky bisphenyl-amidinato ligand. In addition, the presence of a NH moiety in the BHetA ligands in complexes **7** and **9** was confirmed by ^{1}H-^{15}N HSQC NMR experiments (see Figure 2 for **7**)

The different disposition observed for the asymmetric BHetA ligands within the square planar structures follows some trends. Thus, the S-donor atom is located *cis* to IPr in all cases (**6**, **9** and **10**). However, the arrangement of N,O ligands seems to be directed by the bulkiness of the substituent on N-donor atom. The acetanilidato ligand in complex **8** is disposed with the phenyl group towards the smaller coe, whereas two isomers in 84:16 ratio were observed for the NH acetamidato complex **7** with the major isomer corresponding to that in which the NH substituent points to the bulkier IPr ligand (Figure 2). Exchange peaks between the two isomers were observed at room temperature indicating a dynamic process. A similar behavior has been observed for **11** in ^{1}H-^{1}H NOESY and TOCSY experiments (see Figures S63 and S64 in Supporting Information).

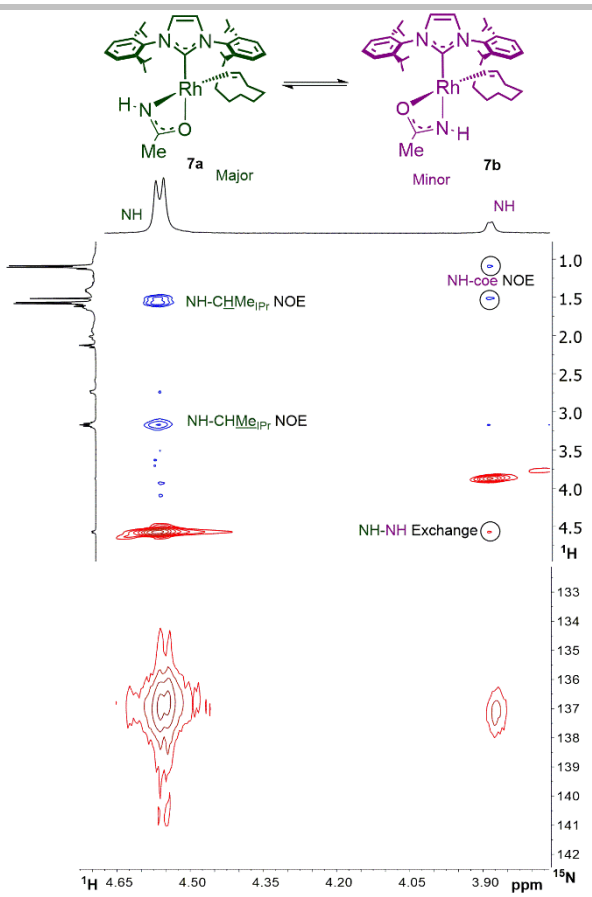

Figure 2. ^{1}H-^{1}H-NOESY (up) and ^{1}H-^{15}N HSQC (down) spectra for the NH signals of **7**.

Catalytic Alkyne Dimerization

The catalytic activity of the Rh^{I}-NHC complexes **2**-**11** was evaluated using phenylacetylene as a benchmark substrate. Catalytic reactions were monitored in NMR tubes using 2 mol % of catalyst loading in C_6D_6 at 25 ºC. Unfortunately, carboxylato catalysts **2**-**5** were not efficient in alkyne dimerization. However, all of them exhibited good catalytic performance in the presence of pyridine, comparable to that previously reported for chlorido-dimer **1** (entries 1-6). In contrast, the acetanilidato catalyst **8** reacted very fast with phenylacetylene. Pleasingly, complete and selective conversion to *gem*-enyne was observed after only 3 min of reaction, displaying a $TOF_{1/2}$ of 726 h^{-1} (entry 11). Catalyst loading can be reduced to 0.5 mol % with only slight decrease of conversion ($TOF_{1/2}$ of 2500 h^{-1}, entry 14). Catalyst **8** exceeds by two orders of magnitude the activity reported for **1** and, as far as we are aware, presents the highest TOF ever reported at room temperature in alkyne dimerization. Related acetamido catalyst **7** is much less efficient than **8** (entry 9). Rather surprisingly, the more basic amidinato complex **11** is also less active (entry 19). Interestingly, similarly to carboxylato species, the activity of both catalysts significantly increased in the presence of pyridine with excellent selectivity (entries 10 and 20). On the other hand, S-donor BHetA

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catalysts **6**, **9**, and **10** were moderately active in the absence of pyridine but did not show regioselectivity, thus pointing to an alternative operational mechanism. Moreover, the previously reported hydroxo-dimer [Rh(μ-OH)(IPr)(η^2-coe)]$_2$ (**12**)[28b] was also inefficient, but becomes activated in the presence of pyridine as additive (entries 21-22). These results indicate that basicity of the ligand is not the only factor influencing catalytic activity. Indeed, the presence of both N- and O- donor atoms in the ancillary ligand seems to be crucial for an efficient catalytic system.

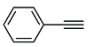
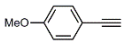
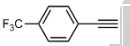
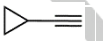
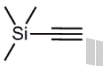
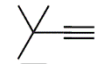
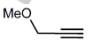
Table 1. Catalyst screening for phenylacetylene dimerization.[a]

Entry	Catalyst	Additive[b]	t(h)	Conv(%)	*gem*/*E*	TOF$_{1/2}$(h^{-1})[c]
1	**1**	py	15	99	89/1/10[d]	12
2	**2**	-	20	5	99/1	-
3	**2**	py	2	86	98/2	12
4	**3**	py	4	98	97/3	10
5	**4**	py	4	98	98/2	12
6	**5**	py	6	78	98/2	7
7	**6**	-	1.5	94	67/33	53
8	**6**	py	7.5	97	81/19	16
9	**7**	-	24	34	97/3	-
10	**7**	py	1.4	>99	98/2	48
11	**8**	-	0.05	>99	>99	726
12	**8**	py	0.7	>99	>99	385
13[e]	**8**	-	0.6	97	>99	1023
14[f]	**8**	-	1	71	>99	2500
15	**9**	-	1.5	91	39/61	34
16	**9**	py	1	97	40/60	53
17	**10**	-	0.5	43	55/45	-
18	**10**	py	5	87	60/40	8
19	**11**	-	22	16	99/1	-
20	**11**	py	1	95	99/1	49
21	**12**	-	26	2	-	-
22	**12**	py	2	>99	99/1	20

[a] Reaction conditions: 0.5 mL of C_6D_6, 0.5 mmol of phenylacetylene, 0.01 mmol of catalyst, 25 °C. [b] 10 eq. per mole of rhodium. [c] TOF$_{1/2}$: turnover frequency at 50 % conversion. [d] (*Z*)-hexa-3,5-dien-1-yne-1,3,5-R trimer [e] 1 mol % of catalyst. [f] 0.5 mol % of catalyst.

Catalytic performance of **8** was evaluated for a range of alkynes (Table 2). The introduction of an electron-donating group at the *para* position of the aromatic ring of phenylacetylene slightly increased the reaction rate (entry 2), whereas an electron-withdrawing group slowed down the reaction (entry 3). The dimerization of aliphatic alkynes was slower, although maintaining excellent selectivity (entries 4-5). Highly encumbered alkynes reacted even more slowly displaying low selectivity and the presence of hexa-3,5-dien-1-yne trimers was observed. Finally, only trace amounts of enyne were observed for methyl propargyl ether.

Table 2. Dimerization of terminal alkynes catalyzed by **8**.[a]

Entry	Substrate	t(h)	Conv(%)	*gem*/*E*	Trimer	TOF$_{1/2}$(h^{-1})[b]
1		0.05	>99	>99	-	726
2		0.05	>99	>99	-	725
3		0.1	>99	>99	-	720
4		1	95	97/3	-	195
5		2	72	99/1	-	405
6		20	62	23/21	56[c]	3
7		24	52	77/9	14[d]	-
8		24	0	-	-	-

[a] Reaction conditions: 0.5 mL of C_6D_6, 0.5 mmol of alkyne, 0.01 mmol of **8**, 25 °C. [b] TOF$_{1/2}$: turnover frequency at 50 % conversion. [c] (*Z*)-hexa-3,5-dien-1-yne-1,3,5-R. [d] (*E*)-hexa-3,5-dien-1-yne-1,3,6-R.

Mechanistic Proposal and Discussion

In order to shed light on the operative mechanism for alkyne dimerization by the Rh-NHC-BHetA catalysts, low temperature stoichiometric reactions were performed. As shown in Scheme 2, the expected mechanism entails deprotonation of a coordinated alkyne, alkyne insertion into the Rh-alkynyl bond and protonolysis. Unfortunately, catalyst **8** dimerized phenylacetylene very fast, even at 213 K, thus no relevant catalytic intermediate could be detected except the complex Rh[κ^2-N,O-{N(Ph)C(O)Me}]{CH$_2$=C(Ph)-η^2-C≡CPh}(IPr) (**13**), that results from the η^2-triple-bond coordination of the enyne reaction product (Scheme 4). A similar behavior was observed for less reactive terminal alkynes such as 1-hexyne or trimethylsilyl acetylene. However, reaction with dimethyl acetylenedicarboxylate, an internal alkyne unable to dimerize, afforded the π-alkyne complex Rh[κ^2-N,O-{N(Ph)C(O)Me}]{η^2-MeOOCC≡CCOOMe}(IPr) (**14**), as a result of the coe-alkyne exchange, which is proposed as the first step of the catalytic cycle (Scheme 2). In the same way, the π-phenylacetylene complex Rh[κ^2-S,O-{SC(O)Me}](η^2-HC≡CPh)(IPr) (**15**) could be detected by using the less efficient catalyst **6** as precursor. The ^{13}C{^{1}H}-APT NMR spectra of complexes **13**-**15** display the typical doublets between δ 81-89 ppm with J_{Rh-C} coupling constants around 15 Hz, characteristic of a triple bond π-coordinated to a rhodium center.

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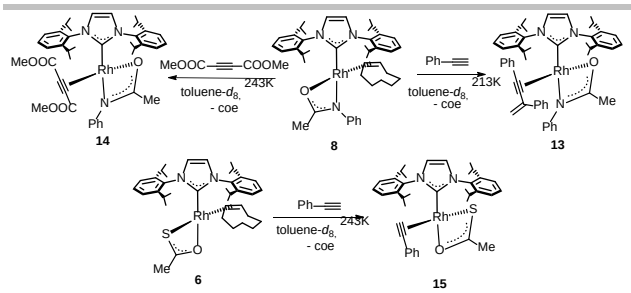
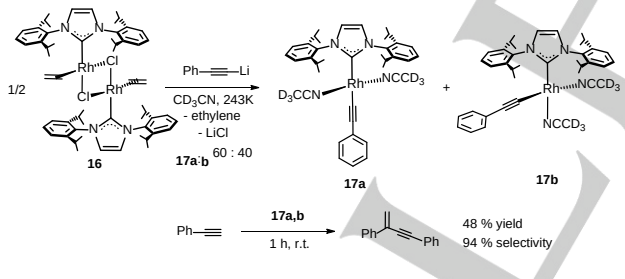


Scheme 4. Stoichiometric reactions of Rh-NHC-BHetA complexes with alkynes.

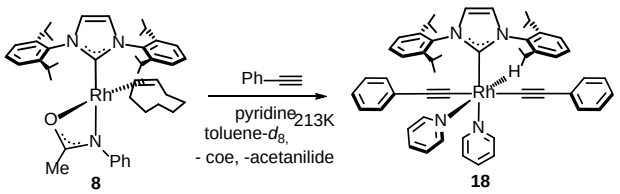
After coordination of the alkyne to the rhodium center, two competitive pathways are possible: oxidative addition to generate Rh^{III}-hydride-alkynyl intermediates or deprotonation by the internal base to yield Rh^{I}-alkynyl species. Oxidative addition process has already been demonstrated to be operative for alkyne dimerization in Rh-NHC systems via alkyne insertion into Rh^{III}-hydride bond.[15n] In order to prove that Rh^{I}-alkynyl species are feasible dimerization initiators, complex $Rh(C{\equiv}CPh)(IPr)(NCCD_3)_2$ (**17**) was prepared by treatment of the dinuclear precursor $[Rh(\mu\text{-}Cl)(IPr)(\eta^2\text{-ethylene})]_2$ (**16**) with lithium phenylacetylide in CD_3CN (Scheme 5). Two isomers **17a/b** in 60:40 ratio were obtained. We assume that the isomer with the lowest Rh-C(alkynyl) coupling constant in $^{13}C\{^1H\}$-APT NMR spectrum (58.2 *vs* 73.7 Hz) should correspond to that with the IPr ligand *trans* to the alkynyl moiety (**17a**).[28d] Interestingly, the **17a/b** mixture was proved to be active in the dimerization of phenylacetylene, although with lower activity than **8**.



Scheme 5. *In-situ* formation and catalytic activity of Rh-alkynyl species **17**.

Once it was demonstrated that the Rh^{I}-alkynyl pathway is a feasible route for alkyne dimerization, it remains to analyze the very different behavior observed for the distinct Rh-NHC-BHetA complexes. The classification of the BHetA ligands according to the pKa values of the protonated form is as follows, thioacetato << carboxylato << acetanilidato < acetamidato < amidinato < hydroxo, whereas the trend in catalytic activity is, acetanilidato >>> thioacetato > acetamidinato > amidinato > carboxylato ≈ hydroxo. Basicity of ligand is a relevant parameter for initial deprotonation in the CMD/AMLA process,[11] whereas the capacity of the protonated ligand to release the proton is key for the final step (Scheme 2). A compromise between these two factors seems essential for efficient catalysis. In this way, highly basic ligands such as hydroxo (**12**) or amidinato (**11**) should promote the first step but protonolysis would not be favored. On the contrary, carboxylate ligands in **2**-**5** seems to be inefficient in deprotonation. The success of acetanilidato catalyst **8** might be derived from its ability to both deprotonotate and protonate in an efficient manner, as a consequence of the presence of a N,O framework in the BHetA ligand. Thus, the more basic nitrogen atom should favor the deprotonation step. Then, a 1,3-prototropic shift to the oxygen atom of the BHetA ligand could take place rendering the OH moiety prone to trigger the final protonolysis step. On the other hand, catalytic behavior of S-based BHetA points to an alternative reaction pathway in which thiolato-bridged dimeric species could be involved (see Fig S4 in Supporting Information).

The less efficient carboxylato-based catalysts become active after addition of pyridine. Careful analysis of the NMR kinetic experiments revealed the presence of a shielded doublet at δ -16.48 ppm with $J_{H\text{-}Rh}$ coupling of 25.2 Hz, which can be ascribed to a rhodium-hydride ligand resulted from oxidative addition of phenylacetylene. Interestingly, the same signal was observed under the same experimental conditions regardless on the O,O; N,O; or N,N BHetA catalyst precursor employed, even for the acetanilidato complex **8**. This resonance has been assigned to the bis-alkynyl rhodium-hydrido species $RhH(C{\equiv}CPh)_2(IPr)(py)_2$ (**18**), which has been independently prepared by treatment of **8** with ten-fold and five-fold excess of phenylacetylene and pyridine, respectively (Scheme 6). Formation of **18** can be rationalized by initial deprotonation of phenylacetylene by the internal base and subsequent oxidative addition of a second molecule of alkyne with release of N-phenylacetamide. A similar behavior has been previously observed in the reaction of thiophenol with the rhodium-hydroxo complex **12**.[28b] Hydride species **18** could be initiators for alkyne dimerization following pathway *ii* depicted in Scheme 1. The fact that the TOFs values are similar regardless of the anionic ligand supports the participation of active species lacking the BHetA ligand.



Scheme 6. *In-situ* formation of Rh-bis-alkynyl-hydride species **18**.

In view of these data, a plausible mechanism for alkyne dimerization in the presence or absence of pyridine is proposed in Scheme 7. The first step would be the alkyne–coe exchange similarly to what observed in intermediates **14**-**15**. Then, the basic BHetA ligand deprotonates the alkyne in a CMD/AMLA process to give a rhodium-alkynyl species similar to **17**. From this point two pathways are available. In the absence of pyridine, pathway **a** is followed which entails a N-

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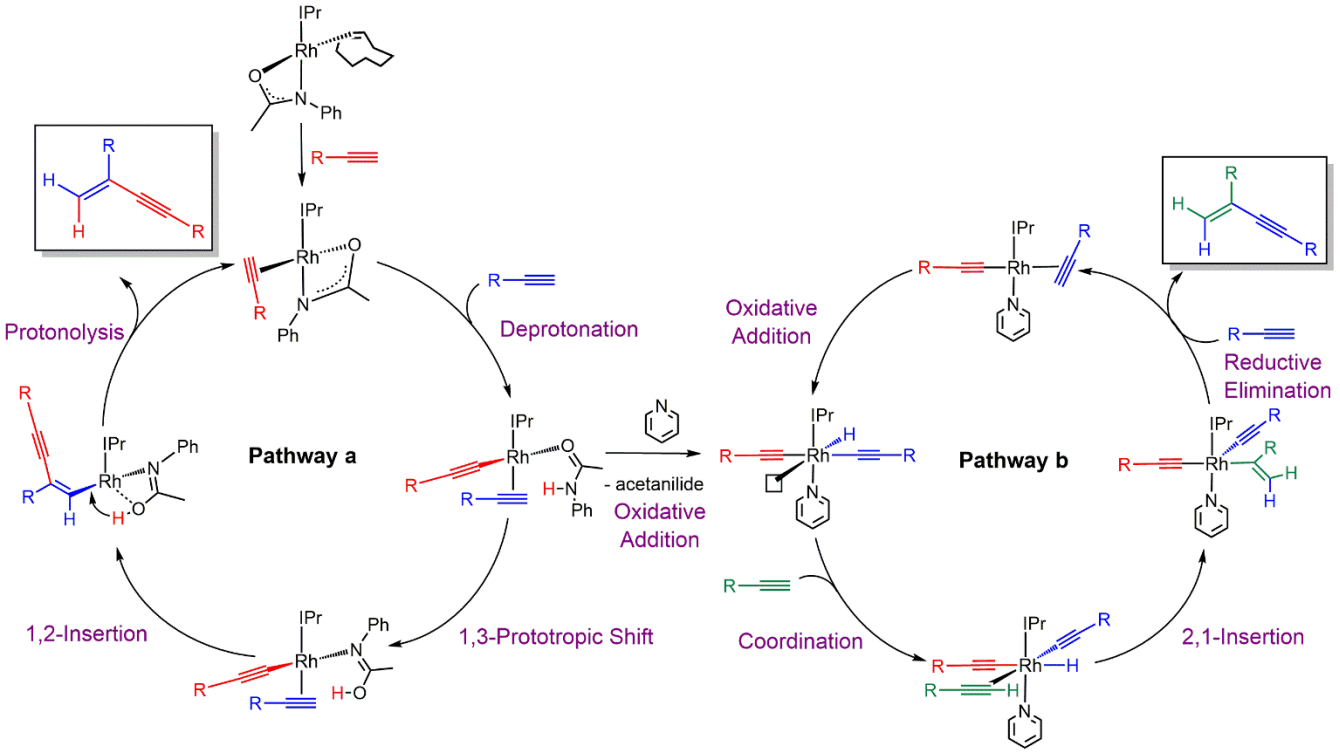
O 1,3-prototropic shift and subsequent insertion of an alkyne into rhodium-alkynyl bond. Then, protonolysis from the oxygen atom releases the enyne and regenerates the active species. However, in the presence of pyridine pathway **b** becomes operative. Replacement of the acetanilide ligand by pyridine is followed by oxidative addition of the coordinated alkyne to generate a Rh^{III}-hydride bis-alkynyl species similar to **18**. Then, coordination of an alkyne at the vacant site, insertion into the rhodium-hydride bond followed by reductive elimination affords the *gem*-enyne product. Subsequent oxidative addition will close the catalytic cycle. It is noteworthy to point out that both catalytic pathways result in the formation of the same head-to-tail enyne isomer despite displaying opposite insertion modes in the selectivity-determining step. This fact can be explained by the different structural nature of the six coordinate octahedral Rh^{III}-H intermediates *versus* four coordinate square planar Rh^{I}-alkynyl species. In pathway **b**, coordination of alkyne before insertion into the Rh^{III}-H bond takes place *cis*-to-NHC, as pyridine blocks the *trans*-to-NHC position.[28d] Thus, the sterical hindrance of the bulky carbene ligand results in the unusual 2,1 alkyne insertion into Rh^{III}-H bond, which is in agreement with our previous observations in related rhodium(III) systems.[15n] In contrast, along pathway **a**, the only position available for coordination of alkyne in square planar Rh^{I}-alkynyl species is *trans*-to-NHC, where the carbene ligand is not exerting a sterical influence thereby resulting in the electronically preferred 1,2 insertion.



Scheme 7. Plausible catalytic cycle for alkyne dimerization in the absence **(pathway a**) or presence of pyridine **(pathway b**).

Conclusions

A series of Rh(κ^2-BHetA)(η^2-coe)(IPr) complexes bearing LX-type 1,3-hetereoatomic acidato (O,O; O,S; O,N; N,S and N,N) ligands have been prepared by reaction of the dinuclear complex [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ with the corresponding anionic BHetA species. The different disposition of the asymmetric BHetA ligands related to IPr and coe within the mononuclear Rh^{I} square planar complexes depends on the nature of the heteroatoms and steric factors. Thus, S-donor atom is invariably located *cis* to IPr in all cases whereas an equilibrium between both configurations was observed for N,O-BHetA complexes with the isomer having the bulky substituent on N-atom directed to the smaller coe ligand being predominant.

The Rh-NHC-BHetA complexes are efficient catalyst for alkyne dimerization displaying high selectivity towards the head-to-tail enynes. Particularly, the acetanilidato catalyst is highly active reaching TOF values of 2500 h^{-1}, never reported before for this transformation. The proposed mechanism follows a CMD/AMLA non-oxidative pathway involving the deprotonation of the alkyne by the basic BHetA ligand, alkyne insertion into the newly formed rhodium-alkynyl bond and protonolysis by the κ^1-HBHetA ligand. In this sense, basicity of the BHetA ligand is a relevant parameter for initial deprotonation, whereas the capacity of the coordinated HBHetA species for proton transfer is key for the final step. A compromise between these two factors seems to be essential for efficient catalysis. Therefore, carboxylate-based catalysts are not

basic enough whereas amidinato species are less efficient in the protonolysis step. Addition of pyridine triggers the oxidative addition pathway operating via a common $Rh^{III}H(C{\equiv}CPh)_2(IPr)(py)_2$ intermediate. The excellent performance of the acetanilidato catalyst might be derived from its ability to both deprotonotate and protonate in an efficient manner, which could be related to the presence of a N,O donor set in the BHetA ligand. Further work on the potential applications both in synthesis and catalysis is in progress in our group and results will be reported in due course.

Experimental Section

General Considerations. All reactions were carried out with rigorous exclusion of air and moisture using Schlenk-tube techniques and dry box when necessary. The organometallic precursor $[Rh(\mu\text{-Cl})(IPr)(\eta^2\text{-coe})]_2$ (**1**) was prepared as previously described in the literature.[27] Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H and $^{13}C\{^1H\}$), NH_3 (^{15}N), or $CFCl_3$ (^{19}F). Coupling constants, *J*, are given in Hz. Spectral assignments were achieved by combination of ^1H-^1H COSY, $^{13}C\{^1H\}$-APT and ^1H-^{13}C HSQC/HMBC experiments.

Preparation of Rh{κ^2-O,O'-(O_2CCH_3)}{η^2-coe)(IPr) (2). A solution of dinuclear complex **1** (200 mg, 0.16 mmol) in THF (10 mL) was treated with CH_3COOK (32 mg, 0.34 mmol) and stirred for 2 h at r.t. After evaporation to dryness, the residue was dissolved in toluene (10 mL) and was filtered through Celite. Then, the resulted solution was evaporated to dryness. Addition of hexane at -40 ºC induced the precipitation of a yellow solid, which was washed with cold hexane (3 x 2 mL) and dried in vacuo. Yield: 155 mg (74%). Anal. Calcd for $C_{37}H_{53}N_2O_2Rh$: C, 67.26; H, 8.09; N, 4.24. Found: C, 67.17; H, 8.15; N, 4.37. IR (cm^{-1}): 1519 $\nu(OCO_{asym})$, 1442 $\nu(OCO_{sym})$. ^1H NMR (400.2 MHz, C_6D_6, 298 K): δ 7.32 (m, 2H, $H_{p\text{-}Ph\text{-}IPr}$), 7.24 (m, 4H, $H_{m\text{-}Ph\text{-}IPr}$), 6.48 (s, 2H, =CHN), 3.08 (sept, $J_{H\text{-}H}$ = 7.1, 4H, C<u>H</u>Me_{IPr}), 2.76 (m, 2H, $=CH_{coe}$), 2.1-0.9 (m, 12H, $CH_{2\text{-}coe}$), 1.65 (s, 3H, MeCOO), 1.53 and 1.05 (both d, $J_{H\text{-}H}$ = 7.1, 24H, CH<u>Me</u>$_{IPr}$). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, C_6D_6, 298 K): δ 187.7 (d, $J_{C\text{-}Rh}$ = 1.9, Rh-OO<u>C</u>Me), 183.5 (d, $J_{C\text{-}Rh}$ = 64.5, Rh-C_{IPr}), 146.9 (s, $C_{q\text{-}IPr}$), 137.2 (s, C_qN), 129.9 (s, $CH_{p\text{-}Ph\text{-}IPr}$), 124.4 (d, $J_{C\text{-}Rh}$ = 1.3, =CHN), 124.0 (s, $CH_{m\text{-}Ph\text{-}IPr}$), 57.6 (d, $J_{C\text{-}Rh}$ = 17.3, $=CH_{coe}$), 30.0 and 28.7 (both d, $J_{C\text{-}Rh}$ = 1.6, $CH_{2\text{-}coe}$), 29.2 (s, <u>C</u>HMe_{IPr}), 27.1 (s, $CH_{2\text{-}coe}$), 26.4 and 23.0 (both s, CH<u>Me</u>$_{IPr}$), 23.6 (d, $J_{C\text{-}Rh}$ = 2.4, Rh-OOC<u>Me</u>).

Preparation of Rh{κ^2-O,O'-(O_2CPh)}{η^2-coe)(IPr) (3). The complex was prepared as described for **2** starting from **1** (160 mg, 0.13 mmol) and PhCOONa (40 mg, 0.27 mmol) and isolated as a yellow solid. Yield: 120 mg (66%). Anal. Calcd for $C_{42}H_{55}N_2O_2Rh$: C, 69.79; H, 7.67; N, 3.88. Found: C, 69.71; H, 7.55; N, 4.07. IR (cm^{-1}): 1513 $\nu(OCO_{asym})$, 1418 $\nu(OCO_{sym})$. ^1H NMR (400.2 MHz, C_6D_6, 298 K): δ 8.19 (m, 2H, $H_{o\text{-}Ph}$), 7.27 (m, 2H, $H_{p\text{-}Ph\text{-}IPr}$), 7.20 (m, 4H, $H_{m\text{-}Ph\text{-}IPr}$), 7.10 (m, 3H, H_{Ph}), 6.52 (s, 2H, =CHN), 3.16 (sept, $J_{H\text{-}H}$ = 7.1, 4H, C<u>H</u>Me_{IPr}), 2.87 (m, 2H, $=CH_{coe}$), 2.1-0.9 (m, 12H, $CH_{2\text{-}coe}$), 1.53 and 1.06 (both d, $J_{H\text{-}H}$ = 7.1, 24H, CH<u>Me</u>$_{IPr}$). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, C_6D_6, 298 K): δ 183.4 (d, $J_{C\text{-}Rh}$ = 64.0, Rh-C_{IPr}), 182.3 (d, $J_{C\text{-}Rh}$ = 1.7, Rh-OOC), 146.8 (s, $C_{q\text{-}IPr}$), 137.1 (s, C_qN), 135.0 (s, $C_{q\text{-}Ph}$), 131.4 (s, $CH_{p\text{-}Ph}$), 130.0 (s, $CH_{p\text{-}Ph\text{-}IPr}$), 129.3 (s, $CH_{o\text{-}Ph}$), 127.9 (s, $CH_{m\text{-}Ph}$), 124.5 (s, =CHN), 124.1 (s, $CH_{m\text{-}Ph\text{-}IPr}$), 57.8 (d, $J_{C\text{-}Rh}$ = 17.4, $=CH_{coe}$), 29.9 and 28.7 (both d, $J_{C\text{-}Rh}$ = 1.3, $CH_{2\text{-}coe}$), 29.2 (s, <u>C</u>HMe_{IPr}), 27.1 (s, $CH_{2\text{-}coe}$), 26.4 and 23.0 (both s, CH<u>Me</u>$_{IPr}$).

Preparation of Rh{κ^2-O,O'-{O_2CC^tBu)}{η^2-coe)(IPr) (4). The complex was prepared as described for **2** starting from **1** (160 mg, 0.13 mmol) and $^tBuCCOOK$ (40 mg, 0.28 mmol) and isolated as a yellow solid. Yield: 110 mg (61%). IR (cm^{-1}): 1505 $\nu(OCO_{asym})$, 1427 $\nu(OCO_{sym})$. ^1H NMR (400.2 MHz, C_6D_6, 298 K): δ 7.31 (m, 2H, $H_{p\text{-}Ph\text{-}IPr}$), 7.23 (m, 4H, $H_{m\text{-}Ph\text{-}IPr}$), 6.46 (s, 2H, =CHN), 3.17 (sept, $J_{H\text{-}H}$ = 6.8, 4H, C<u>H</u>Me_{IPr}), 2.74 (m, 2H, $=CH_{coe}$), 2.1-0.9 (m, 12H, $CH_{2\text{-}coe}$), 1.56 and 1.05 (both d, $J_{H\text{-}H}$ = 6.8, 24H, CH<u>Me</u>$_{IPr}$), 1.13 (s, 9H, CMe_3). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, C_6D_6, 298 K): δ 195.2 (d, $J_{C\text{-}Rh}$ = 1.8, Rh-OOC), 183.4 (d, $J_{C\text{-}Rh}$ = 64.1, Rh-C_{IPr}), 146.8 (s, $C_{q\text{-}IPr}$), 137.2 (s, C_qN), 129.8 (s, $CH_{p\text{-}Ph\text{-}IPr}$), 124.4 (s, =CHN), 124.0 (s, $CH_{m\text{-}Ph\text{-}IPr}$), 57.8 (d, $J_{C\text{-}Rh}$ = 17.4, $=CH_{coe}$), 39.9 (s, <u>C</u>Me_3), 29.9 and 28.6 (both d, $J_{C\text{-}Rh}$ = 1.4, $CH_{2\text{-}coe}$), 29.1 (s, <u>C</u>HMe_{IPr}), 27.6 (s, C<u>Me</u>$_3$), 27.0 (s, $CH_{2\text{-}coe}$), 26.2 and 23.1 (both s, CH<u>Me</u>$_{IPr}$).

Preparation of Rh{κ^2-O,O'-(O_2CCF_3)}{η^2-coe)(IPr) (5). A mixture of CF_3COOH (13 µL, 0.17 mmol) and ^tBuOK (18 mg, 0.17 mmol) in THF (5 mL) was stirred for 30 min at r.t. Then, a solution of dinuclear complex **1** (100 mg, 0.08 mmol) in THF (5 mL) was cannulated over the suspension containing the deprotonated carboxylate and the mixture was stirred for additional 2 h at r.t. After evaporation to dryness, the residue was dissolved in toluene (10 mL) and was filtered through Celite. Then the resulted solution was evaporated to dryness. Addition of hexane at -40 ºC induced the precipitation of a yellow solid, which was washed with cold hexane (3 x 2 mL) and dried in vacuo. Yield: 40 mg (71%). Anal. Calcd for $C_{37}H_{50}N_2F_3O_2Rh$: C, 62.18; H, 7.05; N, 3.92. Found: C, 61.87; H, 7.09; N, 3.95. IR (cm^{-1}): 1611 $\nu(OCO_{asym})$, 1463 $\nu(OCO_{sym})$. ^1H NMR (400.2 MHz, C_6D_6, 298 K): δ 7.29 (m, 2H, $H_{p\text{-}Ph\text{-}IPr}$), 7.19 (m, 4H, $H_{m\text{-}Ph\text{-}IPr}$), 6.44 (s, 2H, =CHN), 2.94 (sept, $J_{H\text{-}H}$ = 6.9, 4H, C<u>H</u>Me_{IPr}), 2.89 (m, 2H, $=CH_{coe}$), 2.1-0.9 (m, 12H, $CH_{2\text{-}coe}$), 1.49 and 1.00 (both d, $J_{H\text{-}H}$ = 6.9, 24H, CH<u>Me</u>$_{IPr}$). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, C_6D_6, 298 K): δ 177.5 (d, $J_{C\text{-}Rh}$ = 66.6, Rh-C_{IPr}), 169.8 (qd, $J_{C\text{-}F}$ = 37.8, $J_{C\text{-}Rh}$ = 1.4, Rh-OO<u>C</u>CF_3), 146.7 (s, $C_{q\text{-}IPr}$), 136.4 (s, C_qN), 130.8 (s, $CH_{p\text{-}Ph\text{-}IPr}$), 125.0 (s, =CHN), 124.1 (s, $CH_{m\text{-}Ph\text{-}IPr}$), 116.6 (q, $J_{C\text{-}F}$ = 284.7, Rh-OOC<u>C</u>F_3), 58.3 (d, $J_{C\text{-}Rh}$ = 18.1, $=CH_{coe}$), 29.5 and 28.3 (both d, $J_{C\text{-}Rh}$ = 1.5, $CH_{2\text{-}coe}$), 29.2 (s, <u>C</u>HMe_{IPr}), 26.8 (s, $CH_{2\text{-}coe}$), 26.3 and 22.8 (both s, CH<u>Me</u>$_{IPr}$). ^{19}F NMR (282.3 MHz, C_6D_6, 298 K): δ -75.7 (s, CF_3).

Preparation of Rh[κ^2-S,O-{$SC(O)CH_3$}]{η^2-coe)(IPr) (6). The complex complex was prepared as described for **2** starting from **1** (150 mg, 0.12 mmol) and CH_3COSK (30 mg, 0.26 mmol) and isolated as a yellow solid. Yield: 115 mg (68%). Satisfactory elemental analysis could not be obtained. HRMS (ESI^+): *m/z* Calcd for $RhC_{29}H_{40}N_2O3S$ (M^++H+O_2-coe): 599.1809, Found: 599.1796. IR (cm^{-1}): 1507 $\nu(SCO_{sym})$, 1463 $\nu(SCO_{asym})$. ^1H NMR (400.2 MHz, C_6D_6, 298 K): δ 7.29 (m, 2H, $H_{p\text{-}Ph\text{-}IPr}$), 7.21 (m, 4H, $H_{m\text{-}Ph\text{-}IPr}$), 6.45 (s, 2H, =CHN), 3.25 (m, 6H, C<u>H</u>Me_{IPr}, $=CH_{coe}$), 2.1-0.9 (m, 12H, $CH_{2\text{-}coe}$), 1.85 (s, 3H, SC(O)<u>Me</u>), 1.62 and 1.04 (both d, $J_{H\text{-}H}$ = 6.9, 24H, CH<u>Me</u>$_{IPr}$). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, C_6D_6, 298 K): δ 228.1 (d, $J_{C\text{-}Rh}$ = 1.8, Rh-S<u>C</u>(O)Me), 166.1 (d, $J_{C\text{-}Rh}$ = 66.2, Rh-C_{IPr}), 146.6 (s, $C_{q\text{-}IPr}$), 137.9 (s, C_qN), 129.8 (s, $CH_{p\text{-}Ph\text{-}IPr}$), 124.5 (s, =CHN), 124.2 (s, $CH_{m\text{-}Ph\text{-}IPr}$), 65.7 (d, $J_{C\text{-}Rh}$ = 14.8, $=CH_{coe}$), 36.7 {d, $J_{C\text{-}Rh}$ = 1.2, Rh-SC(O)<u>Me</u>}, 30.0, 27.8, and 27.1 (all s, $CH_{2\text{-}coe}$), 29.2 (s, <u>C</u>HMe_{IPr}), 26.2 and 23.3 (both s, CH<u>Me</u>$_{IPr}$).

Preparation of Rh[κ^2-N,O-{$HNC(O)CH_3$}]{η^2-coe)(IPr) (7a,b). A mixture of CH_3CONH_2 (15 mg, 0.20 mmol) and ^tBuOK (23 mg, 0.21 mmol) in THF (5 mL) was stirred for 30 min at r.t. Then a solution of dinuclear complex **1** (120 mg, 0.09 mmol) THF (5 mL) was cannulated over the suspension containing the deprotonated amide and the mixture was stirred for additional 2 h at r.t. After evaporation to dryness, the residue was dissolved in hexane (20 mL) and was filtered through Celite. Slow evaporation of hexane resulted in the formation of a microcrystalline yellow solid. Yield: 90 mg (73%). IR (cm^{-1}): 1517 $\nu(OCN_{sym})$, 1458 $\nu(OCN_{asym})$. NMR data evidenced the presence of two isomers, **7a** and **7b** (84:16), in equilibrium. Data for complex **7a**: ^1H NMR (400.2 MHz, toluene-d_8, 243 K): δ 7.30 (m, 2H, $H_{p\text{-}Ph\text{-}IPr}$), 7.19 (m, 4H, $H_{m\text{-}Ph\text{-}IPr}$), 6.44 (s, 2H, =CHN), 4.59 (d, $J_{H\text{-}Rh}$ = 6.0, 1H, NH), 3.17 (sept, $J_{H\text{-}H}$ = 7.1, 4H, C<u>H</u>Me_{IPr}), 2.76 (m, 2H, $=CH_{coe}$), 2.1-0.9 (m, 12H, $CH_{2\text{-}coe}$), 1.59 and 1.11 (both d, $J_{H\text{-}H}$ = 7.1, 24H, CH<u>Me</u>$_{IPr}$), 1.48 {s, 3H, OC(NH)<u>Me</u>}. $^{13}C\{^1H\}$-APT NMR (100.4 MHz, toluene-d_8, 243

K): δ 185.3 {d, $J_{C\text{-}Rh}$ = 3.3, Rh-O<u>C</u>(NH)Me}, 184.8 (d, $J_{C\text{-}Rh}$ = 66.1, Rh-C_{IPr}), 146.1 (s, $C_{q\text{-}IPr}$), 137.2 (s, C_qN), 129.3 (s, $CH_{p\text{-}Ph\text{-}IPr}$), 123.6 (s, $CH_{m\text{-}Ph\text{-}IPr}$), 123.4 (s, =CHN), 60.7 (d, $J_{C\text{-}Rh}$ = 14.7, =CH_{coe}), 30.0, 27.8, and 26.9 (all s, $CH_{2\text{-}coe}$), 28.7 (s, <u>C</u>HMe$_{IPr}$), 25.7 and 22.9 (both s, CH<u>Me</u>$_{IPr}$), 24.7 {d, $J_{C\text{-}Rh}$ = 1.5, Rh-OC(NH)<u>Me</u>}. ^{1}H–^{15}N HSQC (40.5 MHz, toluene-d_8, 243 K): δ 189.6 (N_{IPr}), 136.8 (HNCOMe). Data for complex **7b**: ^{1}H NMR (400.2 MHz, toluene-d_8, 243 K): δ 7.3-7.0 (6H, $H_{Ph\text{-}IPr}$), 6.55 (s, 2H, =CHN), 3.85 (d, $J_{H\text{-}Rh}$ = 2.9, 1H, NH), 3.17 (sept, $J_{H\text{-}H}$ = 7.1, 4H, C<u>H</u>Me$_{IPr}$), 2. 59 (m, 2H, =CH_{coe}), 2.1-0.9 (m, 12H, $CH_{2\text{-}coe}$), 1.62 and 1.13 (both d, $J_{H\text{-}H}$ = 7.1, 24H, CH<u>Me</u>$_{IPr}$), 1.58 (s, 3H, OC(NH)<u>Me</u>). ^{13}C{^{1}H}-APT NMR (100.4 MHz, toluene-d_8, 243 K): δ 184.7 (d, $J_{C\text{-}Rh}$ = 62.4, Rh-C_{IPr}), 184.3 (d, $J_{C\text{-}Rh}$ = 3.0, Rh-O<u>C</u>(NH)Me), 146.6 (s, $C_{q\text{-}IPr}$), 137.5 (s, C_qN), 123.5 (s, =CHN), 54.7 (d, $J_{C\text{-}Rh}$ = 18.0, =CH_{coe}), 30.2, 27.8, and 26.9 (all s, $CH_{2\text{-}coe}$), 28.7 (s, <u>C</u>HMe$_{IPr}$), 26.1 and 22.7 (both s, CH<u>Me</u>$_{IPr}$), 24.6 {d, $J_{C\text{-}Rh}$ = 1.5, Rh-OC(NH)<u>Me</u>}. ^{1}H–^{15}N HSQC (40.5 MHz, toluene-d_8, 243 K): δ 191.4 (N_{IPr}), 136.6 (HNCOMe).

Preparation of Rh[κ^2-N,O-{N(Ph)C(O)CH$_3$}](η^2-coe)(IPr) (8). The complex was prepared as described for **7** starting from $CH_3C(O)NHPh$ (25 mg, 0.19 mmol), ^{t}BuOK (22 mg, 0.20 mmol) and **1** (120 mg, 0.09 mmol) and isolated as a yellow solid. Yield: 77 mg (69%). Anal. Calcd for $C_{43}H_{58}N_3ORh$: C, 70.19; H, 7.94; N, 5.71. Found: C, 70.67; H, 8.10; N, 5.29. HRMS (ESI$^+$): *m*/*z* Calcd for $RhC_{35}H_{43}N_3O$ (M^+-coe-H): 624.2456, Found: 624.2462. IR (cm^{-1}): 1543 ν(OCN$_{sym}$), 1464 ν(OCN$_{asym}$). ^{1}H NMR (400.2 MHz, C_6D_6, 298 K): δ 7.33 (m, 2H, $H_{p\text{-}Ph\text{-}IPr}$), 7.27 (m, 4H, $H_{m\text{-}Ph\text{-}IPr}$), 6.94 (vt, 2H, *N* = 15.5, $H_{m\text{-}Ph\text{-}N}$), 6.76 (t, $J_{H\text{-}H}$ = 7.7, 1H, $H_{p\text{-}Ph\text{-}N}$), 6.65 (d, $J_{H\text{-}H}$ = 7.8, 2H, $H_{o\text{-}Ph\text{-}N}$), 6.52 (s, 2H, =CHN), 3.20 (sept, $J_{H\text{-}H}$ = 6.7, 4H, C<u>H</u>Me$_{IPr}$), 2.67 (m, 2H, =CH_{coe}), 2.1-0.9 (m, 12H, $CH_{2\text{-}coe}$), 1.60 and 1.08 (both d, $J_{H\text{-}H}$ = 6.7, 24H, CH<u>Me</u>$_{IPr}$), 1.56 (s, 3H, OC(NPh)<u>Me</u>). ^{13}C{^{1}H}-APT NMR (100.4 MHz, C_6D_6, 298 K): δ 185.7 (d, $J_{C\text{-}Rh}$ = 61.7, Rh-C_{IPr}), 180.7 {d, $J_{C\text{-}Rh}$ = 3.2, Rh-O<u>C</u>(NPh)Me}, 148.8 (s, $C_{q\text{-}Ph\text{-}N}$), 146.8 (s, $C_{q\text{-}IPr}$), 137.2 (s, C_qN), 129.5 (s, $CH_{p\text{-}Ph\text{-}IPr}$), 128.1 (s, $CH_{m\text{-}Ph\text{-}N}$), 125.9 (s, $CH_{o\text{-}Ph\text{-}N}$), 123.9 (s, =CHN), 123.7 (s, $CH_{m\text{-}Ph\text{-}IPr}$), 122.9 (s, $CH_{p\text{-}Ph\text{-}N}$), 56.5 (d, $J_{C\text{-}Rh}$ = 16.5, =CH_{coe}), 30.1 and 29.7 (both d, $J_{C\text{-}Rh}$ = 1.3, $CH_{2\text{-}coe}$), 28.8 (s, <u>C</u>HMe$_{IPr}$), 26.7 (s, $CH_{2\text{-}coe}$), 26.2 and 22.9 (both s, CH<u>Me</u>$_{IPr}$), 19.7 {d, $J_{C\text{-}Rh}$ = 1.1, Rh-OC(NPh)<u>Me</u>}.

Preparation of Rh[κ^2-N,S-{HNC(S)CH$_3$}](η^2-coe)(IPr) (9). The complex was prepared as described for **7** starting from $CH_3C(S)NH_2$ (11 mg, 0.19 mmol), ^{t}BuOK (22 mg, 0.20 mmol) and **1** (120 mg, 0.09 mmol) and isolated as a yellow solid. Yield: 63 mg (61%). Anal. Calcd for $C_{37}H_{54}N_3SRh$: C, 65.76; H, 8.05; N, 6.22. Found: C, 66.02; H, 7.98; N, 6.05. HRMS (ESI+): m/z Calcd for $RhC_{29}H_{40}N_3S$: (M+-coe): 565.1992, Found: 565.1991 IR (cm^{-1}): 3076 ν(NH), 1556 ν(SCN$_{sym}$), 1460 ν(SCN$_{asym}$). ^{1}H NMR (400.2 MHz, C_6D_6, 298 K): δ 7.28 (m, 2H, $H_{p\text{-}Ph\text{-}IPr}$), 7.21 (m, 4H, $H_{m\text{-}Ph\text{-}IPr}$), 6.48 (s, 2H, =CHN), 5.83 (br, 1H, NH), 3.33 (sept, $J_{H\text{-}H}$ = 6.7, 4H, C<u>H</u>Me$_{IPr}$), 3.01 (m, 2H, =CH_{coe}), 2.1-0.9 (m, 12H, $CH_{2\text{-}coe}$), 1.66 and 1.07 (both d, $J_{H\text{-}H}$ = 6.7, 24H, CH<u>Me</u>$_{IPr}$), 1.53 {d, $J_{H\text{-}H}$ = 1.0, 3H, SC(NH)<u>Me</u>}. ^{13}C{^{1}H}-APT NMR (100.4 MHz, C_6D_6, 298 K): δ 200.1 (d, $J_{C\text{-}Rh}$ = 4.5, Rh-S<u>C</u>(NH)Me), 188.2 (d, $J_{C\text{-}Rh}$ = 58.2, Rh-C_{IPr}), 146.3 (s, $C_{q\text{-}IPr}$), 137.9 (s, C_qN), 129.6 (s, $CH_{p\text{-}Ph\text{-}IPr}$), 123.9 (s, =CHN), 123.7 (s, $CH_{m\text{-}Ph\text{-}IPr}$), 60.8 (d, $J_{C\text{-}Rh}$ = 15.1, =CH_{coe}), 33.8 {d, $J_{C\text{-}Rh}$ = 2.1, Rh-SC(NH)<u>Me</u>}, 30.2 (d, $J_{C\text{-}Rh}$ = 1.4, $CH_{2\text{-}coe}$), 29.4 and 26.9 (both s, $CH_{2\text{-}coe}$), 28.9 (s, <u>C</u>HMe$_{IPr}$), 26.0 and 23.2 (both s, CH<u>Me</u>$_{IPr}$). ^{1}H–^{15}N HSQC (40.5 MHz, toluene-d_8, 243 K): δ 197.9 (HNCSMe), 190.8 (N_{IPr}).

Preparation of Rh[κ^2-N,S-{N(Ph)C(S)CH$_3$}](η^2-coe)(IPr) (10). The complex was prepared as described for **7** starting from $CH_3C(S)NHPh$ (28 mg, 0.19 mmol), ^{t}BuOK (22 mg, 0.20 mmol) and **1** (120 mg, 0.09 mmol) and isolated as a yellow solid. Yield: 82 mg (70%). Satisfactory elemental analysis could not be obtained. HRMS (ESI$^+$): *m*/*z* Calcd for $RhC_{35}H_{44}N_3S$: (M^+-coe): 641.2305 Found: 641.2308. IR (cm^{-1}): 1592 ν(SCN$_{sym}$), 1464 ν(SCN$_{asym}$). ^{1}H NMR (400.2 MHz, C_6D_6, 298 K): δ 7.27 (m, 6H, $H_{Ph\text{-}IPr}$), 6.84 (vt, 2H, *N* = 14.7, $H_{m\text{-}Ph\text{-}N}$), 6.72 (t, $J_{H\text{-}H}$ = 7.7, 1H, $H_{p\text{-}Ph\text{-}N}$), 6.52 (s, 2H, =CHN), 6.48 (d, $J_{H\text{-}H}$ = 8.5, 2H, $H_{o\text{-}Ph\text{-}N}$), 3.32 (sept, $J_{H\text{-}H}$ = 6.7, 4H, C<u>H</u>Me$_{IPr}$), 3.18 (m, 2H, =CH_{coe}), 2.1-0.9 (m, 12H, $CH_{2\text{-}coe}$), 1.72 and 1.09 (both d, $J_{H\text{-}H}$ = 6.7, 24H, CH<u>Me</u>$_{IPr}$), 1.69 (s, 3H, SC(NPh)<u>Me</u>). ^{13}C{^{1}H}-APT NMR (100.4 MHz, C_6D_6, 298 K): δ 196.8 {d, $J_{C\text{-}Rh}$ = 3.3, Rh-S<u>C</u>(NPh)Me}, 185.4 (d, $J_{C\text{-}Rh}$ = 62.8, Rh-C_{IPr}), 149.6 (s, $C_{q\text{-}Ph\text{-}N}$), 146.8 (s, $C_{q\text{-}IPr}$), 138.1 (s, C_qN), 129.7 (s, $CH_{p\text{-}Ph\text{-}IPr}$), 127.9 (s, $CH_{m\text{-}Ph\text{-}N}$), 124.7 (s, $CH_{o\text{-}Ph\text{-}N}$), 124.5 (s, =CHN), 124.2 (s, $CH_{m\text{-}Ph\text{-}IPr}$), 124.1 (s, $CH_{p\text{-}Ph\text{-}N}$), 64.4 (d, $J_{C\text{-}Rh}$ = 14.4, =CH_{coe}), 30.4, 29.7, and 26.9 (all s, $CH_{2\text{-}coe}$), 29.9 {s, Rh-SC(NPh)<u>Me</u>}, 29.3 (s, <u>C</u>HMe$_{IPr}$), 26.5 and 23.5 (both s, CH<u>Me</u>$_{IPr}$).

Preparation of Rh[κ^2-N,N-{N(Ph)C(CH$_3$)NPh}](η^2-coe)(IPr) (11). The yellow complex was prepared as described for **7** starting from $CH_3C(NPh)NHPh$ (40 mg, 0.19 mmol), ^{t}BuOK (22 mg, 0.20 mmol) and **1** (120 mg, 0.09 mmol) and isolated as a yellow solid. Yield: 115 mg (75%). Satisfactory elemental analysis could not be obtained. HRMS (ESI$^+$): *m*/*z* Calcd for $RhC_{41}H_{48}N_4$: (M^+-coe-H): 699.2929, Found: 699.2874. IR (cm^{-1}): 1593 ν(NCN$_{sym}$), 1484 ν(NCN$_{asym}$). ^{1}H NMR (400.2 MHz, C_6D_6, 298 K): δ 7.36 (d, 2H, $H_{m\text{-}Ph\text{-}IPr}$), 7.31 (t, $J_{H\text{-}H}$ = 8.1, 2H, $H_{p\text{-}Ph\text{-}IPr}$), 7.13 (m, 2H, $H_{m\text{-}Ph\text{-}Na}$), 7.09 (m, 2H, $H_{m\text{-}Ph\text{-}IPr}$), 7.00 (vt, *N* = 15.5, 2H, $H_{m\text{-}Ph\text{-}Nb}$), 6.86 (d, $J_{H\text{-}H}$ = 8.1, 2H, $H_{o\text{-}Ph\text{-}Nb}$), 6.82 (t, $J_{H\text{-}H}$ = 7.4, 2H, $H_{p\text{-}Ph\text{-}Nb}$), 6.81 (t, $J_{H\text{-}H}$ = 7.4, 2H, $H_{p\text{-}Ph\text{-}Na}$), 6.55 (s, 2H, =CHN), 6.53 (d, $J_{H\text{-}H}$ = 8.1, 2H, $H_{o\text{-}Ph\text{-}Na}$), 4.29 and 2.02 (both sept, $J_{H\text{-}H}$ = 6.7, 4H, C<u>H</u>Me$_{IPr}$), 2.66 (m, 2H, =CH_{coe}), 1.83 (s, N(Ph)C(<u>Me</u>)NPh), 2.1-0.9 (m, 12H, $CH_{2\text{-}coe}$), 1.41, 1.24, 1.01, and 0.97 (all d, $J_{H\text{-}H}$ = 6.7, 24H, CH<u>Me</u>$_{IPr}$). ^{13}C{^{1}H}-APT NMR (100.4 MHz, C_6D_6, 298 K): δ 193.0 (d, $J_{C\text{-}Rh}$ = 57.9, Rh-C_{IPr}), 172.3 {d, $J_{C\text{-}Rh}$ = 4.0, Rh-N(Ph)<u>C</u>(Me)NPh}, 150.1 and 148.7 (both s, C_qN_{Ph}), 148.2 and 146.6 (both s, $C_{q\text{-}IPr}$), 137.8 (s, C_qN_{IPr}), 129.7 (s, $CH_{p\text{-}Ph\text{-}IPr}$), 128.3 and 128.2 (both s, $CH_{m\text{-}Ph\text{-}N}$), 127.3 (s, $CH_{o\text{-}Ph\text{-}Nb}$), 124.8 and 123.7 (both s, $CH_{m\text{-}Ph\text{-}IPr}$), 124.6 (s, =CHN), 123.4 (s, $CH_{p\text{-}Ph\text{-}Nb}$), 122.8 (s, $CH_{o\text{-}Ph\text{-}Na}$), 118.9 (s, $CH_{p\text{-}Ph\text{-}Na}$), 57.5 (d, $J_{C\text{-}Rh}$ = 15.6, =CH_{coe}), 30.5 (d, $J_{C\text{-}Rh}$ = 1.8, $CH_{2\text{-}coe}$), 29.6 and 27.0 (both s, $CH_{2\text{-}coe}$), 29.2 and 28.6 (s, <u>C</u>HMe$_{IPr}$), 26.9, 27.1, 23.7, and 22.4 (all s, CH<u>Me</u>$_{IPr}$), 17.1 (s, Rh-N(Ph)C(<u>Me</u>)NPh).

***In situ* Formation of Rh[κ^2-N,O-{N(Ph)C(O)CH$_3$}]{η^2-PhC≡C(Ph)C=CH$_2$}(IPr) (13).** A solution of **8** (31 mg, 0.042 mmol) in toluene-d_8 at 213 K (0.5 mL, NMR tube) was treated with phenylacetylene (46 µL, 0.42 mmol). Complex **14** was detected immediately at low temperature. Conversion reached 90 % after 24 h at 298 K. ^{1}H NMR (400.2 MHz, toluene-d_8, 298 K): δ 7.4-6.9 (16H, H_{Ph}), 6.51 (s, 2H, =CHN), 5.65 and 5.22 (both d, $J_{H\text{-}H}$ = 2.1, 2H, =CH_2), 3.03 and 2.92 (both sept, $J_{H\text{-}H}$ = 6.7, 4H, C<u>H</u>Me$_{IPr}$), 1.41, 1.12, 1.04, and 1.01 (all d, $J_{H\text{-}H}$ = 6.7, 24H, CH<u>Me</u>$_{IPr}$), 1.76 (s, 3H, OC(NPh)<u>Me</u>). ^{13}C{^{1}H}-APT NMR (100.4 MHz, toluene-d_8, 298 K): δ 184.0 (d, $J_{C\text{-}Rh}$ = 58.0, Rh-C_{IPr}), 181.6 (d, $J_{C\text{-}Rh}$ = 3.1, Rh-O<u>C</u>(NPh)Me), 147.2 and 147.1 (both s, $C_{q\text{-}IPr}$), 141.1 (s. <u>C</u>=CH_2), 138.0 (s, C_qN), 136.4 (s, $C_{q\text{-}Ph}$), 130-120 (CH_{Ph}), 122.3 (s, =CHN), 123.6 (s, $C_{q\text{-}Ph}$), 120.1 (s, =CH_2), 86.0 (d, $J_{C\text{-}Rh}$ = 18.3, Ph<u>C</u>≡CC(Ph)CH_2), 82.6 (d, $J_{C\text{-}Rh}$ = 19.3, PhC≡<u>C</u>C(Ph)CH_2), 28.8 and 28.6 (both s, <u>C</u>HMe$_{IPr}$), 26.2, 26.1, 23.2, and 22.7 (all s, CH<u>Me</u>$_{IPr}$), 19.6 {s, Rh-OC(NPh)<u>Me</u>}.

***In situ* Formation of Rh[κ^2-N,O-{N(Ph)C(O)Me}]{η^2-MeOOCC≡CCOOMe)(IPr) (14).** A solution of **8** (21 mg, 0.029 mmol) in toluene-d_8 at 243 K (0.5 mL, NMR tube) was treated with dimethylacetylendicarboxylate (4 µL, 0.32 mmol). NMR measurements were made immediately. ^{1}H NMR (400.2 MHz, toluene-d_8, 243 K): δ 7.19 (m, 2H, $H_{p\text{-}Ph\text{-}IPr}$), 7.08 (m, 4H, $H_{m\text{-}Ph\text{-}IPr}$), 7.01 (vt, 2H, *N* = 15.7, $H_{m\text{-}Ph\text{-}N}$), 6.75 (t, $J_{H\text{-}H}$ = 7.4, 1H, $H_{p\text{-}Ph\text{-}N}$), 6.56 (d, $J_{H\text{-}H}$ = 8.3, 2H, $H_{o\text{-}Ph\text{-}N}$), 6.26 (s, 2H, =CHN), 3.54 and 2.93 (both sept, $J_{H\text{-}H}$ = 6.7, 4H, C<u>H</u>Me$_{IPr}$), 3.18 (s, 6H, COOMe), 1.82, 1.69, 1.17, and 1.12 (all d, $J_{H\text{-}H}$ = 6.7, 24H, CH<u>Me</u>$_{IPr}$), 1.31 (s, 3H, OC(NPh)<u>Me</u>). ^{13}C{^{1}H}-APT NMR (100.4 MHz, toluene-d_8, 243 K): δ 183.4 (s, Rh-O<u>C</u>(NPh)Me), 176.0 (d, $J_{C\text{-}Rh}$ = 56.7, Rh-C_{IPr}), 157.8 (s, <u>C</u>OOMe), 147.3 and 146.5 (both s, $C_{q\text{-}IPr}$), 145.1 (s, $C_{q\text{-}Ph\text{-}N}$), 135.9 (s, C_qN), 130.0 (s, $CH_{p\text{-}Ph\text{-}IPr}$), 128.8 (s, $CH_{m\text{-}Ph\text{-}N}$), 124.9 (s, =CHN), 124.8 and 124.2 (both s, $CH_{m\text{-}Ph\text{-}IPr}$), 124.0 (s, $CH_{o\text{-}Ph\text{-}N}$), 122.9 (s, $CH_{p\text{-}Ph\text{-}N}$), 86.1 (d, $J_{C\text{-}Rh}$ =

18.8, C≡C), 51.8 (s, COOMe), 29.8 and 28.9 (both s, CHMe$_{IPr}$), 26.8, 26.4, 24.1, and 23.5 (all s, CHMe$_{IPr}$), 22.2 (d, $J_{C\text{-}Rh}$ = 1.1, Rh-OC(NPh)Me).

***In situ* Formation of Rh[κ^2-S,O-{SC(O)CH$_3$}](η^2-HC≡CPh)(IPr) (15).** A solution of **6** (20 mg, 0.030 mmol) in toluene-d_8 at 243 K (0.5 mL, NMR tube) was treated with phenylacetylene (9 µL, 0.086 mmol). NMR measurements were made immediately. ^{1}H NMR (400.2 MHz, toluene-d_8, 243 K): δ 7.74 (d, $J_{H\text{-}H}$ = 7.2, 2H, H$_{o\text{-}Ph}$), 7.1-6.8 (9H, H$_{Ph}$), 6.34 (s, 2H, =CHN), 4.59 (br, 1H, HC≡CPh), 3.51 and 2.74 (both sept, $J_{H\text{-}H}$ = 6.7, 4H, CHMe$_{IPr}$), 1.79, 1.45, 1.06, and 1.00 (all d, $J_{H\text{-}H}$ = 6.7, 24H, CHMe$_{IPr}$), 1.69 (s, 3H, SC(O)Me). ^{13}C{^{1}H}-APT NMR (100.4 MHz, toluene-d_8, 243 K): δ 227.8 {s, Rh-SC(O)Me}, 179.4 (d, $J_{C\text{-}Rh}$ = 64.6, Rh-C$_{IPr}$), 146.4 and 145.9 (both s, C$_{q\text{-}IPr}$), 137.2 (s, C$_q$N), 131.3 (s, CH$_{o\text{-}Ph}$), 130.1, 129.2, 127.8, 126.7, and 124.6 (all s, CH$_{Ph}$), 124.5 (s, =CHN), 121.2 (s, C$_{q\text{-}Ph}$), 89.1 (d, $J_{C\text{-}Rh}$ = 15.9, HC≡CPh), 82.6 (d, $J_{C\text{-}Rh}$ = 13.0, HC≡CPh), 37.1 (s, Rh-SC(O)Me), 29.7 and 29.5 (both s, CHMe$_{IPr}$), 26.9, 26.2, 23.7, and 23.1 (all s, CHMe$_{IPr}$).

***In situ* Formation of Rh(-C≡CPh)(IPr)(NCCH$_3$)$_2$ (17a,b).** A solution of dinuclear complex [Rh(μ-Cl)(IPr)(η^2-etilene)]$_2$ (**16**) (31 mg, 0.03 mmol) in CD$_3$CN (0.5 mL, NMR tube) was cannulated over the lithium phenylacetylide (6 mg, 0.06 mmol) contained in another NMR tube at 243 K. Low temperature measurements revealed the presence of two new isomers **17a**,**b** in 60:40 ratio. After warming the NMR tube at 298 K for 30 min, conversion to **17** was increased to 56%. Data for **17a**: ^{1}H NMR (400.2 MHz, CD$_3$CN, 298 K): δ 7.46 (t, $J_{H\text{-}H}$ = 7.7, 2H, H$_{p\text{-}Ph\text{-}IPr}$), 7.31 (d, $J_{H\text{-}H}$ = 7.7, 4H, H$_{m\text{-}Ph\text{-}IPr}$), 7.13 (s, 2H, =CHN), 7.02 (t, $J_{H\text{-}H}$ = 7.6, 2H, H$_{m\text{-}Ph}$), 6.90 (d, $J_{H\text{-}H}$ = 7.6, 2H, H$_{o\text{-}Ph}$), 6.87 (t, $J_{H\text{-}H}$ = 7.6, 1H, H$_{p\text{-}Ph}$), 3.29 (sept, $J_{H\text{-}H}$ = 6.8, 4H, CHMe$_{IPr}$), 1.19 and 1.06 (both d, $J_{H\text{-}H}$ = 6.8, 24H, CHMe$_{IPr}$). ^{13}C{^{1}H}-APT NMR (100.4 MHz, C$_6$D$_6$, 298 K): δ 193.8 (d, $J_{C\text{-}Rh}$ = 58.7, Rh-C$_{IPr}$), 147.0 (s, C$_{q\text{-}IPr}$), 138.6 (s, C$_q$N), 132-122 (C$_{Ph}$), 128.7 (d, $J_{C\text{-}Rh}$ = 58.2, Rh-C≡C), 106.4 (d, $J_{C\text{-}Rh}$ = 18.1, Rh-C≡C), 28.8 (s, CHMe$_{IPr}$), 25.9 and 22.6 (both s, CHMe$_{IPr}$). Data for **17b**: ^{1}H NMR (400.2 MHz, CD$_3$CN, 298 K): 7.12 (s, 2H, =CHN), 3.25 (sept, $J_{H\text{-}H}$ = 6.8, 4H, CHMe$_{IPr}$), 1.21 and 1.08 (both d, $J_{H\text{-}H}$ = 6.8, 24H, CHMe$_{IPr}$). ^{13}C{^{1}H}-APT NMR (100.4 MHz, C$_6$D$_6$, 298 K): δ 193.9 (d, $J_{C\text{-}Rh}$ = 57.2, Rh-C$_{IPr}$), 131.8 (d, $J_{C\text{-}Rh}$ = 73.7, Rh-C≡C), 108.5 (d, $J_{C\text{-}Rh}$ = 15.0, Rh-C≡C).

***In situ* Formation of RhH(-C≡CPh)$_2$(IPr)(py)$_2$ (18).** A solution of **8** (20 mg, 0.028 mmol) in toluene-d_8 at 213 K (0.5 mL, NMR tube) was treated with phenylacetylene (30 µL, 0.27 mmol) and pyridine (11 µL, 0.136 mmol). Complex **15** was detected immediately at low temperature. After warming the NMR tube at 263 K for 2 h complex **15** was formed in 42% yield. ^{1}H NMR (400.2 MHz, toluene-d_8, 223 K): δ 9.40 (d, $J_{H\text{-}H}$ = 5.4, 2H, H$_{2\text{-}py\text{-}cis}$), 9.07 (d, $J_{H\text{-}H}$ = 5.8, 2H, H$_{2\text{-}py\text{-}trans}$), 7.65 (d, $J_{H\text{-}H}$ = 7.6, 4H, H$_{o\text{-}Ph}$), 7.5-6.7 (14H, H$_{Ph}$, =CHN), 6.58 (d, $J_{H\text{-}H}$ = 7.7, 1H, H$_{4\text{-}py\text{-}cis}$), 6.39 (d, $J_{H\text{-}H}$ = 7.7, 1H, H$_{4\text{-}py\text{-}trans}$), 6.15 (vt, N = 13.1, 2H, H$_{4\text{-}py\text{-}cis}$), 6.07 (vt, N = 13.5, 2H, H$_{4\text{-}py\text{-}trans}$), 4.07 and 3.95 (both sept, $J_{H\text{-}H}$ = 6.7, 4H, CHMe$_{IPr}$), 1.67, 1.49, 1.26, and 1.15 (all d, $J_{H\text{-}H}$ = 6.7, 24H, CHMe$_{IPr}$), -16.48 (d, $J_{H\text{-}H}$ = 25.2, 1H, Rh-H). ^{13}C{^{1}H}-APT NMR (100.4 MHz, toluene-d_8, 223 K): δ 178.4 (d, $J_{C\text{-}Rh}$ = 50.0, Rh-C$_{IPr}$), 154.8 (s, C$_{2\text{-}py\text{-}trans}$), 153.4 (s, C$_{2\text{-}py\text{-}cis}$), 147.2 and 146.7 (both s, C$_{q\text{-}IPr}$), 137.7 (s, C$_q$N), 133-120 (CH$_{Ph}$), 131.2 (d, $J_{C\text{-}Rh}$ = 31.2, Rh-C≡C), 107.3 (d, $J_{C\text{-}Rh}$ = 8.3, Rh-C≡C), 30-22 (CHMe$_{IPr}$).

Crystal Structure Determination. Single crystals suitable for the X-ray diffraction studies were grown by slow difusion of hexane over saturated toluene solutions (**2**, **3**, and **6**) or alternatively slow evaporation of saturated hexane soultion of complexes (**7a**, **8** and **10**). X-ray diffraction data were collected at 100(2) K on the diffractometers Bruker SMART APEX CCD (**2**, **3**, **6**) and Bruker APEX DUO CCD (**7a**, **8**, **10**) with graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å) using ω rotations. Intensities were integrated and corrected for absorption effects with SAINT–PLUS[31] and SADABS[32] programs, both included in APEX2 package. The structures were solved by the Patterson method with SHELXS-97[33] and refined by full matrix least-squares on F^2 with SHELXL-2014,[34] under WinGX.[35]

Crystal data and structure refinement for 2. $C_{37}H_{53}N_2O_2Rh$, M = 660.72 g mol^{-1}, monoclinic, $P2_1$, a = 9.7412(4) Å, b = 16.3135(7) Å, c = 10.7745(5) Å, β = 99.0330(10)°, V = 1690.97(13) Å^3, Z = 2, D_{calc} = 1.298 g cm^{-3}, μ = 0.538 mm^{-1}, F(000) = 700, yellow prism, 0.365 x 0.230 x 0.190 mm^3, $\theta_{min}/\theta_{max}$ 1.914/28.610°, index ranges –12≤h≤12, –21≤k≤21, –14≤l≤14, reflections collected/independent 37450/8057 [R(int) = 0.0226], semiempirical absorption correction from equivalents, T_{max}/T_{min} 0.9006/0.8307, data/restraints/parameters 8057/1/388, GOF(F^2) = 1.028, R_1 = 0.0181 [I > 2 σ(I)], wR_2 = 0.0446 (all data), absolute structure parameter 0.012(5), largest diff. peak/hole 0.750/–0.429 e Å^{-3}. CCDC deposit number: 1986674.

Crystal data and structure refinement for 6. $C_{37}H_{53}N_2ORhS\cdot(C_6H_{14})_{0.5}$, M = 719.87 g mol^{-1}, monoclinic, $P2_1/c$, a = 10.4646(7) Å, b = 19.4622(13) Å, c = 19.2387(12) Å, β = 103.3010(10)°, V = 3813.1(4) Å^3, Z = 4, D_{calc} = 1.254 g cm^3, μ = 0.534 mm^{-1}, F(000) = 1532, orange prism, 0.200 x 0.140 x 0.120 mm^3, $\theta_{min}/\theta_{max}$ 2.000 to 26.365°, index range –13≤h≤13, –24≤k≤24, –24≤l≤24, reflections collected/independent 37524/7784 [R(int) = 0.0417], semi-empirical absorption correction from equivalents, T_{max}/T_{min} 0.9158/0.8018, data/restraints/parameters 7784/0/416, GOF(F^2) = 1.044, R_1 = 0.0330 [I > 2 σ(I)], wR_2 = 0.0785 (all data), largest diff. peak/hole 0.731/–0.562 e Å^{-3}. CCDC deposit number: 1986671.

Crystal data and structure refinement for 7a. $C_{37}H_{54}N_3ORh$, M = 659.74 g mol^{-1}, monoclinic, $P2_1$, a = 9.7638(15) Å, b = 16.282(3) Å, c = 10.7500(17) Å, β = 98.691(2)°, V = 1689.3(5) Å^3, Z = 2, D_{calc} = 1.297 g cm^3, μ = 0.538 mm^{-1}, F(000) = 700, yellow prism 0.220 x 0.120 x 0.040 mm^3, $\theta_{min}/\theta_{max}$ 1.916/26.407°, index range –12≤h≤12, –16≤k≤20, –13≤l≤13, reflections collected/independent 16344/5524 [R(int) = 0.0501], semi-empirical absorption correction from equivalents, T_{max}/T_{min} 0.9376/0.8142, data/restraints/parameters 5524/1/392, GOF(F^2) = 1.030, R_1 = 0.0338 [I > 2 σ(I)], wR_2 = 0.0631 (all data), absolute structure parameter 0.03(2), largest diff. peak/hole 0.511/–0.589 e Å^{-3}. CCDC deposit number: 1986670.

Crystal data and structure refinement for 8. $C_{43}H_{58}N_3ORh$, M = 735.83 g mol^{-1}, orthorhombic, $P2_12_12_1$, a = 11.4003(10) Å, b = 12.5967(11) Å, c = 27.588(3) Å, V = 3961.9(6) Å^3, Z = 4, D_{calc} = 1.234 g cm^3, μ = 0.466 mm^{-1}, F(000) = 1560, orange prism 0.370 x 0.240 x 0.080 mm^3, $\theta_{min}/\theta_{max}$ 1.476/28.343°, index range –15 ≤h≤15, -16 ≤k≤16, -36 ≤l≤36, reflections collected/independent 78405/9868 [R(int) = 0.0530], semi-empirical absorption correction from equivalents, T_{max}/T_{min} 0.8997/0.7503, data/restraints/parameters 9868/15/461, GOF(F^2) = 1.180, R1 = 0.0317 [I > 2 σ(I)], wR2 = 0.0779 (all data), absolute structure parameter 0.000(8), largest diff. peak/hole 1.155/–0.942 e Å^{-3}. CCDC deposit number: 1986673.

Standard Conditions for the Catalytic Alkyne Dimerization. In a NMR tube, 0.01 mmol of catalyst and 0.16 mmol of toluene as internal standard were dissolved in 0.5 mL of C$_6$D$_6$ and placed inside a dewar containing isopropanol at 193 K. Then, 0.50 mmol of alkyne were added to the freezed mixture that was allowed to warm up to room temperature just before the first NMR spectrum was recorded. The reaction course was monitored by ^{1}H NMR spectroscopy and the conversion was determined by integration of the corresponding resonances of the alkyne and the products.

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[1] a) G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **1980**, *33*, 227-250; b) G. I. Dzhardimalieva, A. D. Pomogailo, *Russ. Coord. Chem.* **2008**, *77*, 259-301.

[2] a) D. H. Kerridge, *Chem. Soc. Rev.* **1988**, *17*, 181-227. b) M. W. Drover, J. A. Love, L. L. Schafer, *Chem. Soc. Rev.* **2017**, *46*, 2913-2940.

[3] a) J. Baker, M. Kilner, *Coord. Chem. Rev.* **1994**, *133*, 219-300; b) F. T. Edelmann, *Adv. Organomet. Chem.* **2008**, 57, 183-352.

[4] a) R. Fandos, C. Hernández, A. Otero, A. Rodríguez, M. J. Ruíz, *Organometallics* **1999**, *18*, 2718-2723; b) J. J. Vittal, M. T. Ng, *Acc. Chem. Res.* **2006**, *139*, 869-877; c) M. J. D. Champion, R. Solanki, L. Delaude, A. J. P. White, J. D. E. T. Wilton-Ely, *Dalton Trans.* **2012**, *41*, 12386-12394; d) Y. Mutoh, M. Sakigawara, I. Niiyama, S. Saito, Y. Ishii, *Organometallics* **2014**, *33*, 5414-5422.

[5] a) G.-L. Xu, M. C. DeRosa, R. J. Crutchley, T. Ren, *J. Am. Chem Soc.* **2004**, *126*, 3728-3729; b) H. Arora, R. Mukherjee, *New J. Chem.* **2010**, *34*, 2357-2365; c) G. Beobide, O. Castillo, J. Cepeda, A. Luque, S. Pérez-Yáñez, P. Román, J. Thomas-Gipson, *Coord. Chem. Rev.* **2013**, *257*, 2716-2736. d) K. Sanada, H. Ube, M. Shionoya, *J. Am. Chem. Soc.* **2016**, *138*, 2945-2948.

[6] a) K. M. L. Taylor-Pashow, J. Della Rocca, Z. Xie, S. Tran, W. Lin, *J. Am. Chem. Soc.* **2009**, *131*, 14261-14263; E. Gabano, M. Ravera, I. Zanellato, S. Tinello, A. Gallina, B. Rangone, V. Gandin, C. Marzano, M. G. Bottone, D. Osella, *Dalton Trans.* **2017**, *46*, 14174-14185; (c) J. Ohata, Z. T. Ball, *Dalton Trans.* **2018**, *47*, 14855-14860.

[7] a) K. Ahlford, J. Ekström, A. B. Zaitsev, P. Ryberg, L. Eriksson, H. Adolfsson, *Chem. Eur. J.* **2009**, *15*, 11197-11209; b) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315-1345; c) S. A. Ryken, L. L. Schafer, *Acc. Chem. Res.* **2015**, *48*, 2576-2586; d). Y.-S. Huang, G.-T. Huang, Y.-L. Liu, J.-S. K. Yu, Y.-C. Tsai, *Angew. Chem. Int. Ed.* **2017**, *56*, 15427-15431; e) W. G. Whitehurst, J. H. Blackwell, G. N. Hermann, M. J. Gaunt, *Angew. Chem. Int. Ed.* **2019**, *58*, 9054-9059.

[8] a) J. Hansen, H. M.L. Davies, *Coord. Chem. Rev.* **2008**, *252*, 545-555; b) S. Tanaka, H. Tsurugi, K. Mashima, *Coord. Chem. Rev.* **2014**, *265*, 38-51; b) S. A. Beach, L. H. Doerrer, *Acc. Chem. Res.* **2018**, *51*, 1063-1072.

[9] a) C.-W. Hsu, J.-S. K. Yu, C.-H. Yen, G.-H. Lee, Y. Wang, Y.-C. Tsai, *Angew. Chem. Int. Ed.* **2008**, *47*, 9933-9936; b) M. Carrasco, N. Curado, C. Maya, R. Peloso, A. Rodríguez, E. Ruiz, S. Alvarez, E. Carmona, *Angew. Chem. Int. Ed.* **2013**, *52*, 3227-3231.

[10] a) C. S. Sevov, J. Zhou, J. F. Hartwig. *J. Am. Chem. Soc.* **2012**, *134*, 11960-11963; b) M. Zabransky, I. Cisařova, P. Štěpnička, *Eur. J. Inorg. Chem.* **2017**, 2557-2572; c) J. M. Clarkson, L. L. Schafer, *Inorg. Chem.* **2017**, *56*, 5553-5566.

[11] a) S. I. Gorelsky, D. Lapointe, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 10848-10849; b) Y. Boutadla, D. L. Davies, S. A. Macgregor, A. I. Poblador-Bahamonde, *Dalton Trans.* **2009**, 5820-5831.

[12] a) S. E. García-Garrido, In *Modern Alkyne Chemistry: Catalytic and Atom-Economic Transformations*; B. M. Trost and C.-J. Li, Eds.; Wiley-VCH, Weinheim, Germany, 2015; pp 301−334; b) B. M. Trost, J. T. Masters, *Chem. Soc. Rev.* **2016**, *45*, 2212−2238; c) Y. Zhou, Y. Zhang, J. Wang, *Org. Biomol. Chem.* **2016**, *14*, 6638−6650.

[13] a) R. Duchateau, C. T. van Wee, J. H. Teuben, *Organometallics* **1996**, *15*, 2291-2302; b) A. Haskel, T. Straub, A. K. Dash, M. S. Eisen, *J. Am. Chem. Soc.* **1999**, *121*, 3014-3024; c) M. Nishiura, Z. Hou, Y. Wakatsuki, T. Yamaki, T. Miyamoto, *J. Am. Chem. Soc.* **2003**, *125*, 1184-1185; d) S. Ge, A. Meetsma, B. Hessen, *Organometallics* **2009**, *28*, 719-726; e) R. J. Batrice, J. McKinven, P. L. Arnold, M. S. Eisen, *Organometallics* **2015**, *34*, 4039-4050.

[14] a) M. Akita, H. Yasuda, A. Nakamura, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 480-487; b) M. Yoshida, R. F. Jordan, *Organometallics* **1997**, *16*, 4508-4510; c) G. V. Oshovsky, B. Hessen, J. N. H. Reek, B. De Bruin, *Organometallics* **2011**, *30*, 6067-6070; d) R. H. Platel, L. L. Schafer, *Chem. Commun.* **2012**, *48*, 10609-10611.

[15] a) I. P. Kovalev, K. V. Yevdakov, Y. A. Strelenko, M. G. Vinogradov, G. I. Nikishin, *J. Organomet. Chem.* **1990**, *386*, 139-146; b) C. Bianchini, M. Peruzzini, F. Zanobini, P. Frediani, A. Albinati, *J. Am. Chem. Soc.* **1991**, *113*, 5453-5454; c) B. M. Trost, M. T. Sorum, C. Chan, A. E. Harms, G. Rühter, *J. Am. Chem. Soc.* **1997**, *119*, 698-708; d) C. S. Yi, N. Liu, *Organometallics* **1998**, *17*, 3158-3160; e) T. Ohmura, S.-I. Yorozuya, Y. Yamamoto, N. Miyaura, *Organometallics* **2000**, *19*, 365-366; f) W. Baratta, W. A. Herrmann, P. Rigo, J. Schwarz, *J. Organomet. Chem.* **2000**, *593-594*, 489-493; g) M. Rubina, V. Gevorgyan, *J. Am. Chem. Soc.* **2001**, *123*, 11107-11108; h) C. Yang, S. P. Nolan, *J. Org. Chem.* **2002**, *67*, 591-593; i) R. Gosh, X. Zhang, P. Achord, T. J. Emge, K. Krogh-Jespersen, A. S. Goldman, *J. Am. Chem. Soc.* **2007**, *129*, 853-866; j) T. Katagiri, H. Tsurugi, T. Satoh, M. Miura, *Chem. Commun.* **2008**, 3405-3407; k) M. Ciclosi, F. Estevan, P. Lahuerta, V. Passarelli, J. Pérez-Prieto, M. Sanau, *Adv. Synth. Catal.* **2008**, *350*, 234-236; l) H. M. Peng, J. Zhao, X. Li, *Adv. Synth. Catal.* **2009**, *351*, 1371-1377; m) S. Sun, J. Kroll, Y. Luo, L. Zhang, *Synlett* **2012**, *23*, 54-56; n) L. Rubio-Pérez, R. Azpíroz, A. Di Giuseppe, V. Polo, R. Castarlenas, J. J. Pérez-Torrente, L. A. Oro, *Chem. Eur. J.* **2013**, *19*, 15304-15314; o) T. Chen, C. Guo; M. Goto, L.-B. Han, *Chem. Commun.* **2013**, *49*, 7498-7500; p) C. J. Pell, O. V. Ozerov, *ACS Catal.* **2014**, *4*, 3470-3480; q) O. V. Zatolochnaya, E. G. Gordeev, C. Jahier, V. P. Ananikov, V. Gevorgyan, *Chem. Eur. J.* **2014**, *20*, 9578-9588; r) G. Kleinhans, G. Guisado-Barrios, D. C.; Liles, G. Bertrand, D. I. Bezuidenhout, *Chem. Commun.* **2016**, *52*, 3504-3507; s) M. G. Lauer, B. R. Headford, O. M. Gobble, M. B. Weyhaupt, D. L. Gerlach, M. Zeller, K. H. Shaughnessy, *ACS Catal.* **2016**, *6*, 5834-5842; t) N. Endo, M. Kanaura, M. P. Schramm, T. Iwasawa, *Eur. J. Org. Chem.* **2016**, 2514-2521; u) R. Salvio, F. Juliá-Hernández, L. Pisciottani, R. Mendoza-Meroño, S. García-Granda, M. Bassetti, *Organometallics* **2017**, *36*, 3830-3840; v) P. Żak, M. Bołt, J. Lorkowski, M. Kubicki, C. Pietraszuk, *ChemCatChem* **2017**, *9*, 3627-3631; w) C. M. Storey, M. R. Gyton, R. E. Andrew, A. B. Chaplin, *Angew. Chem. Int. Ed.* **2018**, *57*, 12003-12006; x) S. Ostrowska, N. Szymaszec, C. Pietraszuk, *J. Organomet. Chem.* **2018**, *856*, 63-69.

[16] A. K. Dash, M. S. Eisen, *Org. Lett.* **2000**, *2*, 737-740.

[17] a) G. C. Midya, S. Paladhi, K. Dhara, J. Dash, *Chem. Commun.* **2011**, *47*, 6698-6700; b) S. Ventre, E. Derat, M. Amatore, C. Aubert, M. Petit, *Adv. Synth Catal.* **2013**, *355*, 2584-2590; c) O. Rivada-Wheelaghan, S. Chakraborty, L. J.W. Shimon, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2016**, *55*, 6942-6945; d) Q. Liang, K. M. Osten, D. Song, *Angew. Chem. Int. Ed.* **2017**, *56*, 6317-6320; e) F. Xue, X. Song, T. T. Lin, K. Munkerup, S. F. Albawardi, K.-W. Huang, T. S. A. Hor, J. Zhao, *ACS Omega* **2018**, *3*, 5071-5077; f) N. Gorgas, B. Stöger, L. F. Veiros, K. Kirchner, *ACS Catal.* **2018**, *8*, 7973-7982; g) Q. Liang, K. Sheng, A. Salmon, V. Y. Zhou, D. Song, *ACS Catal.* **2019**, *9*, 810-818; h) X. Zhuang, J.-Y. Chen, Z. Yang, M. Jia, C. Wu, R.-Z. Liao, C.-H. Tung, W. Wang, *Organometallics* **2019**, *38*, 3752-3759; i) J.-C. Grenier-Petel, S. K. Collins, *ACS Catal.* **2019**, *9*, 3213-3218.

[18] a) G. C. Midya, B. Parasar, S. Maiti, J. Dash, *ChemistrySelect* **2017**, *2*, 5032-5037; b) M. Hasenbeck, T. Müller, U. Gellrich, *Catal. Sci. Tech.* **2019**, *9*, 2438-2444; c) J. Ahmed, A. K. Swain, A. Das, R. Govindarajan, M. Bhuniaand, S. K. Mandal, *Chem. Commun.* **2019**, *55*, 13860-13863.

[19] M. Angoy, M. V. Jiménez, P. García-Orduña, L. A. Oro, E. Vispe, J. J. Pérez-Torrente, *Organometallics* **2019**, *38*, 1991-2006.
[20] L. Leroyer, M. Maraval, R. Chauvin, *Chem. Rev.* **2012**, *112*, 1310-1343.
[21] O. Torres, M. Fernàndez, A. Diáz-Jiménez, A. Pla-Quintana, A. Roglans, M. Solà, *Organometallics* **2019**, *38*, 2853-2862.
[22] V. Claus, M. Schukin, S. Harrer, M. Rudolph, F. Rominger, A. M. Asiri, J. Xie, S. K. Hashmi, *Angew. Chem. Int. Ed.* **2018**, *57*, 12966-12970.
[23] a) V. Gevorgyan, U. Radhakrishnan, A. Takeda, M. Rubina, M. Rubin, Y. Yamamoto, *J. Org. Chem.* **2001**, *66*, 2835-2841; b) R. V. Lerum, C. M. Ruso, J. E. Marquez, J. D. Chisholm, *Adv. Synth. Catal.* **2013**, *355*, 3485-3491; c) T. Chen, C.-Q. Zhao, L.-B. Han, *J. Am. Chem. Soc.* **2018**, *140*, 3139-3155; d) C. M. Storey, A. Kalpokas, M. R. Gyton, T. Krämer, A. B. Chaplin, *Chem. Sci.* **2020**, *11*, 2051-2057.
[24] Y. Gao, R. J. Puddephatt, *Inorg. Chim. Acta* **2003**, *350*, 101-106.
[25] a) W. Hermann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290-1309; b) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612-3676; c) D. J. Müller, C. Schlepphorst, F. Glorius, *Chem. Soc. Rev.* **2017**, *46*, 4845-4854; d) E. Peris, *Chem. Rev.* **2018**, *118*, 9988-10031; e) J. Lee, H. Hahm, J. Kwak, M. Kim, *Adv. Synth. Catal.* **2019**, *361*, 1479-1499; e) Q. Zhao, G. Meng, S. P. Nolan, M. Szostak, *Chem. Rev.* **2020**, *120*, 1981-2048.
[26] R. Azpíroz, L. Rubio-Pérez, R. Castarlenas, J. J. Pérez-Torrente, L. A. Oro, *ChemCatChem.* **2014**, *6*, 2587-2592.
[27] X.-Y. Yu, B. O. Patrick, B. R. James, *Organometallics* **2006**, *25*, 4870-4877.
[28] a) L. Palacios, A. Di Giuseppe, A. Opalinska, R. Castarlenas, J. J. Pérez-Torrente, F. J. Lahoz, L. A. Oro, *Organometallics* **2013**, *32*, 2768-2744; b) L. Palacios, M. J. Artigas, V. Polo, F. J. Lahoz, R. Castarlenas, J. J. Pérez-Torrente, L. A. Oro, *ACS Catal.* **2013**, *3*, 2910-2919; c) R. Azpíroz, L. Rubio-Pérez, A. Di Giuseppe, V. Passarelli, F. Lahoz, R. Castarlenas, J. J. Pérez-Torrente, L. A. Oro, *ACS Catal.* **2014**, *4*, 4244-4253; d) L. Palacios, A. Di Giuseppe, R. Castarlenas, F. J. Lahoz, J. J. Pérez-Torrente L. A. Oro, *Dalton Trans.* **2015**, *44*, 5777-5789; e) L. Palacios, A. Di Giuseppe, M. J. Artigas, V. Polo, F. J. Lahoz, R. Castarlenas, J. J. Pérez-Torrente, L. A. Oro, *Catal Sci. Technol.* **2016**, *6*, 8548-8561; f) R. Azpíroz, A. Di Giuseppe, V. Passarelli, J. J. Pérez-Torrente, L. A. Oro, R. Castarlenas *Organometallics* **2018**, *37*, 1695-1707.
[29] a) J. M. Praetorius, M. W. Kotyk, J. D. Webb, R. Wang, C. M. Crudden, *Organometallics* **2007**, *26*, 1057-1061; b) J. Thongpaen, R. Manguin, V. Dorcet, T. Vives, C. Duhayon, M. Maudit, O. Baslé, *Angew. Chem. Int. Ed.* **2019**, *58*, 15244-15248.
[30] H. Amouri, M. Gruselle, M. *Chirality in transition metal chemistry*, **2008**, John Wiley & Sons Ltd, UK.
[31] *SAINT+: Area-Detector Integration Software*, version 6.01; Bruker AXS: Madison, WI, **2001**.
[32] G. M. Sheldrick, *SADABS program*; University of Göttingen: Göttingen, Germany, **1999**.
[33] G. M. Sheldrick, *SHELXS 97,* University of Göttingen: Göttingen, Germany, **1997**.
[34] G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3−8.
[35] L. J. Farrugia, *J. Appl. Crystallogr*. **2012**, *45*, 849−854.

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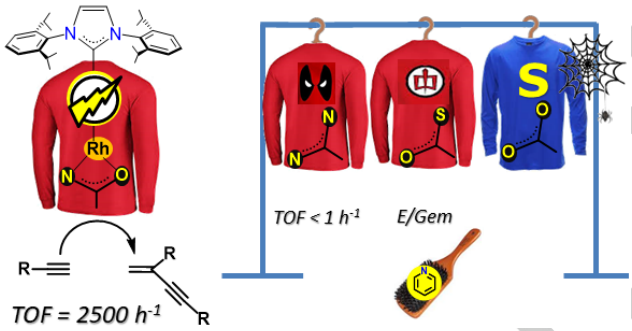
Flash Catalyst: Several rhodium-NHC-BHetA complexes has been prepared and compared as alkyne dimerization catalysts. The N,O framework of acetanilidato ligand is essential for a very high activity



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Rhodium(I)-NHC Complexes Bearing Bidentate Bis-Heteroatomic Acidato Ligands as *gem*-Selective Catalysts for Alkyne Dimerization