ORGANOMETALLICS
Article
Cite This: Organometallics XXXX, XXX, XXX−XXX
pubs.acs.org/Organometallics

# Rh(III)Cp* and Ir(III)Cp* Complexes of 1-[(4-Methyl)phenyl]-3-[(2-methyl-4′-R)imidazol-1-yl]triazenide (R = *t*-Bu or H): Synthesis, Structure, and Catalytic Activity

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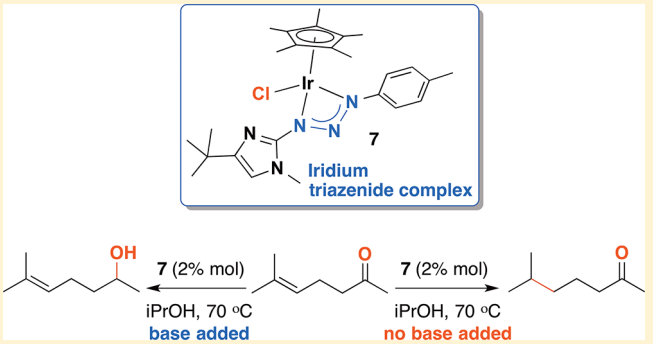
Supporting Information

**ABSTRACT:** A series of iridium and rhodium complexes have been synthesized using as ligand a triazenide monofunctionalized with an imidazole substituent. Steric hindrance at the imidazole moiety induced differences in the coordination modes as well in the catalytic behavior of complexes **4**−**7**. Complexes **4**−**7** were tested in the transfer hydrogenation of acetophenone and 5-alken-2-ones. The hydrogenation of either the double bond or the carbonyl group in 5-alken-2-ones, showed to be selective in the presence of **6**, **7**, and **10** and has a dependence on the presence or absence of base. Control experiments point out that the imidazole moiety in the structure of complexes **4**−**7** speeds-up the catalysis.

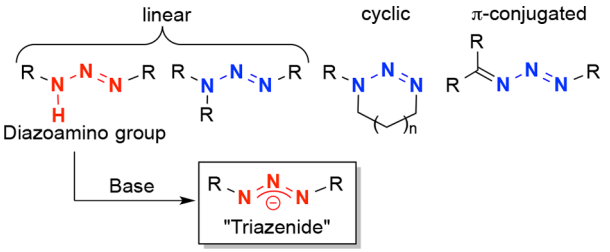



## INTRODUCTION

Triazenes have been described as versatile and very useful molecules in many areas of chemistry.[1] Recently, triazenes have been classified as linear, cyclic and π-conjugated molecules.[2] Linear triazenes containing the diazoamine group are important molecules in coordination chemistry due to their ability to form triazenide anions after deprotonation with base (Chart 1).[3] As ligands, triazenides are also very versatile due to their ability to coordinate to alkali metals,[3c,d] alkaline earth metals,[3b] and early[3e] and late transition metals.[3f]

Aryl groups have been the most common substituents of the triazenide system in triazenide complexes of transition metals.[4] In contrast, *N*-heterocyclic groups have been less studied as substituents on the triazenide ligand.[5] Nevertheless, there are a few examples of complexes where the triazenide ligand is mono- or disubstituted with pyridine,[5] tetrazol,[6] benzothiazole,[7] and triazole[8] heterocyclic groups. Here we report on the synthesis and characterization of Ir(III) and Rh(III) complexes of triazenide ligands monofunctionalized with sterically hindered or unhindered imidazole moiety as well as their catalytic properties in transfer hydrogenation of acetophenone and 5-alken-2-ones.

**Chart 1. Classification of Triazenes**




## RESULTS AND DISCUSSION

Triazenes **2** and **3** are new compounds, which were synthesized according to previously reported methodology[9] by reaction of 2-lithioimidazoles with 4-azidotoluene, followed by hydrolysis (eq 1).

**Received:** November 13, 2018






DOI: 10.1021/acs.organomet.8b00834
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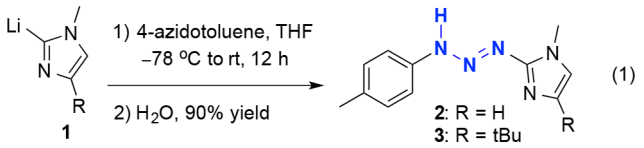



(1)

Compounds **2** and **3** were fully characterized by means of spectroscopic and spectrometric techniques. The $^{1}$H NMR data of both triazenes are consistent with the proposed structures **2** and **3**, wherein the characteristic NH of the triazene group was observed as a broad singlet at 10.92 and 9.99 ppm, respectively. Moreover, the identity of **2** and **3** in the solid state was, unambiguously, resolved by X-ray studies (Figures 1 and 2). Interestingly, the asymmetric unit of **2** showed two triazene molecules connected to each other by hydrogen bonding, wherein the planes are almost perpendicular to each other. Both triazenes adopt an (*E*)-configuration around the N=N double bond, which is a common feature in related 1,3-disubstituted triazenes.[4] For compound **2**, the N2=N3 bond distance [1.276(2) Å] is longer than the typical value for a double bond distance (1.222 Å), whereas the N3−N4 bond distance [1.328(2) Å] is shorter than the typical value for a single bond (1.420 Å).[10] The same behavior in bond distances is observed for triazene **3** (Figure 2). These differences in bond distances at the triazene system have been described as certain degree of $\pi$-delocalization across the linear triazene moiety.[11]

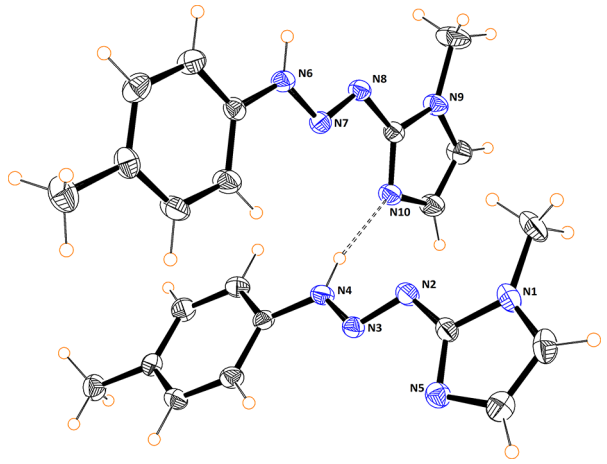



**Figure 1.** Molecular structure of triazene **2**. Selected bond distances (Å): N(2)=N(3), 1.276(2); N(3)−N(4), 1.328(2); N(4)···N(10), 2.99. Selected bond angles (deg): N(2)−N(3)−N(4), 111.3(1).

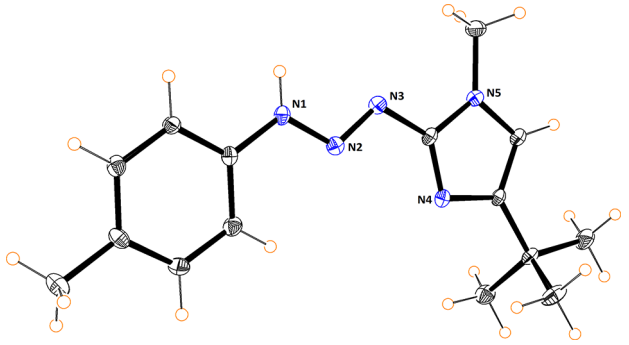
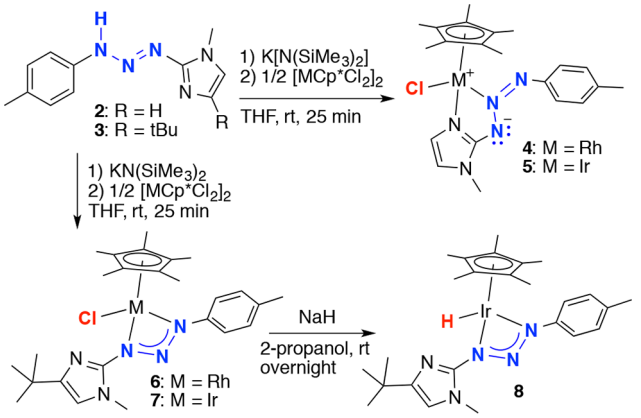


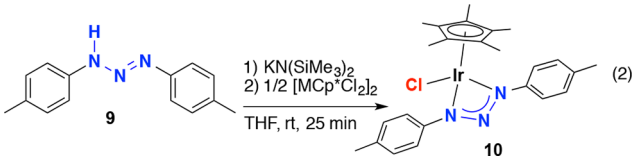

**Figure 2.** Molecular structure of triazene **3**. Selected bond distances (Å): N(2)=N(3), 1.260(2); N(1)−N(2), 1.354(2). Selected bond angles (deg): N(2)−N(3)−N(4), 111.7(2).

Treatment of a solution of **2** or **3** in dry THF with K[N(SiMe$_3$)$_2$] led to the formation of a potassium triazenide, which can be directly converted into complexes **4**−**7** by a transmetalation reaction with [MCp*Cl$_2$]$_2$ (Scheme 1). The $^{1}$H and $^{13}$C NMR of complexes **4** and **5** showed a very similar spectrum, as can be expected from their hypothetical structures. The $^{1}$H spectra of **4** showed two resonances at 7.84 and 7.18 ppm (d, $J$ = 8.3 Hz) assigned to the aromatic hydrogens of the A$_2$B$_2$ system, as well as two doublets at 6.80 and 6.34 ppm ($J$ = 1.8 Hz) due to the imidazole hydrogens. In addition, the C*H*$_3$-*N*, C*H*$_3$-Ph, and Cp* hydrogens appear as singlets at 3.49, 2.37, and 1.70 ppm, respectively. However, the appearance of the aromatic A$_2$B$_2$ system of **6** and **7** is very different when compared to the A$_2$B$_2$ system observed in complexes **4** and **5**. These resonances are centered at 7.08 and 7.12 ppm, respectively and exhibited a typical second-order effect with a $\Delta\nu/J$ = 1.5 (Figures S26 and S32).

**Scheme 1. Synthesis of Triazenide Complexes 4−8 Functionalized with Imidazole**




The ability of complexes to be converted into metal hydrides was examined by reaction of **7** with NaH in 2-propanol. The single organometallic product was formulated as **8** since its $^{1}$H NMR spectrum exhibited a high-field signal at −7.72 ppm. Moreover, a metal hydride was also observed (−14.62 ppm) in the absence of base when **7** was heated to 70 °C for 4 h in 2-propanol (Figure S69). In addition, compound **10** was synthesized from triazene **9**[12] in the same manner as complexes **4**−**7** (eq 2).




(2)

The purpose of preparing **10**, which features a triazenide ligand 1,3-disubstituted with 4-methylphenyl groups, was to study the effect of the absence of the imidazole moiety in the coordination mode as well as its catalytic activity. As a result of the symmetry of **10**, its $^{1}$H NMR spectrum showed only three resonances at 7.11, 2.33, and 1.78 ppm, which were assigned to the aromatic hydrogens, the methyl groups and the Cp*, respectively. Interestingly, the aromatic signal centered at 7.11 ppm exhibits the same second-order effect



DOI: 10.1021/acs.organomet.8b00834
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(with $\Delta\nu/J$ = 1.3), which was observed in **6** and **7** (Figure S43).

A detailed analysis of the $^{13}C$ NMR data of triazenes (**2**−**3**) and complexes (**4**−**8**) allowed to infer the coordination mode of the triazenide ligand in complexes **4**−**8**. For example, it was found that the imidazole-carbon resonance (C4−Im) in complexes **4** and **5** is shifted upfield (4.4 to 5.5 ppm) in comparison with the C4−Im resonance in triazene **2**. Furthermore, the signal of C4−Im in **4** has the appearance of a doublet at 121.9 ppm ($^2J_{Rh-C4}$ = 1.7 Hz). These findings may be considered as direct evidence of imidazole nitrogen coordination in complexes **4** and **5**. In contrast, there is no evidence for imidazole nitrogen coordination in complexes **6**−**8**, whose $^{13}C$ NMR data showed no significant changes in chemical shifts of the C4−Im resonance (149.6, 149.9, and 149.0 ppm, respectively) in comparison with the same signal in triazene **3** (149.5 ppm). Additional data that is consistent with the structure of **6**, shown in Scheme 1, is that both *ipso* carbons C2−Im and C1−Ph in **6** are coupled with rhodium and give two doublets at 147.7 ($^2J_{Rh-C2}$ = 2.8 Hz) and 144.7 ppm ($^2J_{Rh-C1}$ = 2.1 Hz), respectively. Ultimately, a single crystal of complexes **4**, **5**, and **10** were analyzed by X-ray diffraction (Figures 3, S55, and 4).

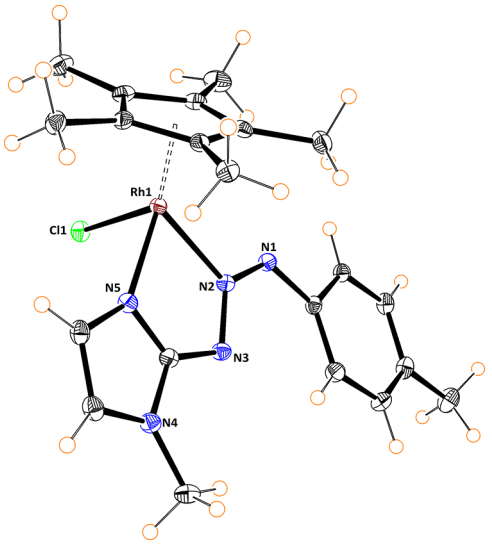



**Figure 3.** Molecular structure of complex **4**. Selected bond distances (Å): N(1)═N(2), 1.281(2); N(2)−N(3), 1.29(5); N(2)−Rh(1), 2.103(1); N(5)−Rh(1), 2.070(1); Cl(1)−Rh(1), 2.4051(4). Selected bond angles (deg): N(2)−Rh−N(5), 75.62(5)°; N(2)−Rh(1)−Cl(1), 87.27(4)°; N(5)−Rh(1)−Cl(1), 90.60(4)°.

The crystalline structures of **4** and **5** showed a distorted octahedral geometry around the metal with a Cp*, chloride, and triazenide ligand coordinated to the metal atom. In both complexes, the triazenide ligand is coordinated through the central nitrogen atom and the imidazole nitrogen (N5). Moreover, the five-membered chelate [N(2)−Rh−N(5) = 75.62(5)°; N(2)−Ir−N(5) = 74.82(1)°] favored a (*Z*)-configuration around the N(1)═N(2) double bond in the triazenide ligand [**4**: N(1)═N(2) = 1.281(2) Å **5**: N(1)═N(2) = 1.29(5)]. A similar behavior in the coordination modes has been observed in copper and cobalt complexes where the triazenide is substituted with pyridine.[5b,c] In contrast, the triazenide ligand in complex **10** coordinates to the metal through the terminal nitrogens, forming a four-membered chelate with a bite angle of 58.5(1)°.

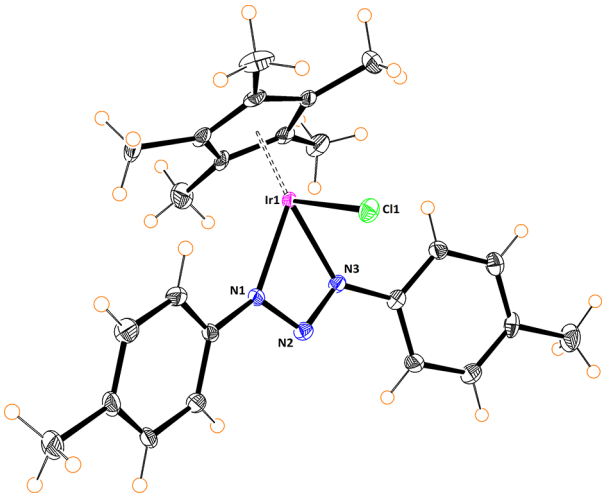
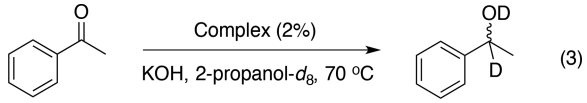



**Figure 4.** Molecular structure of complex **10**. Selected bond distances (Å): N(1)−N(2), 1.310(5); N(2)−N(3), 1.319(5); Ir(1)−N(3), 2.084(3); Ir(1)−N(2), 2.097(3); Ir(1)−Cl(1), 2.387(1). Selected bond angles (deg): N(1)−Ir(1)−N(3), 58.5(1); N(1)−Ir(1)−Cl(1), 87.1(1); N(3)−Ir(1)−Cl(1), 84.2(1).

Complexes **4**−**7** were tested as precatalysts in the transfer hydrogenation of acetophenone to 1-phenylethanol under the conditions shown in eq 3.




(3)

The results of the catalytic evaluation are summarized in Table 1. Complexes **4**−**7** catalyze the reduction of acetophenone to afford 1-phenylethanol in 93−96% yield in the presence of base (42−144 h). In contrast, although a longer time is required (86 h), no base is needed when complex **7** is used as precatalyst (entries 4 and 5). With the aim of evaluating the influence of the imidazole moiety, in a control experiment using complex **10** with base, a significant lower yield was observed, suggesting that the imidazole moiety further assists in the transfer hydrogenation of acetophenone catalyzed by **7** (entries 4 and 6). Surprisingly, in the absence of base, complex **10** catalyzed the hydrogenation of acetophenone in a comparable yield when complex **7** is

**Table 1. Transfer Hydrogenation of Acetophenone Using 4−9 as Precatalysts**[a]

| entry | preCat | subst/preCat/KOH | time (h) | yield (%)[b] |
|---|---|---|---|---|
| 1 | **4** | 100/2/10 | 144 | 96 |
| 2 | **5** | 100/2/10 | 62 | 95 |
| 3 | **6** | 100/2/10 | 89 | 93 |
| 4 | **7** | 100/2/10 | 42 | 95 |
| 5 | **7** | 100/2/- | 86 | 93 |
| 6 | **10** | 100/2/10 | 42 | 57 |
| 7 | **10** | 100/2/10 | 86 | 87 |
| 8 | **10** | 100/2/- | 86 | 98 |
| 9 | **8** | 100/10/- | 4 | 83 |
| 10 | | 100/0/10 | 144 | 30 |

[a]Reaction conditions: 2-propanol-$d_8$, 70 °C. [b]Yields were determined by $^1H$ NMR using 1,3,5-trimethybenzene as internal standard.



DOI: 10.1021/acs.organomet.8b00834
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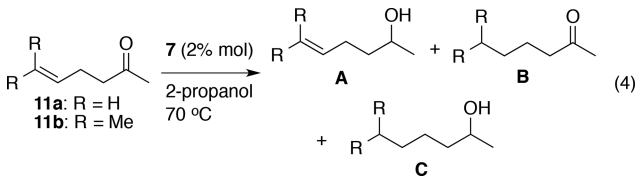
used under the same reaction conditions (entries 5 and 8). The catalytic behavior of **7** and **10** in the absence of base can be explained by the ability of the complexes to form metal hydrides, which are known to be intermediates in the transfer hydrogenation of carbonyl compounds.[13] In this context, when **7** and **10** were heated in 2-propanol at 70 °C, formation of the corresponding metal hydrides was observed by $^1$H NMR (−14.61 and −16.22 ppm, respectively, Figures S69 and S70). Interestingly, using metal hydride **8** in the absence of base, acetophenone was hydrogenated in good yield (83%, entry 9). Complex **10**, although lacking the imidazole substituent on the triazenide ligand showed catalytic activity, probably due to the deprotonated triazene nitrogen, which may act as a Lewis base accepting one proton, thus forming a Noyori's type of hydride complex. Therefore, catalysis may well operate by a ligand-assisted outersphere mechanism analogous to that reported by Noyori for transfer hydrogenation.[13] The base alone mediated the transfer hydrogenation of acetophenone, albeit with lower conversion (entry 10).

Further catalytic studies with 5-alken-2-ones (**11a,b**), as substrates, showed that complexes **6**, **7**, and **10** are selective precatalysts in the hydrogenation of either the double bond or the carbonyl group (eq 4.)




The results summarized in Table 2 show that the selectivity of transfer hydrogenation is sensitive to the presence of base

**Table 2. Transfer Hydrogenation of 5-Hexen-2-one (11a) and 6-Methyl-5-hepten-2-one (11b)[a]**

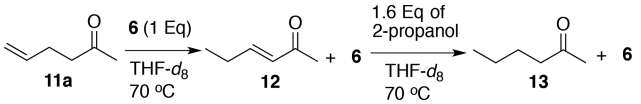
| entry | substrate | preCat/KOH | time (h) | yield (%)[b] | ratio A/B/C |
|---|---|---|---|---|---|
| 1 | **11a** | **6**/KOH | 33 | 33 | 33/0[c] |
| 2 | **11a** | **6**/- | 1 | 100 | 0/97/3 |
| 3 | **11a** | **7**/KOH | 33 | 99 | 58/41[c] |
| 4 | **11a** | **7**/- | 3 | 96 | 0/96/0 |
| 5 | **11a** | **10**/KOH | 22 | 50 | 46/0[c] |
| 6 | **11a** | **10**/- | 3 | 76 | 0/76/0 |
| 7 | **11a** | -/KOH | 68 | 10[d] | 10/0/0 |
| 8 | **11b** | **6**/KOH | 38 | 88 | 70/5/13 |
| 9 | **11b** | **6**/- | 6 | 95 | 2/73/20 |
| 10 | **11b** | **7**/KOH | 38 | 96 | 83/3/10 |
| 11 | **11b** | **7**/- | 6 | 100 | 0/95/5 |
| 12 | **11b** | **10**/KOH | 22 | 13 | 11/2/0 |
| 13 | **11b** | **10**/- | 6 | 42 | 0/40/0 |
| 14 | **11b** | -/KOH | 68 | 0[d] | |

[a]Reaction conditions: 2-propanol, 70 °C. [b]Yields were determined by GC-MS. [c]Mixture of **A** and **B**. [d]Yields were determined by $^1$H NMR using 1,3,5-trimethybenzene as internal standard.

(KOH). In the absence of KOH, the double bond in **11a-b** is selectively hydrogenated to give **B** in higher to moderate yields (entries 2, 4, 6, 11, and 13). In contrast, if KOH is added, then the carbonyl group is hydrogenated instead (entries 8 and 10). Interestingly, the hydrogenation of **11a** in the presence of KOH by complexes **6**, **7**, or **10** is not selective and gave either a mixture of **A**/**B** or **A**/**B**/**C** (entries 1, 3, and 5). In addition, the ratio between products **A**, **B**, and **C** showed to be time dependent and could be controlled by adjusting the reaction time.

Control experiments showed that the base itself mediated the hydrogenation of the carbonyl group in substrate **11a** in low yield (entry 7). In addition, the presence of the imidazole moiety in the structure of precatalysts **6** and **7** accelerate the catalytic hydrogenation of **11a,b** to give species **B**. Moreover, species **A** was not detected in most of the experiments conducted without base, suggesting that the hydrogenation follows the order **11a,b** → **B** → **C**. For instance, when complex **6** was treated with 1 equiv of **11a** in THF-$d_8$ at 70 °C, isomerization of the double bond took place over two positions to produce 3-hexen-2-one (**12**), which gives rise to a new set of olefinic signals in the $^1$H NMR spectrum at 6.81 and 5.99 ppm (Figures S115 and S116). Under these reactions conditions, the isomerization of **11a** to **12** was slow (≈16% in 3 h). Further, when 2-propanol was added, an increase of the concentration of **12** was observed (≈55% in 1 h), which was then hydrogenated to product **13** (**B** analogue) and the full reaction sequence completed in 16.5 h (Scheme 2).

**Scheme 2. Stoichiometric Hydrogenation Reaction of 11a with Complex 6**




In summary, precatalysts **6**, **7**, and **10** have shown a dual behavior in the catalytic hydrogenation of 5-alken-2-ones, which is sensitive to the presence of base. Most importantly, the hydrogenation of **11a,b** to give **B** in the absence of base is very selective and the product of the double hydrogenation (**C**) is only detected (5−20%) after a longer reaction time (6 h).

## CONCLUSIONS

In summary, we have synthesized iridium(III) and rhodium(III) complexes **4**−**8** bearing a triazenide ligand monofunctionalized with the imidazole moiety. The coordination mode of the triazenide ligand is sensitive to the substituents of the imidazole ring. In this context, the lack of steric hindrance at the imidazole ring in complexes **4** and **5** has as a consequence its coordination to the metal ion. However, the steric hindrance imposed by the *tert*-butyl group on the imidazole ring prevents its coordination in complexes **6**−**8**. These observations were supported by the crystalline structures of **4** and **5**, as well as the NMR data of **4**−**8**. All complexes were active as precatalysts in the transfer hydrogenation of acetophenone, with **7** being the most active. In this sense, the ability of complexes to form metal hydrides was illustrated by the conversion of **7** into hydride **8**. Complexes **6** and **7** show promising use as precatalyst for selective hydrogenation of 5-alken-2-ones. The catalytic behavior of **7** depends on the presence of a base; if a base is present, then the carbonyl group will be selectively hydrogenated in the first place. However, in the absence of base the double bound is preferably hydrogenated, which was confirmed by stoichiometric studies. Additional reactivity studies and applications are in progress.



DOI: 10.1021/acs.organomet.8b00834
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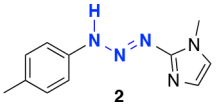
## EXPERIMENTAL SECTION

**General Procedures.** Unless otherwise specified, all manipulations were carried out in an argon-filled glovebox or using Schlenk techniques. Commercially available reagents were used as received from Aldrich Chemical Co. and Alfa Aesar. $[IrCp^*Cl_2]_2$ and $[RhCp^*Cl_2]_2$ were prepared by published procedures.[14] THF-$d_8$ and $C_6D_6$ were purchased from Cambridge Isotope Laboratories (CIL), dried over calcium hydride, and vacuum transferred prior to use. $CD_3CN$ and $CD_2Cl_2$ were used as received from CIL. NMR spectra were recorded at 400 MHz with a Bruker Avance III spectrometer at 30 °C unless otherwise specified. $^1H$ and $^{13}C$ NMR chemical shifts are reported in ppm referenced to residual solvent resonances ($^1H$ NMR: 7.24 for $CHCl_3$ in $CDCl_3$, 5.32 for $CHDCl_2$ in $CD_2Cl_2$, 7.16 for $C_6HD_5$ in $C_6D_6$, 1.94 for $CHD_2CN$ in $CD_3CN$, and 3.58 for H2 of THF-$d_7$. $^{13}C$ $\{^1H\}$ NMR: 77.23, 128.39, and 1.39 for chloroform-$d_1$, benzene-$d_6$, and acetonitrile-$d_3$, respectively). Coupling constants $J$ are given in Hertz (Hz). IR spectra were recorded on a PerkinElmer FT-IR 1605 spectrophotometer (ATR mode). Melting points were measured in an Electrothermal GAC 88629 apparatus. Mass spectra were obtained by direct insertion on an Agilent Technologies 5975C instrument. High-resolution mass spectrometry (HRMS) data were obtained in a micrOTOF-Q III MS instrument with electrospray ionization using sodium formate as calibrant. Elemental analyses were performed at NuMega Resonance Laboratories, San Diego, CA. Metal hydride **8** is air-sensitive; therefore elemental analysis could not be obtained. Although elemental analysis for **2**, **5**, and **10** are slightly off the accepted range, they are provided to illustrate the best values obtained to date. Nevertheless, a complete set of NMR and HRMS spectra has been provided in the Supporting Information, as evidence of bulk purity and identity. X-ray diffraction data for crystals of compounds **2**−**5** and **10** were collected on an Agilent Technologies Supernova AtlasS2 and a Bruker APEX II CCD diffractometers.

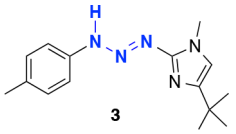
**Synthesis of 1-[(4-Methyl)phenyl]-3-[(2-methyl)imidazol-1-yl]tria-zene (2).**



**2**

1-Methylimidazole (0.5 g, 0.484 mL, 6.08 mmol) was dissolved in dry THF (10 mL) and cooled in a dry-ice−acetone bath to −78 °C; buthyllitium 2.5 M (2.43 mL) was added dropwise and stirred for 2 h. 4-azidotoluene[15] (0.8134 g, 6.1 mmol) was added and stirred at room temperature for 12 h. The reaction was quenched with water and stirred for 1 h. The product was extracted with ethyl acetate (3 × 50 mL), and the organic phase was washed with water (3 × 50 mL), dried over $MgSO_4$, and filtered. The solvent was removed under vacuum to afford an orange solid (1.180 g, yield 90%). Mp 121−123 °C. IR (ATR, $cm^{-1}$): 3140 $\nu$(N−H). $^1H$ NMR (400 MHz, $CD_3CN$): $\delta$ 12.0−10.0 (br s, 1H, N*H*), 7.26 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar*H*), 7.18 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar*H*), 6.95 (d, $^3J_{HH}$ = 1.2 Hz, 1H, Im*H*), 6.91 (d, $^3J_{HH}$ = 1.2 Hz, 1H, Im*H*), 3.69 (s, 3H, NC$H_3$), 2.31 (s, 3H, ArC$H_3$). $^{13}C$ $\{^1H\}$ NMR (100.62 MHz, $CD_3CN$): $\delta$ 151.1 (C2−Im), 141.3 (C1−Ar), 134.5 (C4−Ar), 130.9 (C3−Ar), 126.1 (C4−Im), 121.3 (C5−Im), 116.6 (C2−Ar), 32.9 (NC$H_3$), 20.9 (ArC$H_3$). $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ 11.93.0−9.55 (br s, 1H, N*H*), 7.28 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar*H*), 7.16 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar*H*), 7.01 (s, 1H, Im*H*), 6.87 (d, $^3J_{HH}$ = 1.2 Hz, 1H, Im*H*), 3.75 (s, 3H, NC$H_3$), 2.33 (s, 3H, ArC$H_3$). $^{13}C$ $\{^1H\}$ NMR (100.62 MHz, $CD_2Cl_2$): $\delta$ 150.4 (C2−Im), 139.9 (C1−Ar), 134.3 (C4−Ar), 130.4 (C3−Ar), 126.3 (C4−Im), 120.4 (C5−Im), 116.1 (C2−Ar), 32.9 (NC$H_3$), 21.1 (ArC$H_3$). EIMS (70 eV) $m/z$: $M^+$ 215 (41), 187 (28), 172 (4), 119 (85), 109 (90), 91 (100). HRMS (ESI-TOF) $m/z$: $[M + H]^+$ calcd for $C_{11}H_{14}N_5$: 216.1244. Found 216.1240. Anal. Calcd for $C_{11}H_{13}N_5$ (215.26): C, 61.38; H, 6.09; N, 32.54. Found: C, 61.33; H, 6.51; N, 33.0%.

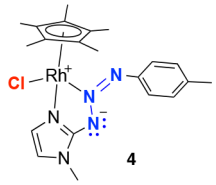
**Synthesis of 1-[(4-Methyl)phenyl]-3-[(4-*tert*-butyl-2-methyl)imi-dazol-1-yl]triazene (3).**



**3**

Compound **3** was synthesized in the same manner as **2**, using 4-*tert*-butyl-1-methylimidazole[16] (1.00 g, 7.24 mmol), buthyllitium 2.5 M (3.2 mL) and 4-azidotoluene (0.964 g, 7.24 mmol) to afford a yellow solid (1.822 g, yield 92%). Mp 126−128 °C. IR (ATR, $cm^{-1}$): 3146 $\nu$(N−H) $^1H$ NMR (400 MHz, $CDCl_2$): $\delta$ 10.33−9.17 (br s, 1H, N*H*), 7.28 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 7.18 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 6.59 (s, 1H, Im*H*), 3.74 (s, 3H, NC$H_3$), 2.34 (s, 3H, ArC$H_3$), 1.31 [s, 9H, C(C$H_3$)$_3$]. $^{13}C$ $\{^1H\}$ NMR (100.62 MHz, $CD_2Cl_2$): $\delta$ 149.5 (C4−Im), 146.8 (C2−Im), 140.0 (C1−Ar), 134.1 (C4−Ar), 130.5 (C3−Ar), 115.9 (C2−Ar), 114.1 (C5−Im), 32.7 (NC$H_3$), 32.3 [C(C$H_3$)$_3$], 30.4 [C(C$H_3$)$_3$], 21.1 (Ar−C$H_3$); EIMS (70 eV) $m/z$: $M^+$ 271 (19), 243 (8), 228 (22), 165 (44), 138 (35), 119 (26), 91 (100). HRMS (ESI-TOF) $m/z$: $[M + H]^+$ calcd for $C_{15}H_{22}N_5$: 272.1870. Found 272.1863. Anal. Calcd for $C_{15}H_{21}N_5$ (271.36): C, 66.39, H, 7.80, N, 25.81. Found: C, 66.35, H, 7.84, N, 26.0%.

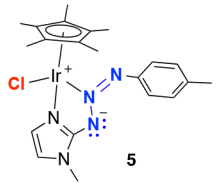
**Synthesis of Complex 4.**



**4**

In the glovebox, triazene **2** (0.125 g, 0.5806 mmol) and K[N(Si$Me_3$)$_2$] (0.116 g, 0.5815 mmol) were dissolved in dry benzene (10 mL). The yellow reaction mixture was stirred for 10 min. Addition of $[RhCl_2Cp^*]_2$ (0.18 g, 0.291 mmol) gave an orange mixture, which was stirred for 2 h at room temperature. After this time, the reaction mixture was filtrated through a plug of Celite. The filtrate was collected in a tared flask and the solvent was removed under vacuum to give **4** as an orange powder (0.27 g, 95%). $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ 7.84 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar*H*), 7.18 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar*H*), 6.80 (d, $^3J_{HH}$ = 1.8 Hz, 1H, Im*H*), 6.64 (d, $^3J_{HH}$ = 1.8 Hz, 1H, Im*H*), 3.49 (s, 3H, NC$H_3$), 2.37 (s, 3H, ArC$H_3$), 1.70 (s, 15H, Cp*). $^{13}C$ $\{^1H\}$ NMR (100.62 MHz, $CD_2Cl_2$): $\delta$ 160.6 (C2−Im), 148.7 (C1−Ar), 135.6 (C4−Ar), 129.0 (C3−Ar), 125.0 (C2−Ar), 121.9 (d, $^2J_{C-Rh}$ = 1.7 Hz, C4−Im), 118.1 (C5−Im), 95.3 (d, $^1J_{C-Rh}$ = 8.0 Hz, Cp*), 33.5 (NC$H_3$), 21.5 (ArC$H_3$), 9.1 (Cp*−C$H_3$). HRMS (ESI-TOF) $m/z$: $[M + H]^+$ calcd for $C_{21}H_{28}ClN_5Rh$ 488.1083. Found 488.1078. Anal. Calcd for $C_{21}H_{27}ClN_5Rh$ (487.83): C, 51.70; H, 5.57; N, 14.35. Found: C, 51.78; H, 5.33; N, 14.32%.

**Synthesis of Complex 5.**



**5**

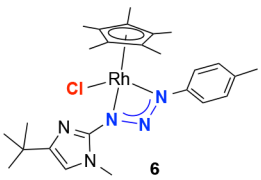
Complex **5** was synthesized in the same manner as **4**, using **2** (0.108 g, 0.5017 mmol), K[N(Si$Me_3$)$_2$] (0.100 g, 0.5013 mmol) and $[IrCl_2Cp^*]_2$ (0.200 g, 0.251 mmol) in dry benzene. After filtration, the solvent was removed under vacuum to give **5** as yellow powder (0.27 g, 93%). $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ 7.80 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar*H*), 7.18 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar*H*), 6.76 (d, $^3J_{HH}$ = 1.8 Hz, 1H, Im*H*), 6.65 (d, $^3J_{HH}$ = 1.8 Hz, 1H, Im*H*), 3.56 (s, 3H, NC$H_3$), 2.38 (s, 3H, ArC$H_3$), 1.71 (s, 15H, Cp*). $^{13}C$ $\{^1H\}$ NMR (100.62 MHz, $CD_2Cl_2$): $\delta$ 165.3 (C2−Im), 149.1 (C1−Ar), 135.9 (C4−Ar), 129 (C3−Ar), 125.4 (C2−Ar), 120.8 (C4−Im), 117.9 (C5−Im), 87.5 (Cp*), 33.7 (NC$H_3$), 21.5 (ArC$H_3$), 8.9 (Cp*−C$H_3$). HRMS (ESI-TOF) $m/z$: $[M + H]^+$ calcd for $C_{21}H_{28}ClN_5Ir$:



DOI: 10.1021/acs.organomet.8b00834
Organometallics XXXX, XXX, XXX−XXX

578.1649. Found 578.1641. Anal. Calcd for $C_{21}H_{27}ClN_5Ir$ (577.14): C, 43.70; H, 4.72; N, 12.13. Found: C, 42.48; H, 4.80; N, 11.33%.

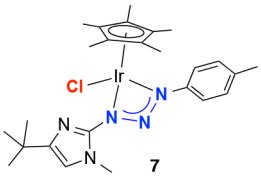
**Synthesis of Complex 6.**




6

Complex **6** was synthesized in the same manner as **4**, using **3** (0.160 g, 0.5896 mmol), $K[N(SiMe_3)_2]$ (0.118 g, 0.5915 mmol), and $[RhCl_2Cp^*]_2$ (0.185 g, 0.2931 mmol) in dry benzene. After filtration, the solvent was removed under vacuum to give **6** as an orange powder (0.30 g, 94%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.11 (d, $^3J_{HH}$ = 8.6 Hz, 2H, Ar*H*), 7.08 (d, $^3J_{HH}$ = 8.6 Hz, 2H, Ar*H*), 6.35 (s, 1H, Im*H*), 3.50 (s, 3H, $NCH_3$), 2.31 (s, 3H, $ArCH_3$), 1.85 (s, 15H, Cp*), 1.27 [s, 9H, $C(CH_3)_3$]. $^{13}$C {$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta$ 149.6 (C4−Im), 147.7 (d, $^2J_{C-Rh}$ = 2.8 Hz, C2−Im), 144.7 (d, $^2J_{C-Rh}$ = 2.1 Hz, C1−Ar), 134.1 (C4−Ar), 129.6 (C3−Ar), 117.8 (C2−Ar), 113.4 (C5−Im), 94.0 (d, $^1J_{C-Rh}$ = 8.2 Hz, Cp*), 34.3 ($NCH_3$), 31.9 [$C(CH_3)_3$], 30.2 [$C(CH_3)_3$], 21.1 ($ArCH_3$), 9.8 (Cp*−$CH_3$). HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{36}ClN_5Rh$: 544.1709. Found 544.1711. Anal. Calcd for $C_{25}H_{35}ClN_5Rh$ (543.93): C, 55.20; H, 6.48; N, 12.87. Found: C, 55.41; H, 6.61; N, 12.47%.

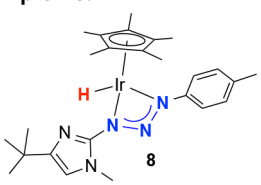
**Synthesis of Complex 7.**




7

Complex **7** was synthesized in the same manner as **4**, using **3** (0.135 g, 0.4975 mmol), $K[N(SiMe_3)_2]$ (0.100 g, 0.5013 mmol) and $[IrCl_2Cp^*]_2$ (0.200 g, 0.251 mmol) in dry benzene. After filtration the solvent was removed under vacuum to give **7** as an orange solid (0.29 g, 92%). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 7.14 (d, $^3J_{HH}$ = 8.5 Hz, 2H, Ar*H*), 7.10 (d, $^3J_{HH}$ = 8.5 Hz, 2H, Ar*H*), 6.43 (s, 1H, Im*H*), 3.58 (s, 3H, $NCH_3$), 2.33 (s, 3H, $ArCH_3$), 1.82 (s, 15H, Cp*), 1.28 [s, 9H, $C(CH_3)_3$]. $^{13}$C {$^1$H} NMR (100.62 MHz, $CD_2Cl_2$): $\delta$ 149.9 (C4−Im), 146.6 (C2−Im), 144.0 (C1−Ar), 135.1 (C4−Ar), 130.0 (C3−Ar), 117.7 (C2−Ar), 114.2 (C5−Im), 87.0 (Cp*), 34.8 ($NCH_3$), 32.3 [$C(CH_3)_3$], 30.4 [$C(CH_3)_3$], 21.2 ($ArCH_3$), 10.1 (Cp*−$CH_3$). HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{36}ClN_5Ir$: 634.2275. Found 634.2280. Anal. Calcd for $C_{25}H_{35}ClN_5Ir$ (633.25): C, 47.41; H, 5.57; N, 11.05. Found: C, 47.13; H, 5.83; N, 10.66%.

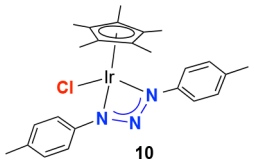
**Synthesis of Complex 8.**




8

To a solution of **7** (0.080 g, 0.126 mmol) in 2-propanol (10 mL), was added solid NaH (0.009 g, 0.375 mmol) at room temperature and stirred overnight. The solvent was evaporated under vacuum to give a dark brown residue, which was redissolved in dry benzene and filtered through a short plug of Celite. The filtrate was collected in a tared flask, and the solvent was removed under vacuum to give a solid, which was washed with hexane (3 × 5 mL) and dried *in vacuo* to give **8** as red solid (0.060 g, 80%). $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.38 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar*H*), 7.06 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar*H*), 5.96 (s, 1H, Im*H*), 3.05 (s, 3H, $NCH_3$), 2.18 (s, 3H, $ArCH_3$), 1.92 (s, 15H, Cp*), 1.52 [s, 9H, $C(CH_3)_3$], −7.73 (s, 1H, Ir*H*). $^{13}$C {$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta$ 149.0 (C4−Im), 147.7 (C2−Im), 147.1 (C1−Ar), 133.3 (C4−Ar), 129.5 (C3−Ar), 117.4 (C2−Ar), 113.3 (C5−Im), 87.3 (Cp*), 34.4 ($NCH_3$), 32.3 [$C(CH_3)_3$], 30.6 [$C(CH_3)_3$], 21.0 ($ArCH_3$), 11.0 (Cp*−$CH_3$). HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{25}H_{35}N_5Ir$: 598.2517. Found 598.2535.

**Synthesis of Complex 10.**




10

Complex **10** was synthesized in the same manner as **4**, using **9** (0.100 g, 0.4438 mmol), $K[N(SiMe_3)_2]$ (0.097 g, 0.486 mmol), and $[IrCl_2Cp^*]_2$ (0.1761 g, 0.221 mmol) in dry benzene. After filtration, the solvent was removed under vacuum to give **10** as yellow solid (0.21 g, 81%). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 7.13 (d, $^3J_{HH}$ = 8 Hz, 4H, Ar*H*), 7.10 (d, $^3J_{HH}$ = 8 Hz, 4H, Ar*H*), 2.33 (s, 6H, $ArCH_3$), 1.78 (s, 15H, Cp*). $^{13}$C {$^1$H} NMR (100.62 MHz, $CD_2Cl_2$): $\delta$ 144.2 (C1−Ar), 134.5 (C4−Ar), 129.9 (C3−Ar), 117.6 (C2−Ar), 86.7 (Cp*), 21.2 ($ArCH_3$), 10.3 (Cp*−$CH_3$). HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{24}H_{29}ClN_3IrNa$: 610.1564. Found 610.1571. Anal. Calcd for $C_{24}H_{29}ClN_3Ir$ (587.18): C, 49.09; H, 4.98; N, 7.16. Found: C, 48.56; H, 4.70; N, 6.96%.

**General Procedure for Transfer Hydrogenation Studies Monitored by $^1$H NMR.** Acetophenone (0.06 mmol), 1,3,5-trimethylbenzene (2 $\mu$L) as internal standard and 0.6 mL of 2-propanol-$d_8$ were transferred into a J. Young NMR tube, and a $^1$H NMR spectrum was recorded. Then, the precatalyst (2 mol %) and KOH (10 mol %) were added. No base was added in the case of entries 5 and 7 (Table 1). The reaction mixture was heated at 70 °C according to the time shown in Table 1. The conversions were quantified by the integration of the $^1$H NMR signals of the alcohol and acetophenone. The value of the integral for the singlet due to the aromatic protons of 1,3,5-trimethylbenzene (internal standard) was set to 10 units in each case.

**General Procedure for Transfer Hydrogenation Studies Monitored by Gas Chromatography−Mass Spectrometry (GC-MS).** 6-Methyl-5-hepten-2-one or 5-hexen-2-one (0.1 mmol), precatalyst (2 mol %), and KOH (10% mol) were stirred in 2-propanol (1 mL) in a 2 mL vial at 70 °C. No base was added in the case of entries 2, 4, 7, and 9 (Table 2). The reaction was monitored at different times by sampling aliquots of 0.05 mL diluted in 1 mL of methylene chloride.

The analytical GC/MS system used was an Agilent 7890A GC coupled to 5975C Mass detector Agilent Technologies, equipped with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 $\mu$m) Agilent Technologies, Inc. An Agilent Technologies 7693 auto sampler was used to inject 1 $\mu$L of a sample solution. The ionization energy was 70 eV with a mass range of 30 to 800 *m*/*z*. The injector temperature was set at 250 °C and the detector to 230 °C. The flow rate of the carrier gas (helium) was 1.0 mL/min injected with a gas dilution of 1:50. Identification of the individual components was done by comparison with the mass spectra library (NIST98). For the substrate 5-hexen-2-one, the initial temperature of the column was set at 60 °C, held for 2 min, and then a ramp of 10 °C/min to 250 °C. For the substrate 6-methyl-5-hepten-2-one, the initial temperature of the column was set at 70 °C, held for 2 min and then a ramp of 10 °C/min to 250 °C.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00834.

Additional experimental information, Nuclear magnetic resonance spectra for all complexes, GC-MS analysis, HRMS spectra, and crystallographic data for complexes **2**−**5** and **10** (PDF)



DOI: 10.1021/acs.organomet.8b00834
*Organometallics* XXXX, XXX, XXX−XXX

### Accession Codes

CCDC 1877017−1877021 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.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

Dedicated to the memory of Professor Pascual Royo. This research was supported by Tecnológico Nacional de México (TecNM, grant 6185.17-P) and Consejo Nacional de Ciencia y Tecnología (CONACyT, grant 162005). JPCD thanks CONACyT for graduate fellowship. We thank CONACyT for ITT NMR, HRMS, and X ray facilities (Grants INFR-2011-3-173395, INFR-2012-01-187686 and INFR-2014-224405).

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DOI: 10.1021/acs.organomet.8b00834
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