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Synthesis and Reactivity of Heteroditopic Dicarbene Rhodium(I) and Iridium(I) Complexes Bearing Chelating 1,2,3-Triazolylidene–Imidazolylidene Ligands

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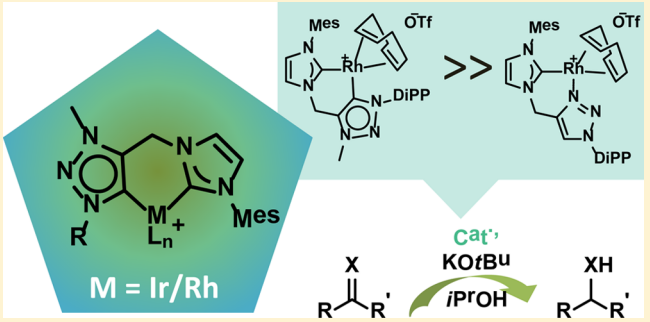
Supporting Information

ABSTRACT: 1,2,3-Triazol-5-ylidenes (tzNHC) have become a popular class of NHC ligands in homogeneous catalysis. Herein, we introduce chelate monovalent Rh- and Ir(cod) complexes bearing bidentate ligands that combine this tzNHC and an Arduengo-type NHC motif. The reactivity of these complexes with H_2 and CO gas has been investigated, leading to an interesting octahedral [Ir(tzNHC-CH_2-NHC)-$(CO)_2(H)_2$]OTf complex and [M(tzNHC-CH_2-NHC)-$(CO)_2$]OTf complexes. The carbonyl stretching frequencies of the latter indicate that the ligand has stronger electron-donating properties than classic di-NHC ligands. The square planar rhodium and iridium NHC-tzNHC complexes have been applied in transfer hydrogenation employing isopropyl alcohol as the hydrogen donor, in which they show moderate activity (Ir > Rh) toward a range of ketones as well as for an aldehyde, an imine, and a diene. The new dicarbene complexes proved to be more active for this reaction than the analogues in which the triazolyl moiety coordinates through a nitrogen donor.



Recently, there has been an increasing interest in 1,2,3-triazol-5-ylidene (tzNHC) ligands in transition metal catalysis.[1−5] Their popularity can be explained by the combination of their specific σ-donor properties, stronger than the most basic normal carbenes yet weaker than imidazol-4-ylidenes,[1,6] and synthetic accessibility and endless possibilities to vary the N1 and C4 position through "click" chemistry.[7−9] The versatility and huge potential were already predicted in the first report on this highly modular class of mesoionic carbenes published by the group of Albrecht in 2008.[6] They coordinated the triazolium salts to Pd(II) as well as Ag(I) and used the latter to transfer the carbene to Rh(I), Ir(I), and Ru(II), underlining the versatility of metal insertion.[6,7] Since then, tzNHCs have indeed proven to be useful ligands for catalytic applications. Their metal complexes have been reported as active catalysts for a wide variety of reactions: oxidation, olefin metathesis, and transfer hydrogenation reactions facilitated by ruthenium;[10−16] Ir(III)-catalyzed water oxidations;[17,18] Pd-catalyzed C−C cross-coupling reactions[19−22] and hydroarylation;[23] and carbene transfer and cyclization reactions by gold complexes.[1,5]

We previously reported zero- and divalent palladium complexes bearing classic dicarbene[25] and heterobidentate NHC triazolyl ligands[26] with various wingtip substituents (Figure 1) for the transfer semihydrogenation of alkynes. An obvious and readily accessible di-NHC alternative to these bidentate ligands is the heteroditopic NHC-tzNHC described in this paper (Figure 1). Although the majority of tzNHC complexes reported so far consist of monodentate species,[16]

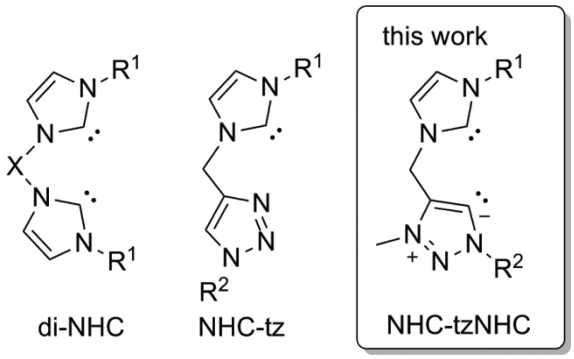


Figure 1. Bidentate NHC ligands of recent interest to our group.

several chelating dicarbene ligands incorporating tzNHCs have been reported.[18,27,28] The group of Cowie previously prepared hybrid NHC-tzNHC ligands to support bimetallic Pd/Rh complexes in a bridging fashion,[29] but similar chelate complexes with these ligands have not yet been reported to date. Herein, we report on the synthesis of a series of NHC-tzNHC ligands bearing various N3 substituents on the triazolyl moiety as well as their coordination to monovalent rhodium and iridium centers. The catalytic activity of the resulting electron-rich complexes in the transfer hydrogenation of ketones and some other unsaturated substrates is also discussed.

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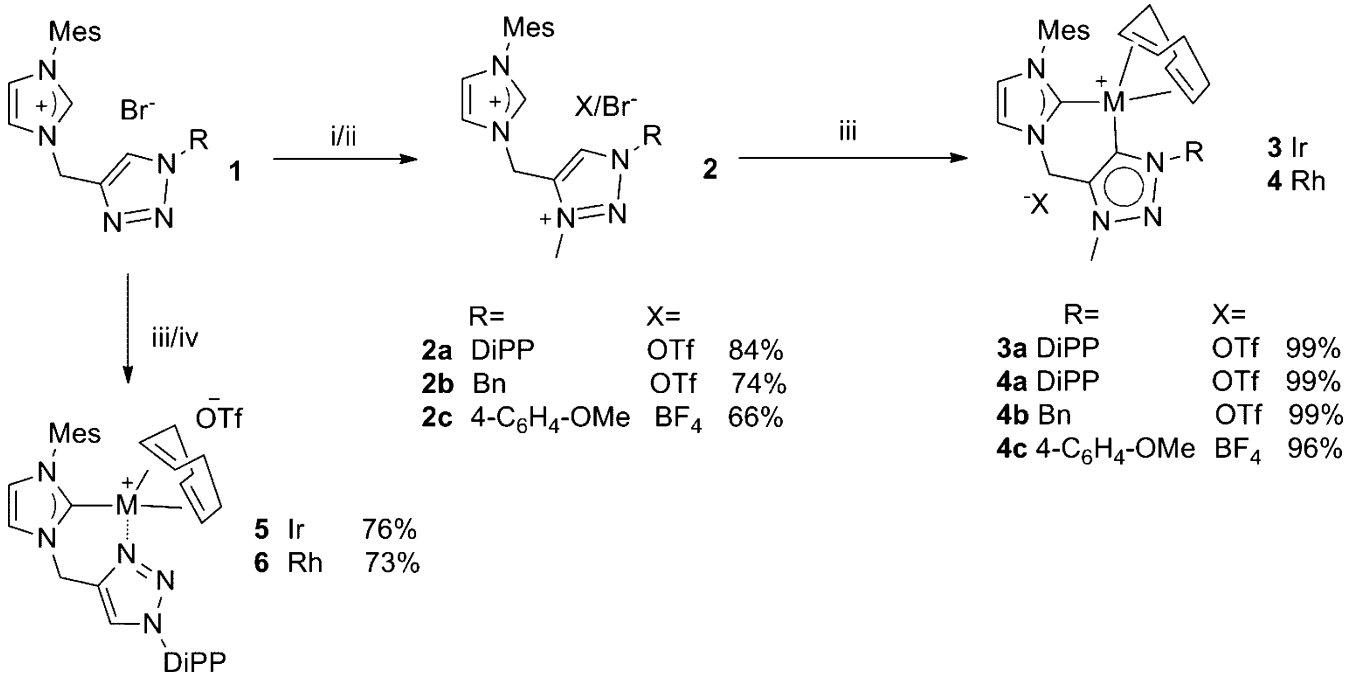
Scheme 1. Synthesis of Imidazolium−Triazolium Salts 2, [M(I)(NHC-tzNHC)(cod)] Complexes 3 and 4, and [M(I)(NHC-tz)(cod)] Complexes 5 and 6[a]



[a]Mes = 2,4,6-trimethylphenyl, DiPP = 2,6-diisopropylphenyl, (i) MeOTf, DCM, −78 °C → RT, (ii) $Me_3O{\cdot}BF_4$, DCM, (iii) 1. NaH, $[M(cod)Cl]_2$, MeOH, 2. L, 50 °C, (iv) 1. KO*t*Bu, $[M(cod)Cl]_2$ in THF, 2. AgOTF, DCM.

RESULTS AND DISCUSSION

Synthesis of Imidazole−Triazolium Salts. The syntheses of the triazolyl-functionalized imidazolium salts, **1**, have been reported by us and others; they can be conveniently prepared in high yields by the copper-catalyzed [3+2] cycloaddition of the appropriate azide to the relevant alkynes, a "click"-like reaction, in either acetonitrile[26] or a *tert*-butanol−water mixture[30] in high yields. In order to obtain a di-NHC precursor, alkylation of the N1 of the triazolyl is necessary, which can be achieved with various alkylating agents. In our hands methyl iodide proved to be ineffective,[23] whereas treatment with methyl triflate did yield the desired compound (Scheme 1) for R = Bn, DiPP.[17] Surprisingly, this procedure did not work with methoxyphenyl as substituent on the triazolyl-N3. Therefore, we turned to a synthetic procedure described by Kilpin et al. using trimethyl oxonium tertrafluoroborate (Meerwein's reagent).[24] Using this stronger alkylating agent we obtained the desired compound in 66% yield.

Heteroditopic NHC-tzNHC Rh(I) and Ir(I) Complexes. Several NHC-tzNHC Rh- and Ir(I)(cod) complexes could be obtained in excellent yields (<99%) by stirring the ligand with *in situ* prepared $[M(cod)(\mu\text{-OMe})_2]_2$ and an additional equivalent of base at 50 °C (Scheme 1). The resulting complexes were the respective monometallic chelate species, as was determined from ^{1}H NMR and high-resolution mass spectrometry (HRMS) analysis. Even without applying additional base only the chelated NHC-tzNHC species (and the remaining ligand in 1:1 ratio) were formed, and monocoordinated (imidazolylidene−triazolium or triazolylidene−imidazolium) metal complexes were not observed. This is in contrast to findings of Cowie et al.,[29] who reported monocoordination to the imidazolylidene moiety using the same ligand, an excess of KI, and $[Rh(\mu\text{-OMe})(cod)]_2$ for the synthesis of dinuclear complexes. Presumably, the addition of the excess iodide leads to coordinatively saturated mono-NHC rhodium complex in their case. However, when ligand **2c** with BF_4^- as counterion was employed, we did observe monocoordination to the imidazolylidene moiety. The desired chelate species could be isolated after addition of one extra equivalent of base in this case.

The formation of the dicarbene complexes was confirmed by the disappearance of both the imidazolium and triazolium proton from the ^{1}H NMR spectra. The bright red (Ir) and orange (Rh) dicarbenes showed broad signals for the linker and cod hydrogens in ^{1}H NMR, implying there is some flexibility in the structure. In the ^{13}C NMR two signals for the cod-CH as well as two indicative carbene signals around 182−179 ppm (NHC) and 167−166 ppm (tzNHC) were observed for all rhodium complexes. The relatively large Rh−C coupling ($^1J_{Rh\text{-}NHC}$ = 53 Hz, $^1J_{Rh\text{-}tzNHC}$ = 49 Hz for **4a**) suggests strong rhodium−carbene bonds. The iridium−carbene carbon shifts (174 and 163 ppm) also fall in the expected range.[6,31,32] The ^{19}F NMR spectra showed resonances that are indicative for noncoordinating anions for all complexes (around −78 ppm).[33] The bidentate coordination mode of the ligand was supported by the HRMS (FAB$^+$) that correspond to the entire cationic metal complex rhodium, ligand, and cod coligand in 1:1:1 ratio.

Unfortunately, the obtained complexes were not very stable. Especially the iridium complex, **3a**, showed fast decomposition, marked by a color change from bright dark red to brown. The compound could be stored under argon at −20 °C up to 1 week. The rhodium complexes could be stored under N_2 for at least a month. Therefore, all complexes were prepared immediately prior to their application in the desired catalytic reaction. This instability also prevented us from obtaining satisfactory elemental analysis data for these complexes.

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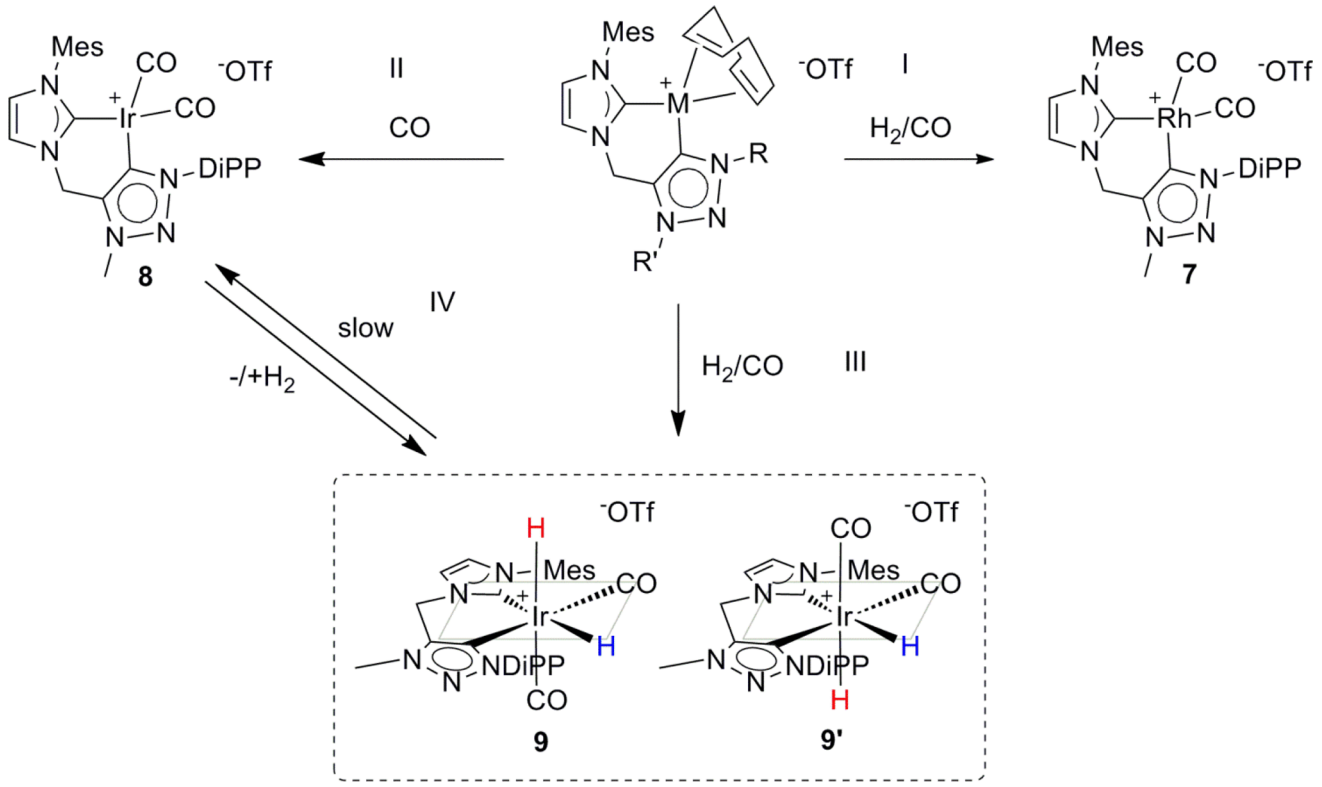
Scheme 2. Reactivity of [M(NHC-tzNHC)(cod)]OTf 3a and 4a Complexes with Carbon Monoxide and Hydrogen Gas[a]



[a]Complexes **9** and **9′** are depicted as two of the possible structures.

For comparison reasons, we were also interested in the iridium and rhodium NHC analogue in which the triazolyl moiety coordinates to the metal via the nitrogen atom (NHC-N), **5** and **6** (Scheme 1). During the course of this research the group of Messerle reported the first rhodium complexes bearing this bidentate NHC-tz ligand for the internal hydroamination.[34] The complexes could be obtained in the same manner as the NHC-tzNHC complexes, **3** and **4**, using the *in situ* prepared precursors containing methoxide as internal base or by addition of one equivalent of KO*t*Bu in the presence of the metal precursor $[M(cod)Cl]_2$ followed by halide abstraction with silver triflate according to Scheme 1.

The ^{1}H NMR spectra confirmed formation of the carbene by disappearance of the imidazolium hydrogen as expected, while the triazolyl-CH showed resonances (8.33 and 8.42 ppm) in the ^{1}H NMR that are comparable to the Pd(II) analogue.[26] The values for the triazolyl-C*H* are significantly shifted downfield compared to the Rh(I) complexes bearing a benzylic functionality reported by Messerle et al.,[34] which is probably caused by shielding of the adjacent aryl group and conjugation in the triazolyl moiety of our ligands. The methylene linker hydrogens give rise to a singlet in the ^{1}H NMR spectrum, indicating the hemilabile character of the nitrogen donor, as was observed by the group of Messerle.[34] The difference in chemical shifts, assigned to the cod-CH signals of **5** and **6**, increased significantly in both ^{1}H and ^{13}C NMR compared to NHC-tzNHC complexes due to the lower donating capacity of the secondary nitrogen donor compared to a mesoionic carbene. The characteristic ^{13}C-imidazolylidene carbon shifts were observed at 173.3 and 176.7 ppm ($^1J_{Rh-C}$ = 52 Hz) for **5** and **6**, respectively. Again, ^{19}F NMR spectroscopy indicated noncoordinating triflate, and MS proved the mononuclear character of the complexes.

Electronic Properties of [(NHC-tzNHC)M] Complexes and Their Reactivity with CO and H_2. Carbonyl stretching frequencies in the infrared provide an adequate measure of the donating strength of ligands in planar Ir/Rh$(CO)_2$ complexes. To this end, one of the rhodium complexes, **4a**, was studied in a Young NMR pressure tube under 5 bar of syngas. Upon contact with the gas, the solution immediately changed color from orange to yellow. The cyclooctadiene ligand was readily replaced by CO, rendering complex **7** (Scheme 2, I); free cod and no hydrogenated ligand (cyclooctane or cyclooctene) were observed in the ^{1}H and ^{13}C NMR spectra of the resulting species. The carbene resonances for the dicarbonyl complex appear at 173.7 ($^1J_{Rh-NHC}$ = 48 Hz) and 163.6 ppm ($^1J_{Rh-tzNHC}$ = 42 Hz) in the ^{13}C NMR, while the carbonyl ligands give rise to a broad singlet at 185 ppm. The decrease in Rh−C coupling constants suggests weakened Rh−carbene bonds caused by the strong *trans* carbonyl coligand. The low average stretching frequency of the carbonyls ($\nu(CO)_{av}$ 2034 cm^{-1}) indicates that the NHC-tzNHC ligand is indeed a very strong electron donor, compared to the "classic" di-NHCs,[35,35] ibitz,[28] and the 1,10-phenanthroline-based "vegi" ligand.[36,36]

The [Ir(NHC-tzNHC)$(CO)_2$] complex **8** could be obtained quantitatively by reacting **3a** with carbon monoxide gas (Scheme 2, II). The IR spectrum showed two strong bands at 2056 and 1992 cm^{-1} ($\nu(CO)_{av}$ 2024 cm^{-1}) corresponding to the two carbonyl stretching modes. In the ^{13}C NMR spectrum the NHC-Ir resonances were found at 171.3 and 162.0 ppm, while two separate signals for the carbonyl ligand were observed at 179.6 and 178.9 ppm. This relatively small difference between the two carbonyl ligand *trans* to the

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different NHC moieties confirms that triazolylidenes are less electron donating than other abnormal carbenes, which is probably due to the presence of three inductively electron-withdrawing nitrogen atoms in the NHC ring.[6]

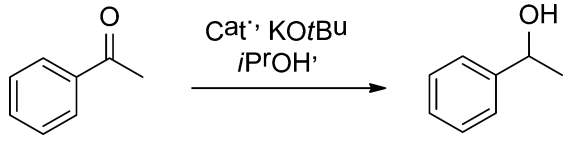
When the iridium analogue **3a** was exposed to syngas under the same reaction conditions as **4a** (Scheme 2, III), we observed three separate signals for all ligand hydrogens (and the free cod ligand), indicating a mixture of species: **8** and two octahedral $[Ir(CO)_2(H)_2(NHC\text{-}tzNHC)]OTf$ complexes, **9** and **9′**, in a 3.2:2.8:1 ratio. The difference in reactivity of the rhodium and iridium complexes with syngas can be explained by the higher basicity of the latter and its greater tendency to form coordinatively saturated octahedral d^6 complexes. The ^1H NMR spectrum showed two pairs of doublets in the hydride region (−10.33 and −12.36 ppm with $^2J_{HH}$ = 3.3 Hz and −10.40 and −11.64 ppm with $^2J_{HH}$ = 2.8 Hz). The IR spectrum showed multiple sharp bands between 2131 and 1993 cm^{-1}, the region in which carbonyl (and metal−hydride) stretching frequencies are expected. The methylene linker of **9** exhibited an AB system in the ^1H NMR, which indicates that the faces above and below the iridium−ligand plane are not equivalent. Thus, one CO and one hydride (red in Scheme 2, ^1H NMR δ −10.33 and −10.40) coligand should occupy the axial positions, while the chelate di-NHC-Ir in the plane ring is not flat but presumably boat-shaped.[37]

Complexes **9** and **9′** converted to carbonyl complex **8** by losing their hydrides slowly over time, while the cyclooctadiene was hydrogenated to give cyclooctane (Scheme 2, IV). The reductive elimination of hydrogen was monitored in time by ^1H NMR at room temperature. The reaction followed first-order kinetics ($t_{1/2}$(**9**) = 456 min and $t_{1/2}$(**9′**) = 462 min) with respect to the disappearance of **9** and **9′** (SI Figure S9). The reaction IV was reversible; when complex **8** was stirred under an atmosphere of hydrogen gas (1 bar), it was completely converted to a mixture of **9** and **9′**. Due to this reactivity, we hypothesize that complex **8** may provide interesting catalytic applications, which will be explored in the near future. Complex **8** could also be obtained directly by reacting the ligand with $[Ir(CO)_2(acac)]$ and two equivalents of potassium *tert*-butoxide.[38]

Catalytic Transfer Hydrogenation with NHC-tzNHC Rh and Ir(I) Complexes. In order to exemplify the catalytic properties of the square planar rhodium and iridium complexes, **3a** and **4a**, their application in the transfer hydrogenation of unsaturated compounds was studied using 2-propanol as hydrogen donor and solvent. It has been described that the catalytic activity in this reaction increases when using Rh(III) complexes bearing di-imidazol-4-ylidenes as catalyst compared to their C2-coordinated analogues,[39] suggesting that electron-rich metal centers are beneficial for this transformation.

Acetophenone was chosen as a benchmark substrate, conversion was followed by GC with *p*-xylene as internal standard, and KO*t*Bu was used as a base to activate the hydrogen donor. All tested complexes were active in this reaction (Table 1), and the transformation proceeded until completion within 24 h at 80 °C. For entries 1 and 2 dynamic light scattering (DLS) measurements of the catalytic mixtures before and after catalysis were performed to check for the presence of nanoparticles. As is described in reviews by Finke[40] and Crabtree,[41] DLS is a powerful method to detect small particles (>1 nm) at concentrations far below those of our catalytic experiments. In none of these measurements was light scattering observed, and therefore we believe that the catalysis

Table 1. Results of Complexes 3−7 in the Transfer Hydrogenation of Acetophenone



entry	cat.	T (°C)	time (h)	yield[d] (%)	TOF[e] (h^{-1})
1[b]	**3a**	80	3	98	641
2[b]	**4a**	80	3	71	190
			24	98	
3[b]	**4b**	80	3	48	37
			24	98	
4[b]	**4c**	80	3	83	178
			24	99	
5[b]	**5**	80	3	98	338
6[b]	**6**	80	3	11	51
			24	96	
7[b]	**7**	80	3	97	n.d.[f]
8[c]	**3a**	25	22	59	n.d.[f]
9[c]	**4a**	25	22	38	n.d.[f]
10[c]	**7**	25	22	11	n.d.[f]

[a]Reaction conditions: 0.1 M acetophenone in 2-propanol, 10 mol % KO*t*Bu at the indicated temperature. [b]0.5 mol % cat. [c]1 mol % cat. [d]Determined by GC analysis using *p*-xylene as an internal standard. [e]Determined around 15% conversion, mol_{sub}/mol_{cat}. [f]Not determined.

is performed by molecular catalysts. At room temperature the complexes still converted the substrate (entries 8−11) albeit significantly more slowly. As expected, the iridium complexes proved to convert acetophenone faster to the corresponding alcohol than their rhodium counterparts (entries 1 and 5 versus 2 and 6). Although there are several rhodium and iridium dicarbene species known that facilitate this transformation extremely efficiently, reaching TOFs up to 50 000,[42−44] the obtained results can compete with known, less active examples of other dicarbene complexes under comparable conditions.[36,39,45−47] Moreover, it is noteworthy that the dicarbene species are more active than the NHC with a secondary N donor for both the rhodium (TOF = 190 h^{-1} against 51 h^{-1}, entries 2 and 7) and iridium catalysts (TOF = 641 h^{-1} against 338 h^{-1}, entries 1 and 6). This might be explained by the higher electron density on the metal for **3a** and **4a** compared to **5** and **6**, which aids the formation of the metal−hydride, in case the monohydride mechanism would be operative similarly to what has been shown for monovalent group 9 TM catalysts.[48,49] The effects of the various substituents on the triazolyl moiety for the rhodium complexes are moderate; however catalyst **4b**, bearing a benzyl substituent on the N3 position of the triazolylidene moiety, is somewhat slower (entry 3 and SI Figure S10) for this reaction.

A small library of substrates was tested for the transfer hydrogenation with complex **3a** and **4a** (Table 2). Other aromatic ketones and cyclohexanone were readily converted by both complexes (entry 1−6), albeit faster by **3a** than by **4a**. The limits of the more active iridium catalyst were further investigated; **3a** also proved active in the transfer hydrogenation of aliphatic ketones, even converting the very hindered pinacolone slowly (entry 8). To test the tolerance of the catalyst to other functional groups, methyl levulinate and levulinic acid were tested (entries 9, 10). The former substrate, having both a ketone and ester functionality, was converted

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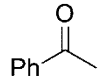
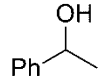
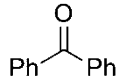
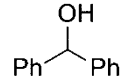
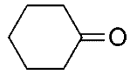
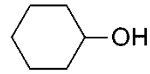
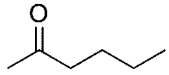
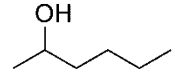
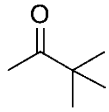
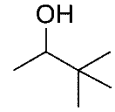
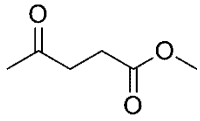
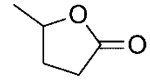
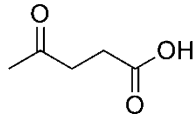
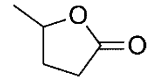
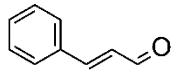
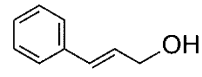
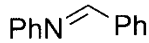
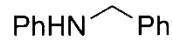
Table 2. Catalytic Results of 3a and 4a in the Transfer Hydrogenation of Various Substrates[d]

Entry	Cat	Substrate	t (h)	Conv. (%)[a]	Product	Yield (%)[a]
1	**3a**		1/2	92		92
2	**4a**		3	98		98
3	**3a**		3	90		97
			23	97		
4	**4a**		3	46		46
			23	94		94
5	**3a**		1/6	100		>99
6	**4a**		3	96		96
7	**3a**		3	66		90
			23	90		
8	**3a**		23	34		34
9	**3a**		23	74		52
10	**3a**		23	0		0
			23[b]	n.d.[c]		23
11	**3a**		3	19		11
			23	66		56
12	**3a**	Cyclooctadiene	3	100	Cyclooctene	84
					Cyclooctane	15
			23	100	Cyclooctene	48
					Cyclooctane	52
13	**3a**		3	82		82
			23	98		98

[a]Determined by GC analysis using *p*-xylene as an internal standard. [b]1 equiv of NEt_3 was added to the reaction mixture. [c]Not determined, could not be detected on GC. [d]Reaction conditions: 0.1 M substrate in 2-propanol, 1 mol % cat., 10 mol % KO*t*Bu, at 80 °C.

slowly to produce mainly γ-valerolactone. The acid functionality, on the other hand, was incompatible with the system, probably inhibiting the transfer hydrogenation by neutralizing the required base. When one equivalent of triethyl amine was added, this substrate was converted slowly as well.

The substrate scope was subsequently expanded beyond ketones. The aldehyde functionality of cinnamaldehyde was mainly converted to yield cinnamylalcohol (entry 11). Also some formation of 3-phenylpropanal, due to the hydrogenation on the alkene moiety, and the completely hydrogenated product 3-phenylpropan-1-ol was observed. The fact that complex **3a** can also be applied to reduce C═C double bonds using 2-propanol as hydrogen donor is further confirmed by the hydrogenation of cyclooctadiene, which was eventually fully hydrogenated to cyclooctane (entry 12). Last but not least, *N*-benzylideneaniline was hydrogenated readily (82% conversion in 3 h, entry 13) under the same reaction conditions.

CONCLUSION

A series of cationic chelate rhodium and iridium complexes bearing mixed tzNHC-NHC ligands are introduced. From the carbonyl stretching frequencies of the [(NHC-tzNHC)M-$(CO)_2$]OTf complexes, the electron-donating properties of the ligand were assessed to be stronger than other examples of dicarbene ligands. In the course of making the carbonyl complexes, the difference in reactivity with syngas between

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iridium and rhodium became apparent, leading to an interesting octahedral [Ir(NHC-tzNHC)$(CO)_2(H)_2$]OTf complex.

All the complexes showed moderate activity in the transfer hydrogenation of acetophenone with 2-propanol as hydrogen donor at elevated temperatures. The various substituents on the tzNHC moiety did not have a large influence on the catalysts' activity. As expected, the iridium complexes were more active than their rhodium analogues in this transformation, and the substrate scope for the iridium system could be expanded to more challenging ketones, cinnamaldehyde, *N*-benzylideneaniline, and cyclooctadiene. More interestingly, the dicarbene tzNHC-NHC complexes converted the substrate significantly faster than the ones with one NHC and a secondary nitrogen donor. This finding strengthened our trust in the potential of this electron-rich and accessible ligand in transition metal catalysis, and we are currently pursuing our studies concerning the coordination of this and similar heteroditopic ligands to other transition metals and the application of the resulting complexes in catalysis.

EXPERIMENTAL SECTION

General Remarks. All reactions were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Solvents were dried and distilled according to standard methods. 2-Propanol was dried over $CaCl_2$, distilled, and degassed prior to use. All reagents were purchased from commercial suppliers and used without further purification. The NMR spectra were recorded on 300 and 400 MHz spectrometers. Data for NMR are reported as follows: chemical shift in parts per million (δ, ppm) relative to TMS, determined by reference to residual ^{1}H and ^{13}C solvent resonances, where applicable, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), number of hydrogens, and coupling constant (Hz). ^{19}F NMR (unreferenced) was used to confirm the (noncoordinating) anion of the compounds: OTf (−78 ppm) and BF_4 (−153 ppm). High-resolution mass spectrometry was performed on a four-sector mass spectrometer (FAB$^+$) orMicrOTOF-Q (ESI$^+$), and GC analyses were performed with a GC instrument using a fused silica capillary column. The azides,[50] [(1-(prop-2-ynyl)-3-mesityl)imidazolium] bromide and the 1,2,3-triazolylmethyleneimidazolium bromide salts **1**,[26] were prepared according to literature procedures.

Synthesis of the Ligands. *[3-(2,6-Diisopropylphenyl)-1-methyl-5-((3-mesitylimidazolium)methyl)1,2,3-triazolium]-trifluoromethanesulfonate Bromide (**2a**).* To a cooled (−78 °C) solution of triazolylimidazolium bromide (125 mg, 0.3 mmol) in dichloromethane (5 mL) was added dropwise methyl triflate (120 mg, 0.73 mmol). The mixture was allowed to warm to room temperature and remained at room temperature for 16 more hours. Upon addition of ether (5 mL), a white crystalline solid precipitated from the mixture, which was collected on a glass frit and washed with ether (3 × 5 mL) to obtain the product (169 mg, 0.25 mmol, 84%). ^{1}H NMR (CD_3CN): 9.09 (s, 1H, NC*H*N), 8.74 (s, 1H, tz-*H*), 7.93 (s, 1H, CH), 7.73 (t, $^3J_{HH}$ = 5.7 Hz, 1H, D*i*PP-*H*), 7.63 (s, 1H, C*H*), 7.51 (d, $^3J_{HH}$ = 5.7 Hz, 2H, D*i*PP-*H*), 7.16 (s, 2H, Mes-C*H*), 5,95 (s, 2H, CH_2), 4.47 (s, 3H, N-CH_3), 2.39 (s, 3H, Mes-CH_3), 2.32 (m, 2H, *i*Pr-C*H*) 2.06 (s, 6H, Mes-CH_3), 1.20−1.16 (m, 12H, *i*Pr-CH_3). ^{13}CNMR (CD_3CN): 145.6 (D*i*PP-C_q), 141.6 (Mes-C_q), 138.4 (tz-C_q), 138.0 (NCN), 134.6 (Mes-CH), 133.2 (Mes-C), 133.0 (D*i*PP-C_q), 130.7 (Mes-C), 130.6 (D*i*PP-CH), 129.6 (D*i*PP-CH), 125.1 (CH), 124.9 (tz-CH), 123.9 (CH), 119.0 (OTf), 43.4 (CH_2), 39.5 (N-CH_3), 28.3 (*i*Pr-CH), 23.5 (*i*Pr-CH_3), 20.1 (Mes-CH_3), 16.6 (Mes-CH_3). MS(FAB$^+$) for $C_{29}H_{37}F_3N_5O_3S$: *m*/*z* calculated 592.2569 [M − Br]$^+$, observed 592.2564.

*[3-((1-Methylbenzene-)-1-methyl-5-(3-mesitylimidazolium)-methyl)1,2,3-triazolium]trifluoromethanesulfonate Bromide (**2b**).* To a cooled (−78 °C) solution of triazolylimidazolium bromide (374 mg, 0.85 mmol) in dichloromethane (10 mL) was added dropwise methyl triflate (350 mg, 2.13 mmol). The mixture was stirred at −78 °C for half an hour and then at room temperature for 16 more hours, during which a white solid precipitated. This precipitate was collected on a glass frit and washed with dichloromethane (3 × 5 mL) and ether (2 × 5 mL). The product was obtained as a white solid (358 mg, 0.60 mmol, 70%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.49 (s, 1H, NC*H*N), 9.09 (s, 1H, tz-*H*), 8.13 (s, 1H, C*H*), 8.04 (s, 1H, C*H*), 7.50−7.46 (m, 5H, Benz), 7.17 (s, 2H, Mes-*H*), 5.94 (s, 2H, CH_2), 5.90 (s, 2H, CH_2), 4.35 (s, 3H, N−CH_3), 2.34 (s, 3H, Mes-CH_3), 2.04 (s, 6H, Mes-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): 140.5 (Mes-C_q), 138.5 (tz-C_q), 137.2 (NCN), 134.3 (Mes-C_q), 132.7 (Benz), 131.3 (Mes-C_q), 130.9 (tz-CH), 129.4 (Mes-CH), 129.3 (tz-CH), 129.1 (Benz), 128.96 (Benz), 124.4 (CH), 123.5 (CH), 119.1 (OTf), 56.3 (CH_2), 40.9 (CH_2), 38.5 (N-CH_3), 20.6 (Mes-CH_3), 16.99 (Mes-CH_3). MS(FAB$^+$) for $C_{24}H_{27}F_3N_5O_3S$: *m*/*z* calculated 522.1787 [M − Br]$^+$, observed 522.1791.

*[3-(4-Methoxyphenyl)-1-methyl-5-((3-mesitylimidazolium)-methyl)-1,2,3-triazolium]tetrafluoroborate Bromide (**2c**).* Triazolylimidazolium bromide (290 mg, 0.64 mmol) and Meerwein's salt ($Me_3O{\cdot}BF_4$, 264 mg, 1.8 mmol) were dissolved in dry dichloromethane, and the reaction mixture was stirred for 2 days at room temperature, during which a white solid precipitated. This was collected on a glass frit and washed with dichloromethane (3 × 5 mL) and ether (1 × 5 mL) to obtain the product as a very hygroscopic white powder (234 mg, 0.42 mmol, 66%). ^{1}H NMR (DMSO-d_6, 300 MHz): 9.58 (s, 1H, NC*H*N), 9.50 (s, 1H, tz-*H*), 8.16 (s, 1H, C*H*), 8.07 (s, 1H, C*H*), 7.93 (d, $^3J_{HH}$ = 8.6 Hz, 2H, Ar-CH), 7.31 (d, $^3J_{HH}$ = 8.6 Hz, 2H, Ar-C*H*), 7.17 (s, 2H, Mes-C*H*), 6.01 (s, 2H, CH_2), 4.45 (s, 3H, N-CH_3), 3.89 (s, 3H, O-CH_3), 2.33 (s, 3H, Mes-CH_3), 2.06 (s, 6H, Mes-CH_3). ^{13}C NMR (DMSO-d_6): 161.7, 154.9, 140.5, 138.2, 137.3, 134.3 (tz/Ar-C_q), 130.9, 129.3 (Ar-*C*H), 129.2 (tz-CH), 127.6 (Ar-Cq), 124.4, 123.7 (CH), 123.1, 115.6 (Ar-CH), 56.0 (O-CH_3), 40.9 (CH_2), 38.7 (N-CH_3), 20.6 (Mes-CH_3), 17.1 (Mes-CH_3). MS(FAB$^+$) for $C_{23}H_{27}N_5OBF_4$: *m*/*z* calculated 476.2249 [M − Br]$^+$, observed 476.2243.

General Procedure for the Synthesis of [M(cod)(NHC-tzNHC)]X. NaH (2 equiv, 60 wt %) was washed three times with pentane. Subsequently, $[M(cod)Cl]_2$ (M = Ir, Rh, 0.5 equiv) in MeOH (c = 20 mM) was added, and the resulting suspension was stirred for half an hour at room temperature. After addition of the appropriate imidazole−triazolium salt (1 equiv), the mixture was stirred for 3 h at 50 °C, after which the resulting orange (rhodium) or red (iridium) solution was concentrated, redissolved in dichloromethane, and filtered over Celite. The solvent was evaporated to yield the product.

*[Ir(I)(cod)(NHC^{Mes}-tzNHC^{DiPP})]OTf (**3a**):* dark red powder (89 mg, 0.1 mmol, 99%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.87 (d, $^3J_{HH}$ = 2.0 Hz, 1H, C*H*), 7.55 (t, $^3J_{HH}$ = 7.8 Hz, 1H, D*i*PP-C*H*), 7.33 (d, $^3J_{HH}$ = 7.8 Hz, 2H, C*H*), 6.98 (s, 2H, Mes-C*H*), 6.92 (d, $^3J_{HH}$ = 2.0 Hz, 1H, C*H*), 5.66 (bs, 2H, CH_2), 4.42 (s, 3H, N-CH_3), 3.58 (s, 4H, COD-C*H*), 2.34 (s, 3H, Mes-CH_3), 2.11 (s, 6H, Mes-CH_3), 2.05−2.00 (m, *i*Pr-C*H*), 1.71−1.45 (bm, 0.8H, COD-CH_2), 1.28 (d, $^3J_{HH}$ = 6.7 Hz, 12H, DiPP-CH_3). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 174.5 (NCN), 162.5 (CCN), 145.3, 139.2, 138.0, 135.9, 135.1, 134.8 (C_q), 131.2, 128.8, 123.9 (CH−Ar), 123.3, 122.4 (CH), 119.2 (OTf), 73.4 (cod-CH), 44.6 (CH_2), 37.3 (N-CH_3), 30.9 (cod-CH_2), 29.6 (*i*Pr-CH_3), 28.6 (cod-CH_2), 25.3 (*i*Pr-CH), 22.1 (*i*Pr-CH_3), 20.6, 18.5 (Mes-CH_3). MS(FAB$^+$): calculated *m*/*z* = 742.3463 for $C_{36}H_{47}N_5Ir$ [M − OTf]$^+$, observed 742.3387.

*[Rh(I)(cod)(NHC^{Mes}-tzNHC^{DiPP})]OTf (**4a**):* bright orange powder (180 mg, 0.22 mmol, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, $^3J_{HH}$ = 1.8 Hz, 1H, C*H*), 7.53 (t, $^3J_{HH}$ = 7.8 Hz, 1H, D*i*PP-C*H*), 7.30 (d, $^3J_{HH}$ = 7.8 Hz, 2H, D*i*PP-C*H*), 6.97 (s, 2H, Mes-C*H*), 6.77 (d, $^3J_{HH}$ = 1.8 Hz, 1H, C*H*), 5.93 (bs, 2H, CH_2), 4.49 (s, 3H, N-CH_3), 3.87 (bs, 4H, cod-C*H*), 2.44−2.38 (m, 2H, *i*Pr-C*H*), 2.35 (s, 3H, Mes-CH_3), 2.12 (s, 6H, Mes-CH_3), 1.88−1.62 (bm, 8H, cod-CH_2), 1.28 (d, $^3J_{HH}$ = 6.7 Hz, 6H, *i*Pr-CH_3) 1.05 (d, $^3J_{HH}$ = 6.7 Hz, 6H, *i*Pr-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 178.7 (d, $^1J_{Rh-C}$ = 53.5 Hz, NCN), 166.1 (d, $^1J_{Rh-C}$ = 48.5 Hz, CCN), 145.4, 139.5, 139.3, 136.3, 135.5, 135.1 (tz/Artz-C_q), 131.4, 129.2, 128.8, 124.1 (Ar-CH), 123.4, 123.0 (CH), 118,9 (OTf), 86.08 (d, $^1J_{Rh-C}$ = 8.3 Hz, cod-CH), 45.2 (CH_2), 37.8 (N-CH_3), 29.8 (COD-CH_2), 28.8 (*i*Pr-CH_3), 28.5 (cod-CH_2), 25.8

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(*i*Pr-CH), 22.6 (*i*Pr-CH_3), 21.2 (Mes-CH_3), 18.8 (Mes-CH_3). MS(FAB^+): calculated m/z = 652.2886 for $C_{36}H_{47}N_5Rh$ [M − OTf]$^+$, observed 652.2885.

*[Rh(I)(cod)(NHC^{Mes}-tzNHC^{Benz})]OTf (**4b**):* orange powder (78 mg, 0.089 mmol, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (bs, 1H, C*H*), 7.48−7.28 (m, 4H, Benz-C*H*), 7.19−7.16 (m, 1H, Benz-C*H*), 6.97 (s, 2H, Mes-C*H*), 6.81 (bs, 1H, C*H*), 5.62 (bs, 2H, CH_2), 5.55 (s, 2H, CH_2), 4.89 (bs, 2H, cod-C*H*), 4.31 (s, 3H, N-CH_3), 3.66 (bs, 2H, cod-C*H*), 2.37 (s, 6H, CH_3), 2.10 (s, 3H, CH_3), 1.93−187 (m, 8H, cod-CH_2). ^{13}C NMR (101 MHz, CD_2Cl_2): 182.1 (d, $^1J_{Rh-C}$ = 42.2 Hz, NCN) 166.7 (d, $^1J_{Rh-C}$ = 48.5 Hz, CCN), 140.4, 139.5, 138.9, 135.0, 134.4 (tz/Ar-C_q), 129.0, 128.9, 128.2, 127.2 (Ar-CH) 122.4, 122.2 (CH), 119.1 (OTf), 95.9 (d, $^1J_{Rh-C}$ = 7.7 Hz, cod-CH), 78.4 (d, $^1J_{Rh-C}$ = 12.2 Hz, cod-CH), 56.5, 55.3 (CH_2), 36.9 (N-CH_3), 29.5, 28.7 (cod-CH_2), 20.6, 18.0 (Mes-CH_3). MS(FAB^+): calculated m/z = 568.1947 for $C_{30}H_{35}N_5Rh$ [M − OTf − CH_3]$^+$, observed 568.1932.

*[Rh(I)(cod)(NHC^{Mes}-tzNHC$^{4\text{-}C_6H_4\text{-}OMe}$)]$BF_4$ (**4c**):* orange powder (98.5 mg, 0.14 mmol, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (bs, 1H, C*H*), 7.58 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar-C*H*), 7.02 (d, J = 8.8 Hz, 4H, Ar-C*H* and overlap Mes-C*H*), 6.77 (s, 1H, C*H*), 5.59 (bs, 2H, CH_2), 4.39 (s, 3H, N-CH_3), 4.02−3.76 (m, 2H, cod-C*H*), 3.90 (s, 3H, O-CH_3), 3.49 (bs, 2H, cod-C*H*), 2.37 (s, 6H, CH_3), 2.35−1.79 (m, 12H, cod-CH_2 and CH_3 overlapping. ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.1 (d, $^1J_{Rh-C}$ = 53,3, NCN), 166.3 (d, $^1J_{Rh-C}$ =47,25, CCN), 161.1 (Ar-C-O), 140.1, 139.2, 136.0, 131.8, 130.4 (tz/Ar-C_q), 129.3, 125.8, 123.2, 122.5, 114.4 (Ar-CH and CH), 77.4 (d, $^1J_{Rh-C}$ = 3.5 Hz, cod-CH), 55.9 (O-CH_3), 45.4 (CH_2), 37.3 (N-CH_3), 28.2, 22.0 (cod-CH_2), 21.2, 17.7 (Mes-CH_3). MS(FAB^+) for $C_{31}H_{47}N_5ORh$: m/z calculated 598.2053 [M − BF_4]$^+$, observed 598.2054.

General Procedure for the Synthesis of [M(cod)(NHC-tz)]OTf. NaH (1 equiv, 60 wt %) was washed three times with pentane. Subsequently $[M(cod)Cl]_2$ (M = Ir, Rh, 0.5 equiv) in MeOH (c = 20 mM) was added, and the resulting suspension was stirred for half an hour at room temperature. After addition of the appropriate triazolyl-imidazolium bromide (1 equiv), the mixture was stirred for 3 h at 50 °C, after which the resulting orange (rhodium) or red (iridium) solution was concentrated, redissolved in dichloromethane, and filtered over Celite. AgOTf (1.1 equiv) was added to the solution, and the mixture was stirred in the dark for 2 h at room temperature, during which it turned to a pale brown suspension. The reaction mixture was filtered over Celite and concentrated to yield the product.

Alternative Procedure for the Synthesis of [M(cod)(NHC-tz)]OTf. The triazolyl-imidazolium bromide salt (1 equiv) and $[M(cod)Cl]_2$ (M = Ir, Rh, 0.5 equiv) were dissolved in THF. Potassium *tert*-butoxide was added, and the mixture was stirred for 3 h, after which the solution was filtered over Celite and concentrated. Subsequently a solution of AgOTf (1.1 equiv) in DCM was added, and the resulting mixture was stirred for another 2 h at room temperature in the dark, during which it turned to a pale brown suspension. The reaction mixture was filtered over Celite and concentrated to yield the product.

*[Ir(I)(cod)(NHC^{Mes}-tz^{DiPP})]OTF (**5**):* red solid (88 mg, 0.1 mmol, 76%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.42 (s, 1H, tz-C*H*), 7.70 (d, $^3J_{HH}$ = 2.0 Hz, 1H, C*H*), 7.59 (t, $^3J_{HH}$ = 7.7 Hz, 1H, DiPP-CH), 7.35 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Di*P*P-C*H*), 7.03 (s, 2H, Mes-C*H*), 6.94 (d, $^3J_{HH}$ = 2.0 Hz, 1H, C*H*), 5.75 (s, 2H, CH_2), 4.59 (bs, 2H, cod-C*H*), 3.54 (bs, 2H, cod-C*H*), 2.37 (s, 3H, Mes-CH_3), 2.07 (s, 6H, Mes-CH_3), 2.08−1.61 (m, 10H, cod-CH_2 and *i*Pr-C*H* overlapping), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 6H, Di*P*P-CH_3), 1.06 (d, $^3J_{HH}$ = 6.8 Hz, 6H, Di*P*P, CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 173.3 (NCN), 146.2, 141.2, 140.3, 135.8, 134.3 (Ar/tz-C_q), 132.4 (Di*P*P-CH), 129.6 (Mes-CH), 127.3 (tz-CH), 124.8 (Di*P*P-CH), 122.6, 123.3 (CH), 117.9 (OTf), 83.8 (cod-CH), 66.3 (cod-CH), 45.2 (CH_2), 33.7 (cod-CH_2), 30.1 (cod-CH_2), 29.4 (*i*Pr-CH), 24.9, 23.4 (Di*P*P-CH_3), 22.6, 18.6 (Mes-CH_3). MS(FAB^+) for $C_{35}H_{47}N_5Ir$: m/z calculated 728.3306 [M − OTf]$^+$, observed 728.3307.

*[Rh(I)(cod)(NHC^{Mes}-tz^{DiPP})]OTF (**6**):* bright orange solid (52 mg, 0.07 mmol, 73%). ^{1}H NMR (300 MHz, CD_2Cl_2): 8.33 (s, 1H, tz-C*H*), 7.67 (d, $^3J_{HH}$ = 1.9 Hz, 1H, C*H*), 7.58 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Di*P*P-C*H*), 7.36 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Di*P*P-C*H*), 7.08 (s, 2H, Mes-C*H*), 6.89 (d, $^3J_{HH}$ = 1.8 Hz, 1H, C*H*), 5.86 (s, 2H, CH_2), 5.01−4.75 (m, 2H, cod-C*H*), 3.91−3.61 (m, 2H, cod-C*H*), 2.40 (s, 3H, Mes-CH_3), 2.12 (s, 6H, Mes-CH_3), 2.11−1.93 (m, 8H, *i*Pr-CH and cod-CH_2 overlapping), 1.84−1.78 (m, 2H, cod-CH_2), 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 6H, *i*Pr-CH_3), 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 6H, *i*Pr-CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 176.7 (d, $^1J_{Rh-C}$ = 51.8 Hz, NCN), 146.3, 141.4, 140.2, 136.19, 135.7 (Ar/tz-C_q), 132.8, 132.3 (Di*P*P-CH), 129.7 (Mes-CH), 126.6 (tz-CH), 124.7 (Di*P*P-CH), 123.6, 123.2 (CH), 118.9 (OTf), 96.7 (d, $^1J_{Rh-C}$ = 7.8 Hz, cod-CH), 79.6 (d, $^1J_{Rh-C}$ = 12.3 Hz, cod-CH), 45.4 (CH_2), 32.7 (cod-CH_2), 29.5 (cod-CH_2), 29.3 (Di*P*P-CH), 24.8, 23.4 (Di*P*P-CH_3), 21.4, 18.5 (Mes-CH_3). MS(FAB^+) for $C_{35}H_{46}N_5Rh$: m/z calculated 638.2730 [M − OTf]$^+$, observed 638.2725.

*[Rh(I)(CO)$_2$(NHC^{Mes}-tzNHC^{DiPP})]OTf (**7**).* A pressure NMR tube containing [Rh(I)(cod)(NHC-Trzl)$^+$]OTf$^-$ **4a** (9.2 mg) in CD_2Cl_2 (0.5 mL) was pressurized with syngas (5 bar). After shaking the tube a color change from bright orange to a darker shade of orange was observed. The NMR spectra showed complete conversion to the carbonyl complex. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.03 (s, 1H, C*H*), 7.60 (t, $^3J_{HH}$ = 7.8 Hz, 1H, C*H*-Di*P*P), 7.36 (d, $^3J_{HH}$ = 7.8 Hz, 2H, C*H*-Di*P*P), 7.10 (s, 1H, C*H*), 7.02 (s, 2H, Mes-C*H*), 5.92 (s, 2H, CH_2), 5.62−5.52 (m, 4H, free cod), 4.51 (s, 3H, N-CH_3), 2.44−2.26 (m, 8H, free cod), 2.27−2.21 (m, $^3J_{HH}$ = 13.5, 6.7 Hz, 2H, *i*Pr-C*H*), 2.03 (s, 6H, Mes-CH_3), 1.27 (s, 3H, Mes-CH_3) 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 6H, *i*Pr-CH_3), 1.10 (d, $^3J_{HH}$ = 6.8 Hz, 6H, *i*Pr-CH_3). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 185.3 (bs, CO), 173.7 (d, $^1J_{Rh-C}$ = 47.5 Hz, NCN), 163.6 (d, $^1J_{Rh-C}$ = 42.4, CCN), 145.7, 141.0, 140.2, 135.9, 135.7, 134.6 (tz/Ar-C_q), 131.9, 129.2, 124.2 (Ar-CH) 124.2 (CH) 123.0 (CH), 118.9 (OTf), 44.8 (CH_2), 37.7 (N-CH_3), 28.5 (*i*Pr-CH), 24.7 (Di*P*P-CH_3), 22.4 (CH_3), 20.7 (Mes-CH_3), 17.9 (Mes-CH_3). MS(FAB^+) for $C_{30}H_{37}N_5O_2Rh$: m/z calculated 602.2002 [M − OTf]$^+$, observed 602.2038/$C_{30}H_{36}N_5O_2Rh$: m/z calculated 601.1924 [M − OTf − H]$^+$, observed 601.1929. IR ν(CO): 2064, 2005 cm^{-1}.

*[Ir(I)(CO)$_2$(NHC^{Mes}-tzNHC^{DiPP})]OTf (**8**).* A pressure NMR tube containing [Ir(I)(cod)(NHC-Trzl)$^+$]OTf$^-$ (**3a**) (40 mg) in CD_2Cl_2 (0.5 mL) was pressurized with carbon monoxide gas (5 bar). After shaking the tube the color changed from red to bright yellow. The NMR spectra showed complete conversion to the carbonyl complex. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.08 (d, $^3J_{HH}$ = 1.9 Hz, 1H, C*H*), 7.68−7.52 (t, $^3J_{HH}$ = 7.9 Hz, 1H, Di*P*P-C*H*), 7.37 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Di*P*P-C*H*), 7.13 (d, $^3J_{HH}$ = 2.0 Hz, 1H, C*H*), 7.02 (s, 2H, Mes-C*H*), 6.00 (s, 2H, CH_2), 5.62−5.52 (m, 4H, free cod), 4.53 (s, 3H, N-CH_3), 2.44−2.26 (m, 8H, free cod), 2.23 (p, $^3J_{HH}$ = 6.8 Hz, 2H, *i*Pr-C*H*) 2.13 (s, 3H, Mes-CH_3), 2.03 (s, 6H, Mes-CH_3), 1.35−1.21 (m, 18H, Di*P*P-CH_3), 1.10 (d, $^3J_{HH}$ = 6.9 Hz, 6H, Di*P*P-CH_3). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 179.6, 178.9 (CO), 171.3 (NCN), 162.0 (CCN), 146.6, 141.9, 141.1, 136.7, 135.9, 134.6 (tz/Ar-C_q),132.8, 129.9, 127.7 (Ar-CH), 125.2 (CH), 125.0 (Ar-CH), 124.9 (CH), 124.0 (OTf), 45.6 (CH_2), 38.5 (N-CH_3), 29.2 (*i*Pr-CH), 25.4 (Di*P*P-CH_3), 23.1 (Di*P*P-CH_3), 21.4 (Mes-CH_3), 18.7 (Mes-CH_3). MS(ESI^+) for $C_{30}H_{35}N_5O_2Ir$: m/z calculated 690.2416 [M − OTf]$^+$, observed 690.2401. IR ν(CO): 2056, 1992 cm^{-1}.

*Alternative Synthesis for [Ir(I)(CO)$_2$(NHC^{Mes}-tzNHC^{DiPP})]OTf (**8**).* Potassium *tert*-butoxide was added to a solution of Ir(CO)$_2$(acac) (35 mg, 0.1 mmol) and **2a** (671 mg, 0.1 mmol) in THF (5 mL), and the resulting brown solution was stirred for 2 h at 50 °C. After the solution was allowed to cool to room temperature, the mixture was filtered over Celite. Then the solution was concentrated to 2 mL, and Et_2O (10 mL) was added to precipitate the remaining ligand. The solution was decanted and concentrated under vacuum to yield the product (50 mg, 0.06 mmol, 60%).

*[Ir(I)(CO)$_2$(H)$_2$(NHC^{Mes}-tzNHC^{DiPP})]OTf (**9** and **9′**).* A pressure NMR tube containing [Ir(I)(cod)(NHC-Trzl)$^+$]OTf$^-$ (**3a**) in CD_2Cl_2 (0.5 mL) was pressurized with syngas (5 bar). After shaking the tube a color change from bright red to yellow occurred. The NMR spectra showed a mixture of [Ir(I)(CO)$_2$(NHC-Trzl)$^+$]OTf$^-$ (**8**) and two different isomers of [Ir(I)(CO)$_2$(H)$_2$(NHC-Trzl)$^+$]OTf$^-$ (**9**) in a 3.2:1:2.8 ratio. Alternatively, **9** could be obtained by stirring complex **8** in CD_2Cl_2 (1 mL) in a Schlenk connected to a balloon with hydrogen gas and stirring for 10 min. Upon release of the pressure, complex **9** converts to **8** by losing H_2, which prevented us from further characterization. The mixture of products prevented us from assigning

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all ^{13}C resonances, and the peaks for CO were not observed. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.03 (d, $^{3}J_{HH}$ = 2.0 Hz, 1H, C*H*), 8.01 (d, $^{3}J_{HH}$ = 1.9 Hz, 1H, C*H*′), 7.65−7.49 (m, 2H, D*i*PP-C*H* and D*i*PP-C*H*′), 7.34−7.28 (m, 4H, D*i*PP-C*H* and D*i*PP-C*H*′), 7.12 (d, $^{3}J_{HH}$ = 2.0 Hz, 1H, C*H*), 7.09 (d, $^{3}J_{HH}$ = 2.0 Hz, 1H, C*H*′), 7.00 (s, 2H, Mes-C*H*), 6.97 (s, 2H, Mes-C*H*′), 6.33 (d, $^{2}J_{HH}$ = 16.8 Hz, 1H, C*H*′$_2$), 6.20 (d, $^{2}J_{HH}$ = 16.8 Hz, 1H, C*H*$_2$), 5.62 (d, $^{2}J_{HH}$ = 16.9 Hz, 1H, C*H*$_2$), 5.57−5.52 (m, 9H, C*H*′$_2$ and free cod-C*H*), 4.51 (s, 3H, N-C*H*$_3$), 4.49 (s, 3H, N-C*H*′$_3$), 2.38−2.33 (m, 16H, free cod), 2.30 (s, 3H), 2.27−2.16 (m, 2H, *i*Pr-C*H*), 2.02 (s, 6H, Mes-C*H*$_3$), 1.97 (s, 6H, Mes-C*H*′$_3$), 1.85 (s, 3H, Mes-C*H*$_3$)), 1.78 (s, 1H, Mes-C*H*′$_3$), 1.30−0.96 (m, 12H, *i*Pr-C*H*$_3$ and *i*Pr-C*H*′$_3$), −10.35 (d, $^{2}J_{HH}$ = 3.3 Hz, 1H, Ir-*H*), −10.41 (d, $^{2}J_{HH}$ = 2.9 Hz, 1H, Ir-*H*′), −11.66 (d, $^{2}J_{HH}$ = 2.9 Hz, 1H, Ir-*H*′), −12.37 (d, $^{2}J_{HH}$ = 3.2 Hz, 1H, Ir-*H*). ^{13}C NMR (126 MHz, CD_2Cl_2): 165.9, 165.2 (NCN), 156.5, 155.2 (CCN), 146.2, 146.1, 141.1, 141.1, 140.2, 136.4, 136.3, 136.0, 134.9, 134.8, 132.1, 132.0, 130.2, 129.8, 129.6, 125.4, 125.3, 124.9, 124.7, 123.5, 123.4, 123.2, 46.2, 46.1, 38.5, 38.3, 29.5, 29.3, 27.2, 25.7, 25.6, 22.1, 21.4, 18.2, 18.1.

General Procedure for Catalytic Transfer Hydrogenation. To a carousel vial or Schlenk equipped with a magnetic stirrer, 0.5 or 1 mol % of catalyst, and 10 mol % of KO*t*Bu were added a degassed stock solution (c = 0.1 M) of the appropriate substrate and *p*-xylene as internal standard in 2-propanol. The mixture was stirred at 80 °C. Aliquots were taken from the mixture during the reaction, subsequently filtered over a plug of silica, and analyzed by GC.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13} C NMR spectra of **3a** and **4a**. Structures of **9**, **9**′, and **10**. ^{1}H NMR spectrum of a mixture of **8** and **9** and distribution of the species over time after the removal of pressure. Graphs of conversion versus time for transfer hydrogenation of acetophenone catalyzed by **3a**, **4a**−**c**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(37) Dihydrogen is oxidatively added in a *cis* fashion as expected. The remaining equatorial carbonyl and hydride (blue in Scheme 2, ^{1}H NMR: δ −11.6 and −12.3 ppm) ligands can in theory be selectively bonded *trans* to one of the carbene donors, as depicted in Scheme 2. Alternatively, two species can be present: one in which the hydride is bonded *trans* to the NHC and one in which it is bonded *trans* to the tzNHC (see SI Figure S5, Option B with alternative complex **10**). In an attempt to elucidate the precise structure, we employed 2D $^{1}H-^{13}C$ heteronuclear multiple-bond correlation (HMBC) NMR experiments under syngas pressure (SI Figure S7). The hydride of the minor complex **9**′ showed coupling (2 Hz < $^{2}J_{CH}$ < 12 Hz) with the imidazolylidene Cq only, indicating that this hydride is coordinated *trans* to the NHC moiety. Unfortunately, the results for the major complex **9** were inconclusive, as in the measured ranges of coupling constants cross-peaks for both the imidazolylidene and triazolylidene

carbene were observed. Further characterization was hampered by the fact that, upon release of hydrogen pressure, the mixture converts to solely complex **8**.
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