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Cyclic Bent Allene Hydrido-Carbonyl Complexes of Ruthenium: Highly Active Catalysts for Hydrogenation of Olefins

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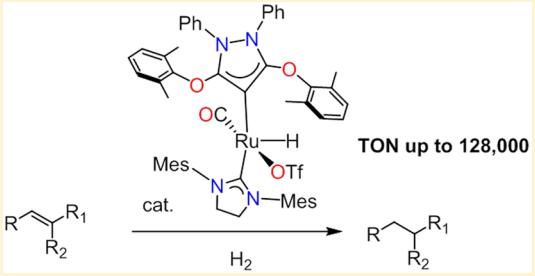
Supporting Information

ABSTRACT: A new family of ruthenium complexes bearing the carbodicarbene-type ligand "cyclic bent allene" (CBA) have been synthesized from the common precursor $RuHCl(CO)(PPh_3)_3$. Complexes were evaluated for catalytic activity in the room-temperature hydrogenation of unactivated olefins and were found to be significantly more active than known ruthenium hydrido-carbonyl phosphine or NHC complexes. In particular, $RuH(OSO_2CF_3)(CO)(SIMes)(CBA)$ was found to be among the most active hydrogenation catalysts, achieving comparable activity to Crabtree's catalyst in the hydrogenation of unactivated trisubstituted olefins and superior activity in the hydrogenation of styrene derivatives in side-by-side catalytic runs. $RuH(OSO_2CF_3)(CO)(SIMes)(CBA)$ was also found to be highly active in olefin selective hydrogenation in the presence of a variety of unsaturated functional groups, and can achieve exceptional diastereoselectivity in functional-group-directed hydrogenations at very low catalyst loadings.



INTRODUCTION

Since their discovery over two decades ago, N-heterocyclic carbenes (NHCs) have earned a prominent position in the toolbox of the organometallic chemist.[1−10] Their high σ-donating ability and steric bulk have proven functional in stabilizing low-coordinate transition metal complexes which have found numerous applications in catalysis. More recently, a number of novel divalent carbon species have been synthesized that are based on other heterocycles,[11−22] offering new avenues to alter one or both of the σ- and π-donor characteristics of the carbene.

In 2008, Bertrand and co-workers[23] reported the synthesis of stable pyrazolin-4-ylidenes that featured heteroatoms at the 3,5 positions of the ring, termed "cyclic bent allenes" (CBAs). It has been shown computationally and experimentally that the introduction of these heteroatoms delocalizes the ring π-electrons exocyclically,[24−26] rendering the central carbon atom of the CBA both strongly σ- and π-basic. CBAs are electronically related to carbodicarbenes and are part of a growing family of nominally carbon(0) compounds (Figure 1).[27−54] The isolation of a Rh-bis(carbonyl)complex bearing this ligand has revealed their significantly greater donating power relative to NHCs.[23] Additionally, CBAs can be isolated in high yields on a large scale and are thermally stable in pure form up to 95 °C under inert atmosphere.[23] Despite these attractive properties, only a small number of CBA metal complexes have been described,[23,55,56] and no examples of catalysis with such systems have been reported. Catalysis employing carbodicarbene ligands also remains very rare.[57,58]

Since the beginnings of organometallic chemistry in the 1960s, homogeneous catalytic olefin hydrogenations have been largely the domain of rhodium- and iridium-based systems,[59]

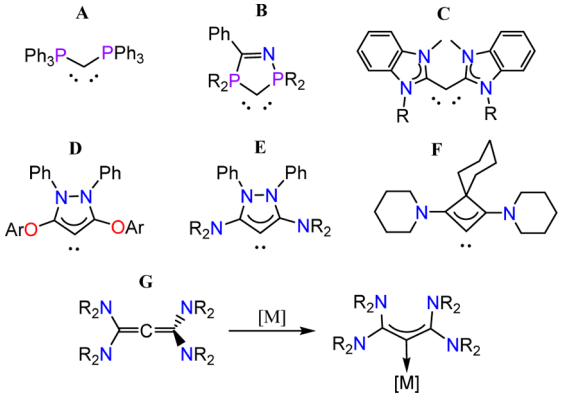


Figure 1. Members of the carbon(0) family: (**A**, **B**) carbodiphosphoranes, (**C**) carbodicarbene, (**D**−**F**) cyclic bent allenes, and (**G**) tetraaminoallene.

two of the most expensive transition metals. Significantly cheaper ruthenium is known as an olefin hydrogenation catalyst, although highly active catalysis is usually restricted to terminal olefins,[60,61] or systems where a directing group is present.[62−65] It has long been known that the complex $Ru(PCy_3)_2(CO)HCl$ will catalyze the hydrogenation of unactivated olefins;[66−71] Nolan and Fogg and co-workers[72] have synthesized mixed NHC-phosphine variants of the type $Ru(NHC)(PR_3)(CO)HCl$, and found that the use of labile phosphines in combination with strongly donating NHCs had a positive effect on rates of catalysis at elevated temperatures.

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Berke and co-workers and others[73,74] have also demonstrated that abstracting or substituting halide for a weakly coordinating anion in related rhenium catalysts can also increase the rates of hydrogenation. On the basis of this precedent, we reasoned that the even more strongly electron-donating nature of CBAs, coupled with their ability to act as four-electron donors, should impart greater stability to a coordinatively unsaturated cationic active species (Figure 2). Herein, we describe the synthesis of a

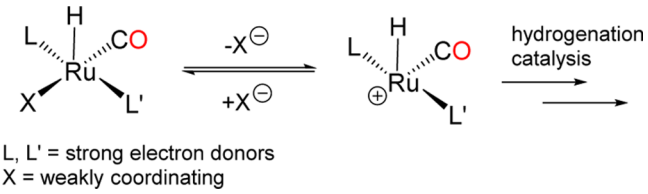


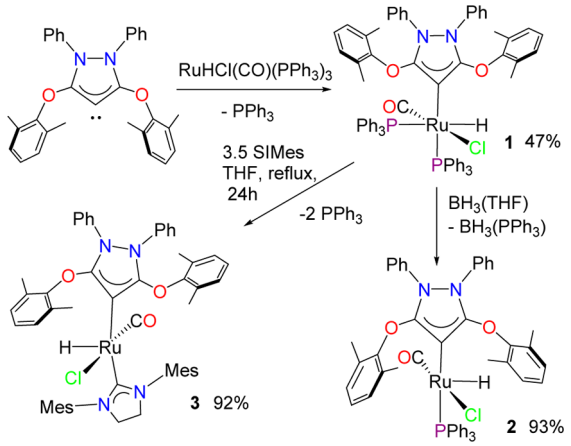
Figure 2. Catalyst pre-equilibrium.

family of hydrido-carbonyl ruthenium complexes featuring CBAs and demonstrate their superior activity in hydrogenation catalysis of both functionalized and unfunctionalized olefins, as well as their utility in diastereoselective reductions.

RESULTS AND DISCUSSION

The CBA ligand and $RuHCl(CO)(PPh_3)_3$ slowly react in toluene over the course of 16 h. Upon concentration of the reaction mixture, single crystals of beige $RuHCl(CO)(CBA)(PPh_3)_2$ **1** precipitated from solution and were isolated in 47% yield (Scheme 1). The molecular structure of **1** reveals a

Scheme 1. Synthesis of Ru−CBA Complexes



distorted octahedral geometry where the CBA and hydride are mutually cis and both mutually trans to a PPh_3 ligand (Figure 3). Steric crowding forces both of the pendant aryloxy groups on the CBA to bend away from the metal center, as has been previously observed by both our group[56] and Bertrand and co-workers.[55]

The Ru−P bond length trans to the hydride, 2.475(1) Å, is notably elongated compared to the other bond trans to the CBA, 2.361(1) Å, likely due to steric congestion. Upon dissolution of complex **1** in CD_2Cl_2, dissociation of PPh_3 trans to hydride is observed, and two signals are observed in the $^{31}P\{^1H\}$MR spectrum, one at 44.6 ppm and the other corresponding to free PPh_3. The ^1H NMR spectrum displays a doublet in the hydride region at −24.22 ppm with a $^2J_{H-P}$

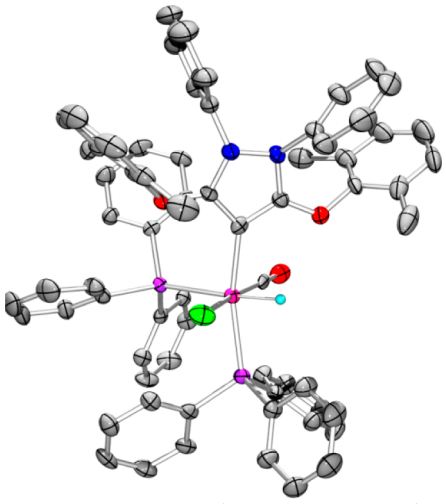


Figure 3. Molecular structure of **1** (50% thermal ellipsoids: Ru, pink; Cl, green; P, purple; O, red; N, blue; and H, turquoise). All hydrogen atoms except hydride are omitted for clarity. Select bond lengths and angles: Ru−C_{CBA} = 2.122(4) Å, Ru−C_{CO} = 1.911(6) Å, Ru−P_{transH} = 2.475(1) Å, Ru−$P_{transCBA}$ = 2.361(1) Å, P−Ru−P = 100.43(4)°, $P_{transCBA}$−Ru−H = 83.5(17)°, Cl−Ru−H = 80.4(17)°, C_{CBA}−Ru−P_{transH} = 96.57(10)°, P_{transH}−Ru−H = 175.8(17)°.

coupling constant of 26.3 Hz, indicating the cis configuration of the hydride and PPh_3.

Subsequent treatment of **1** with 1 equiv of $BH_3(THF)$ sequesters phosphine and allows the isolation of $RuHCl(CO)(CBA)(PPh_3)$ **2** as a bright yellow solid. Formulation of **2** was confirmed by a single-crystal X-ray diffraction study (Figure 4). While the pendant xylyl groups are now canted toward the metal, the Ru−C_{CBA} distance, 2.122(4) Å in **1** and 2.128(2) Å in **2**, remains relatively unchanged. There is no evidence for interaction of the pendant xylyl groups with the open coordination site on ruthenium. Interestingly, ^1H NMR signals

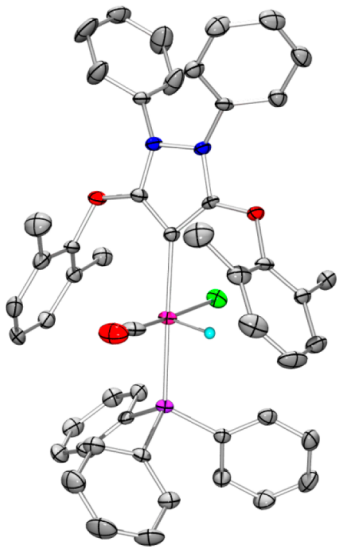


Figure 4. Molecular structure of **2** (50% thermal ellipsoids: Ru, pink; Cl, green; P, purple; O, red; N, blue; and H, turquoise). All hydrogen atoms except hydride are omitted for clarity. Select bond lengths and angles: Ru−C_{CBA} = 2.128(2) Å, Ru−C_{CO} = 1.838(2) Å, Ru−P = 2.3398(10) Å, C_{CO}−O = 1.096(3) Å, C_{CBA}−Ru−P = 175.10(6)°, C_{CO}−Ru−P = 94.28(9)°, C_{CBA}−Ru−Cl = 85.70(7)°.

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attributable to the CBA ligand are significantly broadened at room temperature (Figure 5), implying fluctionality. Upon

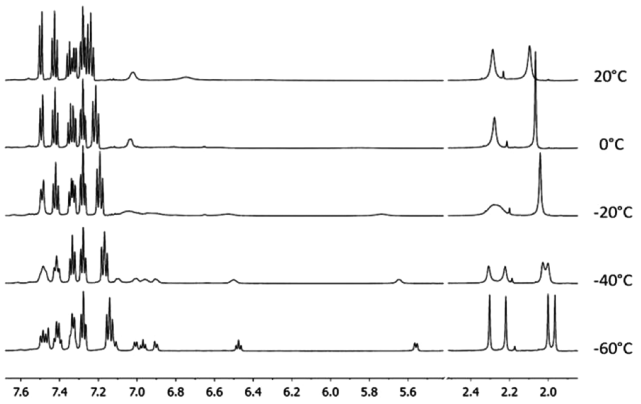


Figure 5. Variable-temperature ^{1}H NMR in CD_2Cl_2 spectra of **2**.

cooling to −60 °C, signals in the methyl region coalesce into four singlets, each integrating equivalently and corresponding to three protons each. The upfield aryl signals observed are consistent with close contact of a xylyl arm with a phenyl group on PPh_3, which is observed in the molecular structure. The IR spectrum of **2** displays a CO stretching frequency at 1892 cm^{-1}, significantly lower than that observed for the related NHC complex RuHCl(CO)(SIMes)(PPh_3) at 1911 cm^{-1}.[72]

Substitution of the phosphine ligand for the stronger donor SIMes can be achieved by refluxing complex **1** with an excess of the NHC in tetrahydrofuran (THF) for 24 h (Scheme 1). The isolated yellow-orange RuHCl(CO)(CBA)(SIMes) **3** displays similar broad resonances for the CBA arms as observed for **2**. A molecular structure confirmed a similar geometry to complex **2** where SIMes is trans to the CBA (Figure 6). Interestingly, the

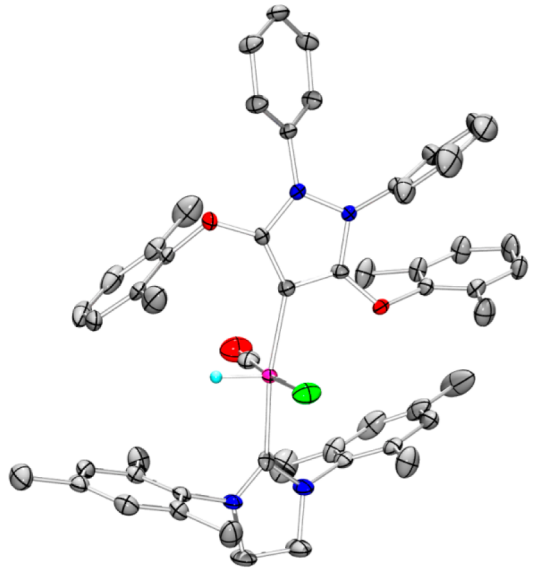
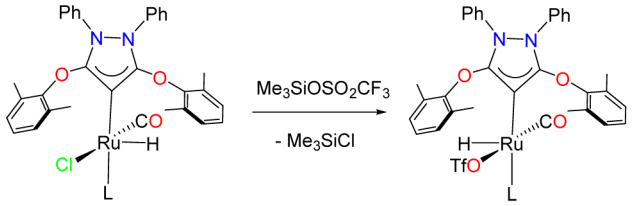


Figure 6. Molecular structure of **3** (50% thermal ellipsoids: Ru, pink; Cl, green; P, purple; O, red; N, blue; and H, turquoise). All hydrogen atoms except hydride are omitted for clarity. Select bond lengths and angles: Ru−C_{CBA} = 2.134(3) Å, Ru−C_{SIMes} = 2.053(4) Å, Ru−C_{CO} = 1.828(4) Å, C_{CO}−O = 1.095(5) Å, C_{CBA}−Ru−C_{SIMes} = 170.8(1)°, C_{CBA}−Ru−C_{CO} = 89.6(2)°, C_{CO}−Ru−Cl = 175.1(1)°, C_{SIMes}−Ru−C_{CO} = 93.7(2)°.

steric environment of the metal center causes one of the xylyl arms of the CBA to bend away from the metal center while the other is bent toward. This "semi-open" conformation of the CBA has not been previously observed. The Ru−C_{SIMes} bond length, 2.134(3) Å, is elongated compared to distances reported for Ru(Ph)Cl(CO)(PCy_3)(SIMes)[75] and $RuCl_2$(CO)(PCy_3)-(SIMes),[76] consistent with the greater donating power of the CBA. The IR spectrum displays a CO stretch at 1881 cm^{-1}, among the lowest reported for complexes of this type.[72,77]

A strategy that has been successfully employed to increase catalytic activity in related hydrogenation catalysis is to replace strongly bound halide with a weakly coordinating anion.[73,74,77] To this end, equimolar combinations of either complex **2** or **3** and $Me_3SiOSO_2CF_3$ (Scheme 2) gave instantaneous reaction in

Scheme 2. Halide Abstraction by $Me_3SiOSO_2CF_3$



2: L= PPh_3
3: L= SIMes
4: L= PPh_3 96%
5: L= SIMes 87%

CH_2Cl_2 at room temperature, generating the species RuH-(OSO_2CF_3)(CO)(CBA)(L) (**4**, L= PPh_3; **5**, L= SIMes). These species were fully characterized by spectroscopic and analytical methods, and the molecular structures have been confirmed by single-crystal diffraction studies (Figure 7). Metric parameters of complexes **2** and **3** and their respective triflate salts **4** and **5** are similar, although there is a slight shortening of the Ru−C_{CBA} bond and corresponding lengthening of the Ru−L (L =

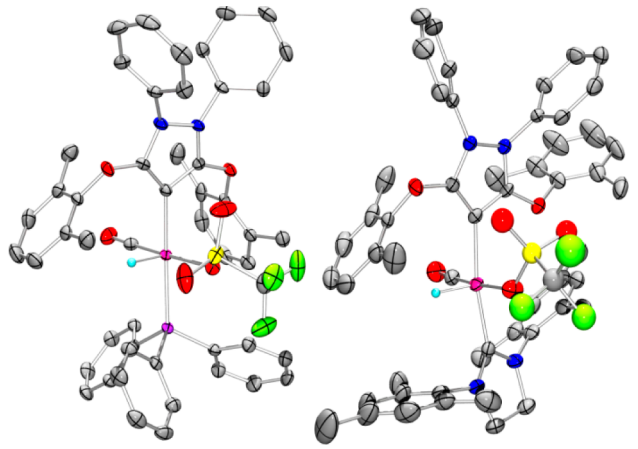


Figure 7. Molecular structures of **4** (left) and **5** (right) (50% thermal ellipsoids: Ru, pink; S, yellow; P, purple; F, yellow-green; O, red; N, blue; and H, turquoise). Disordered triflate in **5** was modeled isotropically, and one position is shown for clarity. All hydrogen atoms except hydride are omitted for clarity. Select bond lengths and angles for **4**: Ru−C_{CBA} = 2.110(3) Å, Ru−C_{CO} = 1.793(3) Å, Ru−P = 2.3539(8) Å, C_{CO}−O = 1.163(4) Å. C_{CBA}−Ru−P = 172.53(8)°, C_{CO}−Ru−P = 94.2(1)°, C_{CBA}−Ru−OTf = 87.34(9)°. For **5**: Ru−C_{CBA} = 2.120(4) Å, Ru−C_{SIMes} = 2.077(4) Å, Ru−C_{CO} = 1.791(5) Å, C_{CO}−O = 1.161(5) Å, C_{CBA}−Ru−C_{SIMes} = 170.28(16)°, C_{CBA}−Ru−C_{CO} = 91.2(2)°, C_{CO}−Ru−OTf = 175.9(2)°, C_{SIMes}−Ru−C_{CO} = 94.1(2)°.

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PPh_3, SIMes) bond distances, reflective of the more electropositive metal center.

Interestingly, in the case of **5**, extremely broad signals in ^{1}H NMR spectrum were observed for both SIMes and CBA ligands at room temperature. This significant broadening is not observed for complex **3**, suggesting that the implied dynamic nature is the result of triflate dissociation in CD_2Cl_2 solution and slow rotation about the Ru−SIMes and Ru−CBA bonds. In addition, the ^{1}H NMR data for **4** are very similar to those of **2**, suggesting that dissociation of triflate occurs in the more electron-rich environment of **5**. When a CD_2Cl_2 solution of **5** is cooled to −80 °C, 10 singlets integrating to three protons each are observed in the methyl region of the ^{1}H NMR spectrum (see Supporting Information). This is consistent with restricted rotation of both the CBA and SIMes ligands about the metal center at reduced temperature. Compounds **4** and **5** give rise to IR νCO stretching frequencies 1919 and 1886 cm^{-1}, respectively. These absorptions are slightly blue-shifted in comparison with those observed for **2** and **3**, reflecting the more electropositive nature of the Ru centers when the electron-poor OSO_2CF_3 anion is incorporated.

Catalytic Hydrogenation of Olefins. Catalytic olefin hydrogenation reactions were performed under 20 bar of H_2 pressure at 25 °C, employing 10 M olefin solutions in CH_2Cl_2, using catalysts **2**−**5** (Table 1). Hydrogenation of 1-hexene proceeded rapidly under these conditions at very low loadings of catalysts **3**, **4**, and **5**. Catalyst **5** proved to be the most active, where quantitative conversion can be achieved in 15 min at 0.01 mol % loading. At 0.005 mol % loading, **5** is capable of 92% conversion to *n*-hexane in 15 min (entry 8). Further reduction of the reaction time to only 5 min (entry 9) reveals 47% conversion and reveals an extremely high average TOF of 31.33/s.

Quantitative hydrogenation of cyclohexene also proceeded in 30 min when catalyst **5** was employed at 0.02 mol % loading (entry 18). Lowering the catalyst loading to 0.01 mol % resulted in 93% conversion to cyclohexane in 30 min (entry 20). Compounds **2**−**4** showed little to no activity under identical conditions. The contrast in the catalytic activities of **5** and **4** is attributed to the lesser lability of triflate in more electron-deficient complex **4** (vida supra).

The unactivated tertiary olefin 2-methyl-2-butene is also hydrogenated to 91% completion in 30 min and completely within 60 min at a loading of 0.1 mol % **5** (entries 25 and 26). Quantitative conversion can also be achieved at 0.05 mol % after 120 min (entry 28). However, only traces of hydrogenated product are detected when the tetrasubstituted olefin 2,3-dimethyl-2-butene is used (entry 31). In addition, several catalytic runs from Table 1 with catalysts **3**−**5** were also repeated in the presence of excess Hg;[78] in all cases, no effect on catalytic turnover was observed, excluding the possibility of heterogeneous Ru(0) acting as a catalyst.

For comparative purposes, hydrogenation catalysis was carried out under the same conditions with the known Ru-based active catalysts $Ru(PCy_3)_2(CO)HCl$ and $Ru(SIMes)(PPh_3)(CO)HCl$ (entries 10, 11, 21, and 22).[72] These catalysts exhibited significantly lower degrees of hydrogenation of 1-hexene and no activity in the hydrogenation of cyclohexene under the same conditions. In addition, Wilkinson's catalyst, $RhCl(PPh_3)_3$, performed poorly in the hydrogenation of cyclohexene at 0.05 mol % (entry 23). In contrast, Crabtree's highly active catalyst,[79] $Ir(COD)(py)(PCy_3)PF_6$, showed activity comparable to **5** under identical conditions for 1-hexene (entries 12 and 13), cyclohexene (entry 24), and 2-methyl-2-butene (entries 29 and 30).

Table 1. Room-Temperature Hydrogenation of Unfunctionalized Olefins[a]

entry	catalyst (mol %)	*T* (min)	% conv[b]	TON
	1-Hexene → Hexane			
1	**2** (0.01)	30	8 (10)[c]	800
2	**3** (0.01)	30	97 (3)	9700
3	**4** (0.01)	30	64 (35)	6400
4	**5** (0.01)	30	100	10 000
5	**5** (0.01)	15	100	10 000
6	**5** (0.01)	5	68 (29)	6800
7	**5** (0.005)	30	92 (6)	18 400
8	**5** (0.005)	15	92 (4)	18 400
9	**5** (0.005)	5	47 (18)	9400
10	[RuP] (0.01)	30	79 (2)	7900
11	[RuSI] (0.01)	30	35 (5)	3500
12	[Ir] (0.01)	30	100	10 000
13	[Ir] (0.005)	30	86 (14)	17 200
	Cyclohexene → Cyclohexane			
14	**2** (0.05)	30	0	
15	**3** (0.05)	30	11	220
16	**4** (0.05)	30	6	120
17	**5** (0.05)	30	100	2000
18	**5** (0.02)	30	100	5000
19	**5** (0.02)	15	71	3550
20	**5** (0.01)	30	93	9300
21	[RuP] (0.05)	30	0	
22	[RuSI] (0.05)	30	<1	
23	[Rh](0.05)	30	18	360
24	[Ir] (0.01)	30	96	9600
	2-Methyl-2-butene → 2-Methylbutane			
25	**5** (0.1)	30	91	910
26	**5** (0.1)	60	100	1000
27	**5** (0.05)	30	56	1120
28	**5** (0.05)	120	100	2000
29	[Ir] (0.1)	30	86	860
30	[Ir] (0.05)	30	59	1180
	2,3-Dimethyl-2-butene → 2,3-Dimethylbutane			
31[c]	**5** (0.5)	30	6	12

[a][Ir] = $Ir(COD)(py)(PCy_3)PF_6$, [RuP] = $Ru(PCy_3)_2(CO)HCl$, [RuSI] = $Ru(SIMes)(PPh_3)(CO)HCl$, [Rh] = $RhCl(PPh_3)_3$. Conditions: *x* mol % catalyst and 10 mmol olefin in 1.00 mL of CH_2Cl_2, 20 bar of H_2, 25 °C. [b]Conversion determined by ^{1}H NMR. Number in parentheses indicates isomerization to 2-hexene. [c]1.0 mmol of substrate in 1.00 mL of CH_2Cl_2 was used.

Hydrogenations were also conducted with various vinylarene derivatives (Table 2). While **5** was found to effect the hydrogenations or various substituted styrenes at very low loadings, Crabtree's catalyst was found to achieve only partial or marginal conversions under identical conditions. The early stages of hydrogenation of styrene to ethylbenzene by 0.005 mol% of catalyst **3**, **5**, and Crabtree's catalyst were examined (Figure 8). While Crabtree's catalyst has the highest initial turnover frequency at the 1 minute mark, it abruptly plateaus at this stage, indicating that catalyst deactivation is occurring. Crabtree's catalyst is outperformed by both **3** and **5** over the course of the 10 minute run with **5** achieving 98% conversion in this time. It should be noted that despite the superiority of **5** over Crabtree's at 20 bar H_2 pressure, Crabtree's catalyst does however outperform **5** at ambient pressures of H_2 in the hydrogenation of styrene at 0.05 mol% catalyst loading (See

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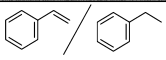
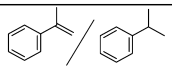
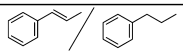
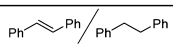
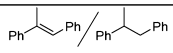
Table 2. Hydrogenation of Styrene Derivatives[a]

	Catalyst (mol%)	Substrate/ Product	T(°C) / t(hr)	Pres (bar)	%Conv (isolated)[a]
1	**5** (0.005)		25/0.5	20	97
2	[Ir] (0.005)		25/0.5	20	63
3	**5** (0.02)		25/1	20	95
4	[Ir] (0.02)		25/1	20	57
5	**5** (0.05)		25/1	20	95
6	[Ir] (0.05)		25/1	20	16
7	**5** (0.05)		80/16	50	100(88)
8	[Ir] (0.05)		80/16	50	56
9[b]	**5** (0.5)		80/16	50	98
10[b]	[Ir] (0.5)		80/16	50	29

[a]Conversion determined by ^{1}H NMR. [b]1.0 mmol of substrate in 0.10 mL of C_6H_5Cl. Conditions: [Ir] = Ir(COD)(py)(PCy_3)PF_6, *x* mol % catalyst and 3.0 mmol substrate in 0.30 mL of CH_2Cl_2 or C_6H_5Cl.

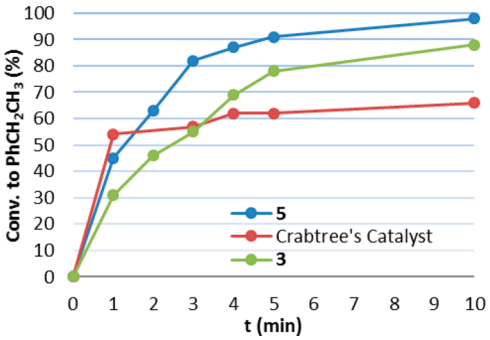


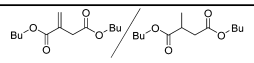
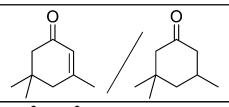
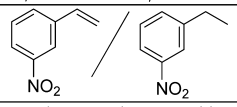
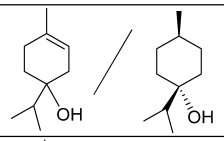
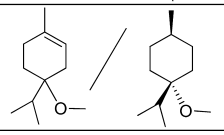
Figure 8. Hydrogenation of styrene to ethylbenzene. Conditions: 0.005 mol % catalyst with 3.0 mmol of styrene in 0.30 mL of CH_2Cl_2, 23 bar of H_2, 25 °C.

Supporting information). Nevertheless, the high degree of activity of **5** under moderate H_2 pressures allows the use of significantly lower catalyst loadings (0.005 mol%) than can be achieved with Crabtree's catalyst either at ambient or elevated pressure. Taken together, these data clearly demonstrate that catalyst **5** among the most active hydrogenation catalysts for unactivated olefins.

Catalyst **5** was also used to hydrogenate several olefins containing functional groups (Table 3). These reactions were carried out at 80 °C under 50 bar of H_2 pressure in neat substrate. Importantly, substrates were not rigorously dried but were only degassed under vacuum prior to catalysis. These catalyzes demonstrate that **5** tolerates ester, carbonyl, nitro, alcohol, and nitrile groups without difficulty. For example, isopherone is hydrogenated selectively to 3,3,5-trimethylcyclohexanone at 0.001 mol % loading (Table 3, entries 3 and 4), with no traces of ketone reduction. Similarly, 3-nitrosytrene is selectively hydrogenated to 3-ethylnitrobenzene at 0.002 mol % loading (Table 3, entries 6 and 7). A chlorobenzene solution of nitrile butadiene rubber is also selectively reduced to HNBR at 0.003 mol % loading (Table 3, entry 8).

Finally, we have explored the utility of catalyst **5** in functional group directed diastereoselective olefin reductions.[81−86] Given the implied four-coordinate nature of the active species in catalyst **5** (Figure 2), it seemed reasonable that **5** should be able to bind a directing group to deliver hydrogen to one face of an olefin. To this end, it was found that catalyst **5** was capable of

Table 3. Hydrogenation of Functionalized Olefins with 5[a]

	Substrate/Product	t(hrs)[b]	Loading (mol%)	%Conv. (isolated)[a]
1		3	0.01	100 (>99)
2		3	0.005	81
3		3	0.004	100 (87)
4		3	0.001	94
6		16	0.005	100 (>99)
7[c]		16	0.002	98
8	Nitrile Butadiene Rubber (NBR)[d]/ HNBR	20	0.003	100
9		20	0.0015	66
10[e,f]		13	0.02	100(92) de: 99
11[e,f]		13	0.01	93 de: 97
12[f]		3	0.05	95 de: 44
13[f]		3	0.02	72 de: 54

[a]Conversion was determined by ^{1}H NMR and/or GC-MS. [b]Reaction times are unoptimized. [c]Minor amounts (~1%) of insoluble polymerized product were also isolated from the reaction mixture by precipitation with MeOH. [d]A 5.0% (w/w) solution of NBR in dry C_6H_5Cl was used, and conversion was determined by the method of Marshall et al.[80] [e]Neat olefin (10 mmol) was used. [f]Identity of directed isomer was established by comparison with literature NMR spectra.[81] Conditions: 50 bar of H_2, 80 °C, 3.0 mmol of neat olefin.

the directed reduction of terpinen-4-ol with loadings as low as 0.02 mol % while achieving a de of 99% (entry 10). Methylated terpinen-4-ol could also be hydrogenationed effectively, although with more modest diastereoselectivitity (entries 12 and 13). Presumably, the weaker coordination of the sterically encumbered ether functionality limits its utility as a directing group.

■ CONCLUSIONS

In summary, we have described the synthesis and characterization of a series of [CBA]Ru complexes and demonstrated that a strongly electron-donating CBA in combination with an NHC is capable of stabilizing an isolable species with a labile OSO_2CF_3 anion. This yields a catalyst exhibiting very high activity for the hydrogenation of unactivated olefins, olefin selective hydrogenation, and functional-group-directed olefin hydrogenation. Comparative catalytic runs indicated the [CBA]Ru species is significantly more active than similar [NHC]Ru and phosphine complexes and displays activity rivaling Crabtree's catalyst in the hydrogenation of unactivated olefins, while outperforming it in styrene derivative reductions. Collectively, these data also illustrate that the exceptional donor abilities of CBA ligands provide a resource for catalyst design that has seen limited use to date. Indeed, we are continuing to explore the utility of CBA ligands in catalysis.

■ EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing a Vacuum Atmospheres glovebox or a Schlenk vacuum line. Solvents were purified with a

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Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Straus flasks equipped with Teflon-valve stopcocks. Deuterated dichloromethane was distilled under reduced pressure from CaH_2 and degassed by successive freeze–pump–thaw cycles. Deuterated benzene was distilled from purple sodium benzophenone ketyl. ^1H and ^{13}C NMR spectra were recorded at 25 °C on Bruker 400 MHz spectrometers, unless otherwise noted. Chemical shifts are reported in parts per million and are given relative to $SiMe_4$ and referenced to the residual solvent signal. Combustion analyses were performed in-house by employing a PerkinElmer CHN analyzer. IR spectra were collected on a Perkin-Elmer Spectrum One FT-IR instrument. Cyclic bent allene, $(C_6H_3Me_2O)_2C_3(NPh)_2$, was prepared according to literature procedures.[24,56] $RuHCl(CO)(PPh_3)_3$ and $Me_3SiOSO_2CF_3$ were purchased from Strem and used without subsequent purification. All commercially available substrates were purchased from Aldrich or Acros and were degassed prior to catalysis but were not dried or further purified. Nitrile butadiene rubber was provided by Lanxess. O-Methylated terpinen-4-ol was synthesized according to literature procedures[86]

Synthesis of Ru(CBA)(PPh$_3$)$_2$(CO)HCl (1). Cyclic bent allene (271 mg, 0.588 mmol) was added to a suspension of $Ru(PPh_3)_3(CO)HCl$ (504 mg, 0.529 mmol) in toluene (10 mL), and the mixture was stirred overnight (16 h). The suspension was then filtered through a plug of Celite and the solvent was removed under vacuum without stirring, causing X-ray-quality crystals of the product to precipitate in a red-brown oil. The mixture was triturated with small successive portions of diethyl ether until the supernatant became yellow in color. The crystalline beige solid obtained was further washed with pentane (2 × 5 mL) and dried under high vacuum (289 mg, 47%). No NMR data could be obtained as the complex readily dissociates triphenylphosphine in solution, forming compound **2**. IR(KBr): 1899 cm^{-1} (νCO). Anal. Calcd for $C_{50}H_{44}ClN_2O_3PRu$ (1150.67): C, 70.98; H, 5.17; N, 2.43. Found: C, 71.24; H, 5.15; N, 2.45.

Synthesis of Ru(CBA)(PPh$_3$)(CO)HCl (2). To a solution of **1** (168 mg, 0.146 mmol) in THF (5 mL) was added $[BH_3]$ (1.0 M in THF, 146 μL, 0.146 mmol). The solution was concentrated to approximately 1 mL, and pentane (15 mL) was added to precipitate the product. The bright yellow solid was collected by filtration and dried under high vacuum (121 mg, 93%). ^1H NMR (CD_2Cl_2): 7.49 (d, $^3J_{H-H}$ = 8.0 Hz, 4H, o-Ph), 7.42 (t, $^3J_{H-H}$ = 8.0 Hz, 4H, m-Ph), 7.37–7.21 (m, 17H, PPh_3 and p-Ph), 7.01 (br s, 2H, m-OAr), 6.74 (br s, 2H, m-OAr), 6.44 (br s, 2H, p-OAr), 2.28 (br s, 6H, $OArCH_3$), 2.09 (br s, 6H, $OArCH_3$), −24.21 (d, $^2J_{H-P}$ = 26.3 Hz, 1H, RuH). ^{13}C NMR (CD_2Cl_2): 201.27 (CO), 151.02, 136.92 (d, $^1J_{C-P}$ = 36.4 Hz, *ipso*-PPh_3), 134.96, 134.66 (d, $^3J_{C-P}$ = 11.3 Hz, o-PPh_3), 129.84, 129.17 (d, $^4J_{C-P}$ = 10.0 Hz, m-PPh_3), 127.67 (d, $^5J_{C-P}$ = 9.1 Hz, p-PPh_3), 126.68, 125.93, 106.38 (d, $^2J_{C-P}$ = 83.2 Hz, C_{CBA}), 17.48 (br, CH_3). ^{31}P NMR(CD_2Cl_2): 44.60 (d, $^2J_{H-P}$ = 23.5 Hz, PPh_3). IR (KBr): 1892 cm^{-1} (νCO). Anal. Calcd for $C_{50}H_{44}ClN_2O_3PRu$ (888.39): C, 67.60; H, 4.99; N, 3.15. Found: C, 67.87; H, 5.34; N, 2.93.

Synthesis of Ru(CBA)(SIMes)(CO)HCl (3). To a solution of **1** (150 mg, 0.130 mmol) in THF (5 mL) was added SIMes (140 mg, 0.457 mmol), and the solution was refluxed for 24 h. The solution was cooled to room temperature and concentrated to approximately 1 mL. Pentane (15 mL) was added to precipitate the product as a bright yellow-orange solid, which was washed with pentane (3 × 10 mL) and dried under high vacuum (111 mg, 92%). ^1H NMR (C_6D_6): 6.88 (br s, 2H, Mes), 6.86–6.77 (m, 6H), 6.75 (d, $^3J_{H-H}$ = 8.0 Hz, 4H, m-OAr), 6.65 (br s, 2H, Mes), 6.60–6.57 (m, 6H), 3.30 (m, 4H, NCH_2CH_2N), 2.73 (br s, $MesCH_3$, 6H), 2.51 (br s, $MesCH_3$, 6H), 2.15 (br s, $OArCH_3$, 12H), 2.05 (br s, $MesCH_3$, 6H), −26.04 (s, 1H, Ru–H). ^{13}C NMR (CD_2Cl_2): 221.40 (NCN), 203.37 (CO), 171.39 (NCO), 152.38, 137.71, 137.64, 137.11, 136.81, 134.91, 130.38, 129.33, 129.30, 129.18, 128.93, 128.76 (br), 127.71, 125.39, 114.08 (C_{CBA}), 51.18 (NCCN), 20.96 ($MesCH_3$), 19.20 ($MesCH_3$), 19.15 ($MesCH_3$), 16.76 (br, $XylCH_3$). IR(KBr): 1881 cm^{-1} (νCO). Anal. Calcd for $C_{53}H_{55}ClN_4O_3Ru$ (932.55): C, 68.26; H, 5.94; N, 6.01. Found: C, 68.22; H, 5.38; N, 5.83.

Synthesis of Ru(CBA)(PPh$_3$)(CO)H(OSO$_2$CF$_3$) (4). In silylated glassware, **2** (50 mg, 0.056 mmol) was dissolved in THF (2 mL) and $Me_3SiOSO_2CF_3$ (10.5 μL, 0.058 mmol) was added. Solvent was removed under high vacuum and yellow solid was washed with pentane (3 × 5 mL) and dried under high vacuum (54 mg, 96%). Small amounts (~5 mol %) of inseparable [CBAH][OTf] are also observed due to minor acid impurities in $Me_3SiOSO_2CF_3$.^1H NMR (CD_2Cl_2): 7.53 (d, $^3J_{H-H}$ = 8.0 Hz, 4H, o-Ph), 7.45–7.31 (m, 15H, o-PPh3, p-PPh_3, m-Ph, and p-Ph), 7.23 (t, $^3J_{H-H}$ = 8.0 Hz, 6H, m-PPh_3), 7.01 (br s, 2H, m-OAr), 6.78 (br s, 2H, m-OAr), 6.09 (br s, 2H, p-OAr), 2.41 (br s, 6H, $OArCH_3$), 2.14 (br s, 6H, $OArCH_3$), −23.38 (d, $^2J_{H-P}$= 23.3 Hz, 1H, RuH). ^{13}C NMR (CD_2Cl_2): 204.37 (d, $^2J_{C-P}$ = 15.3 Hz, CO), 158.77, 150.38, 135.39 (d, $^1J_{C-P}$ = 37.3 Hz, *ipso*-PPh_3), 134.19 (d, $^3J_{C-P}$ = 11.7 Hz, o-PPh_3), 133.80 (br), 130.06, 129.99, 129.80, 129.62 (d, $^5J_{C-P}$ = 1.9 Hz, p-PPh_3), 129.02, 128.17 (br), 128.11 (d, $^5J_{C-P}$ = 9.0 Hz, m-PPh_3), 103.05 (d, $^1J_{C-P}$ = 77.5 Hz, C_{CBA}), 17.25 (br, Me). ^{19}F NMR (CD_2Cl_2): −78.68 (s, OSO_2CF_3). ^{31}P NMR (CD_2Cl_2): 43.16 (d, $^2J_{H-P}$ = 23.5 Hz, PPh_3). IR(KBr): 1919 cm^{-1} (νCO). Anal. Calcd for $C_{54}H_{55}F_3ClN_4O_6PRuS$ (1002.01): C, 61.13; H, 4.43; N, 2.80. Found: C, 61.23; H, 4.84; N, 2.72.

Synthesis of Ru(CBA)(SIMes)(CO)H(OSO$_2$CF$_3$) (5). This was synthesized in an exactly analogous manner to **4** but starting with **3**. The product was obtained as an orange solid (87%). Small amounts (~5 mol %) of inseparable [CBAH][OTf] are also observed due to minor acid impurities in $Me_3SiOSO_2CF_3$.^1H NMR (CD_2Cl_2): 7.46–6.48 (br m, 20H, Ar), 3.90–3.73 (m, 4H, NCH_2CH_2N), 2.66–1.54 (br m, 24H, $ArCH_3$), 2.34 (s, 6H, $ArCH_3$), −26.56 (s, 1H, RuH). ^{13}C NMR (CD_2Cl_2): Very broad low-intensity signals are observed, and select resonances are reported: 217.96 (NCN), 205.83 (CO), 137.41 (br), 131–128.5 (br m), 127.7 (br), 125.3 (br), 109.58 (C_{CBA}), 51.31 (br, NCCN), 20.85 (br, Me), 18.34 (br, Me), 18.14 (br, Me), 16.7 (br, Me).^{19}F NMR (CD_2Cl_2): −77.91 (s, OSO_2CF_3). IR (KBr): 1886 cm^{-1} (νCO). Anal. Calcd for $C_{54}H_{55}F_3ClN_4O_6RuS$ (1046.17): C, 62.00; H, 5.30; N, 5.36. Found: C, 62.02; H, 5.48; N, 5.14.

Hydrogenation Procedure, Table 1 and Table 2 Entries 1–6. Under an inert atmosphere, *x* mmol of catalyst was weighed into a Parr vessel and dissolved in 1.00 or 0.30 mL of CH_2Cl_2. An aliquot (10 mmol or 3.0 mmol) of the appropriate substrate was then added, and the vessel was sealed and rapidly purged three times with 20 bar of H_2. The vessel was then filled to 20 bar of H_2 pressure and allowed to stir at ambient temperature. The pressure was vented after the allotted time, and the vessel was opened in air. The solution was filtered through a small plug of Celite, and conversion was determined by ^1H NMR by integration of the respective product and staring material resonances.

Hydrogenation Procedure, Table 3 and Table 2 Entries 7–10. Under an inert atmosphere, *x* mmol of catalyst was weighed into a Parr vessel and 3.0 mmol of the appropriate substrate was added. The vessel was sealed and rapidly purged three times with 40 bar of H_2, filled to 40 bar of H_2 pressure, and placed in an 80 °C oil bath with rapid stirring for a thermal equilibration period of 15 min. After this time, pressure was adjusted to 50 bar, and the reactor was allowed to stir at this temperature for the allotted time. Upon completion, the reactor was allowed to cool to room temperature over a period of 30 min, the pressure was vented, and the vessel was opened in air. The contents were analyzed by ^1H NMR and/or GC-MS.

■ ASSOCIATED CONTENT

Supporting Information

Additional text and one table with crystallographic details, NMR spectra of **2**–**5** and VT ^1H NMR of **5**, and additional catalytic data for hydrogenation of styrene to ethylbenzene (pdf); crystallographic information (txt). 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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