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A Cis-Bis-Mixed-Carbene Ruthenium Hydride Complex: An Olefin-Selective Hydrogenation Catalyst

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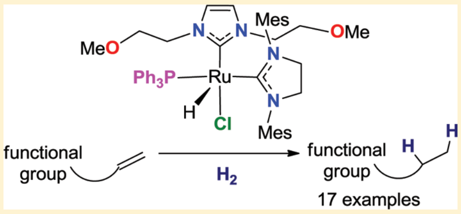
Supporting Information

ABSTRACT: The N-heterocyclic carbene $C_3H_2N_2(CH_2CH_2OMe)_2$ (**1**; IOMe) reacts with $RuHCl(PPh_3)_3$ to give $RuClH(IOMe)(PPh_3)_2$ (**2**), which reacts further with SIMes to give the cis-bis-mixed-carbene complex RuClH(IOMe)-(SIMes)(PPh_3) (**3**). This species has been shown to be a highly effective hydrogenation catalyst that tolerates the presence of a wide range of functional and donor groups.



Heterogeneous hydrogenation catalysis was discovered by Sabatier in the early portion of the 20th century.[1] In the 1960s Wilkinson and co-workers discovered the homogeneous hydrogenation catalyst precursor $(Ph_3P)_3RhCl$.[2] These two findings have been seminal to countless developments and applications. Indeed, hydrogenation catalysis is the most common transformation used in the chemical industry and is employed in the preparation of scores of commercial targets, including natural products and commodity and fine chemicals.[3] A plethora of homogeneous catalysts have emerged since Wilkinson's reports. In the 1970s, Osborn and Schrock[4−6] and subsequently Crabtree and Morris[7] reported the cationic precatalysts $[(COD)Rh(Ph_2PCH_2CH_2PPh_2)]^+$ and $[(COD)Ir(py)(PCy_3)]^+$, respectively. These species have also become commonly used precursors for homogeneous hydrogenations. While perturbations of the Rh and Ir systems for asymmetric catalysis have been widely studied and highly successful over the last 30 years,[8] use of other transition-metal complexes has also garnered attention. In particular, the recent work of Chirik and co-workers[9] has demonstrated the utility of Fe-based systems for olefin hydrogenation.

In the case of Ru, the species $RuHCl(PPh_3)_3$ was reported by Wilkinson and co-workers to be almost as active for catalytic olefin hydrogenation catalysis as $(Ph_3P)_3RhCl$;[10] however, due to its high air sensitivity, the Ru species has not found widespread use. Nonetheless, over the past two decades Ru-based hydrogenation catalysts have emerged as powerful tools for asymmetric hydrogenation of ketones and other polar functional groups.[11−18] Interestingly, it is such reactivity that has precluded Ru hydrogenation catalysts from applications where selectivity for olefinic residues is required.

In our efforts to develop Ru-based, olefin-selective hydrogenation catalysts, we were stimulated by the recent findings of the groups of Nolan and Fogg and others who showed compounds of the form RuHCl(CO)(NHC)(PPh_3) were effective catalysts for the hydrogenation of cyclooctene and cyclododecene and the isomerization of terminal olefins.[19−22] In addition, Albrecht and co-workers demonstrated the ability of chelating bis-carbene Ru complex cations to act as effective hydrogenation catalysts for styrene.[23] On the basis of this and the notion that mimicking the ligand disposition of the active species derived from Wilkinson's catalyst could lead to a general hydrogenation catalyst for olefinic residues, we targeted a cis-bis-NHC Ru hydride complex. However, it was noted that most common bis-carbene Ru species adopt a trans-NHC geometry.[24−34] Cis coordination of carbenes to Ru can be imposed using chelating bis-carbene[23,35,36] and bis-pincer carbene ligands,[37−44] as well as tetrakis-carbene[45−47] and polyoxometalate derivatives.[48] Generally, the challenge of preparing cis-bis-carbene complexes is related to the steric demands of the N-bound substituents. Dixneuf and co-workers were able to overcome this, preparing cis-carbene derivatives of a Ru carborane using the sterically unencumbered carbene $C_3Me_4N_2$.[49] In a related fashion, the Whittlesey group has studied a series of Ru cis-bis-carbene complexes employing NHCs with N-bound isopropyl[50] or cyclohexyl[51] substituents. Herein, we report a new strategy to a cis-bis-carbene hydride complex and demonstrate that the species is an active hydrogenation catalyst for the selective hydrogenation of olefin residues in the presence of a wide variety of functional groups.

Our plan began with the idea of accessing a cis-bis-carbene hydride complex via sequential addition of NHC ligands. However, we noted Morris et al. had reported that reaction of $RuHCl(PPh_3)_3$ with an NHC prompted C−H activation of one of the NHC substituents.[52] While this C−H activation was avoided using the precursor $RuHCl(CO)(PPh_3)_3$, the product was coordinatively saturated.[19,20,53] Thus, we developed a strategy exploiting a pendant labile donor to access a monocarbene Ru hydride synthon. To this end, a precursor to an NHC with pendant ether donors has been readily and quantitatively prepared by refluxing a 2:1 mixture of chloroethyl methyl ether with trimethylsilylimidazole. The isolated imidazolium salt is subsequently treated with Ag_2O to produce the corresponding AgCl adduct of the NHC

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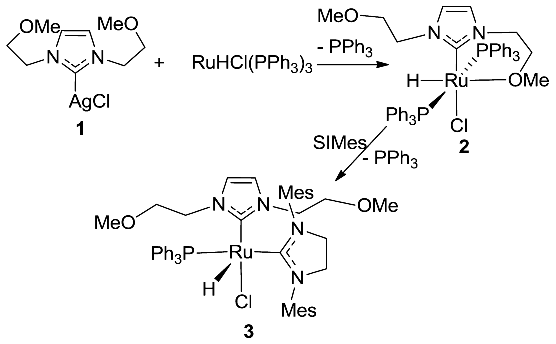
$C_3H_2N_2(CH_2CH_2OMe)_2$ (=IOMe), IOMeAgCl (**1**). Reaction of **1** with $RuHCl(PPh_3)_3$ and the ensuing workup afforded the air-sensitive bright yellow precipitate **2** (Scheme 1). The appearance of a triplet at −23.54 ppm in the ^1H NMR spectrum and a singlet at 44.61 ppm in the ^{31}P NMR spectrum of **2** were consistent with a hydride coupled to two phosphine ligands on Ru. ^1H and ^{13}C NMR spectra also confirmed the presence of the NHC. Single-crystal X-ray analysis of **2** revealed it to be $RuClH(IOMe)(PPh_3)_2$, in which the Ru adopts a pseudo-octahedral coordination sphere comprised of two trans phosphine ligands, a chloride trans to the carbene donor, and a hydride trans to a coordinated ether arm of the NHC ligand (Figure 1). The Ru−P distances average 2.324(1) Å, while the Ru−C and Ru−Cl distances are found to be 1.990(4) and 2.475(1) Å. The Ru−O distance of 2.369(3) Å reflects a weak bonding interaction, while the Ru−H distance was determined to be 1.58(4) Å. The weak Ru−O bond together with the sterically small NHC substituents presumably account for the striking sensitivity of **2** to air. Even under the cover of Paratone oil, crystals of **2** turn black within minutes upon exposure to the atmosphere at room temperature.

Scheme 1. Synthesis of 2 and 3



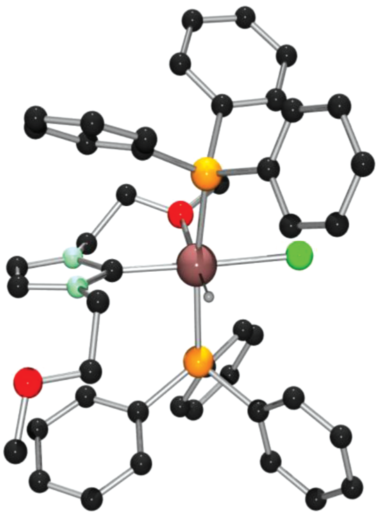


Figure 1. POV-ray depiction of **2**: C, black; O, red; Cl, green; P, orange; N, blue-green; Ru, salmon; H, gray. All hydrogen atoms except the hydride are omitted for clarity.

Subsequent reaction of compound **2** with 1 equiv of the Lewis base 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidine (SIMes) produced an immediate color change from yellow to red. After workup, dark red crystals of **3** were isolated. The ^1H NMR spectrum of **3** revealed a doublet at −28.87 ppm indicative of a hydride coupled to a single phosphine ligand. The upfield shift is also consistent with the absence of a ligand trans to the hydride. In addition, the ipso carbon shifts of the two NHCs were observed at 189.0 and 227.6 ppm for the IOMe and SIMes NHCs, respectively. Single-crystal X-ray analysis of **3** revealed a five-coordinate square-pyramidal ruthenium where the two NHCs, chloride, and phosphine form the base of the pyramid and the hydride occupies the apex: thus, the formulation as $RuClH(SIMes)(IOMe)(PPh_3)$ (Figure 2). The Ru−C distances for SIMes and IOMe were found to be 1.967(1) and 2.069(1) Å. The trans influence of these carbene ligands is reflected in the elongated Ru−P and Ru−Cl distances of 2.3007(4) and 2.4560(4) Å, respectively. The Ru−H distance was determined to be 1.47(2) Å. Interestingly, despite the fact that the ethereal oxygen atoms of the IOMe ligand do not coordinate to Ru, the 16-electron compound **3** is air-stable. This stands in marked contrast to the case for **2**. The cis diposition of the carbene ligands in **3** results in a C−Ru−C angle of 91.44(5)°. To our knowledge, this represents the first Ru cis-bis-mixed-carbene complex. It is the use of the IOMe ligand that permits the incorporation of SIMes in **3**, while the mismatch of the steric conflict between the carbene substituents allows a cis orientation.

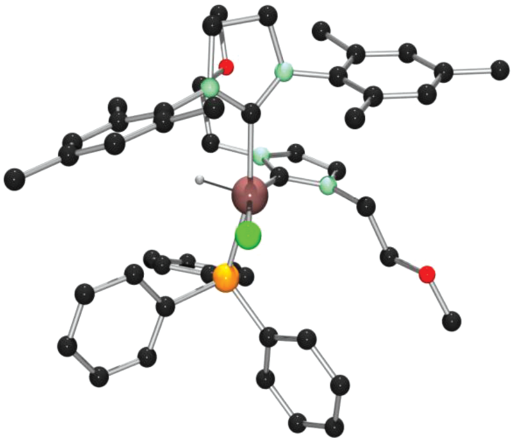
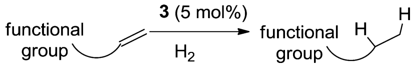


Figure 2. POV-ray depiction of **3**: C, black; O, red; Cl, green; P, orange; N, blue-green; Ru, salmon; H, gray. All hydrogen atoms except the hydride are omitted for clarity.

The utility of **3** as a hydrogenation catalyst was investigated (Table 1). Use of 5 mol % of **3** as a catalyst for the hydrogenation of 1-hexene under 4 atm of H_2 was undertaken. Monitoring this reaction revealed that initially olefin isomerization of 1-hexene to 2-hexene proceeds more quickly than reduction. For example, after 4 h, the product mixture was seen to be a mixture of 2-hexene and hexane in a 32:68 ratio, as determined by NMR spectroscopy. Nonetheless, quantitative reduction of the olefin to the alkane was observed in 8 h at 45 °C. In a similar fashion, styrene was quantitatively reduced in 6 h. The disubstituted olefins cyclohexene and 2-methyl-2-butene were reduced in 100 and 55% yields after 24 and 96 h, respectively, while the tetrasubstituted olefin 2,3-dimethyl-2-butene was not reduced even on prolonged exposure to catalyst and H_2. The corresponding reaction of phenylacetylene results in quantitative reduction to ethylbenzene in 8 h. Interestingly,

Table 1. Hydrogenation Catalysis with 3[a]



substrate	T (h)	product	yield (%)
1-hexene	8	hexane	100
styrene	6	ethylbenzene	100
cyclohexene	72	cyclohexane	100
2-methyl-2-butene	144	2-methylbutane	55
phenylacetylene	8	ethylbenzene	100
acrylonitrile	8	propionitrile	88[b]
allylamine	8	propylamine	93[b]
allyl alcohol	4	propanol	100
phenyl vinyl sulfone	8	ethyl phenyl sulfone	85[b]
2-vinylpyridine	4	2-ethylpyridine	100
1-vinylimidazole	8	1-ethylimidazole	95[b]
acrylaldehyde	8	propionaldehyde	100
3-buten-2-one	4	2-butanone	100
phenyl vinyl thioether	8	ethyl phenyl thioether	98[b]
methyl 3-butenoate	4	methyl butyrate	92[b]
dimethyl 2-methylenesuccinate	8	dimethyl 2-methylsuccinate	79[b]
methyl 2-(acetamido)acrylate	8	methyl 2-(acetylamino)propanoate	59[b]

[a] Conditions: 0.100 mmol of substrate and 5 mol % of catalyst in CD_2Cl_2 or C_6D_5Br, 45 °C, 4 atm of H_2. Yields were determined by NMR spectroscopy. [b] Quantitative reduction was observed in 24 h.

monitoring the reaction by NMR spectroscopy reveals a 50:50 product ratio of styrene and ethylbenzene after 4 h.

The ability of **3** to tolerate the presence of functional and donor groups was also probed. Employing the standard conditions of 4 atm of H_2 and 45 °C, the olefinic residues in acrylonitrile, allylamine, allyl alcohol, phenyl vinyl sulfone, 2-vinylpyridine, 1-vinylimidazole, acrylaldehyde, 3-buten-2-one, phenyl vinyl thioether, 3-methylbuten-2-one, 2-methylenesuccinate, and methyl-2-(acetamido)acrylate were reduced. In all these cases, quantitative reduction was seen in 24 h, although some were complete in as little as 4 h. In addition, hydrogenation occurred exclusively at the olefinic residue, as the functional groups were unaffected. In this regard, prolonged exposure of acetophenone or *N*-*tert*-butylphenylimine to the catalyst **3** and H_2 at elevated temperature led to no reaction, further demonstrating the selectivity for olefin reduction.

Preliminary examination of alternate conditions showed that 3-methylbuten-2-one is hydrogenated to 2-butanone at 45 °C in C_6H_5Br using 0.1 mol % of the catalyst **3** at 50 bar of H_2 pressure in just 30 min. This corresponds to a TON of 1000 and a TOF of 2000 mol/h. This suggests that much lower catalyst loadings are capable of high turnover frequencies when higher pressures of H_2 are used.

Despite the fact that **3** is formally a 16-electron species, it does not react with excess pyridine. This is consistent with the functional group tolerance **3** exhibits in hydrogenation catalysis. The mechanism of hydrogenation is presumed to involve a ligand rearrangement to provide for binding olefin adjacent to the hydride, leading to subsequent insertion. Interestingly the rate of hydrogenation of hexene is unaffected by the presence of a 5-fold excess of PPh_3. These data suggest that phosphine dissociation is not involved in the mechanism. It is also interesting to speculate on the role of the pendant ether arms of IOMe. These donors could act to stabilize transiently generated unsaturated species. The precise mechanistic details are under study.

In summary, on the basis of the use of an NHC with pendant donor ethers, we have developed a synthetic route to a rare cis-bis-mixed-carbene Ru hydride complex. This species has been shown to be a highly effective hydrogenation catalyst that tolerates the presence of a wide range of functional and donor groups. The study of the mechanism of action of **3** and its derivatives and the applications of selective olefin reduction in synthetic chemistry continues to be a focus in our laboratories.

ASSOCIATED CONTENT

Supporting Information

Text, tables, and CIF files giving synthetic, experimental, and crystallographic details. 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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