N-Heterocyclic Carbenes as Activating Ligands for Hydrogenation and Isomerization of Unactivated Olefins

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*Summary: The new hydridoruthenium complexes RuHCl(CO)(NHC)(PPh$_3$) (NHC = IMes (**4a**), H$_2$IMes (**4b**)), conveniently accessible from RuHCl(CO)(PPh$_3$)$_3$, exhibit high activity for hydrogenation of unactivated internal olefins and isomerization of terminal olefins. The lability of the PPh$_3$ ligand is fundamental to the utility of **4**: where this group is replaced by the relatively nonlabile PCy$_3$ ligand, the activating effect of the N-heterocyclic carbene is suppressed.*

N-Heterocyclic carbenes (NHCs) have emerged as an exceptionally versatile class of ligands for transition-metal catalysis. Owing to their enhanced σ-donating ability and thermal stability,[1,2] NHC derivatives display higher reactivity than the corresponding phosphine complexes in many Ru-catalyzed olefin metathesis reactions[3−7] and Pd-catalyzed coupling reactions.[8] They can also offer advantages over the thermally sensitive Crabtree catalyst in the Ir-catalyzed H_2-hydrogenation of olefins.[9,10] While good to excellent activity, typically at high catalyst loadings, has been reported in transfer hydrogenation (or in some cases, direct hydrogenation) via NHC complexes of rhodium,[11] iridium,[9−11] nickel,[12] and ruthenium,[13] deployment of this ligand class in Ru-catalyzed H_2-hydrogenation has so far met with less spectacular success. Indeed, one of us[14] recently pointed out that RuHCl(CO)(IMes)(PCy$_3$) (**2**) (Chart 1; IMes = *N*,*N*′-bis(mesityl)imidazol-2-ylidene) is considerably less active for olefin hydrogenation than the known, highly active[15−17] catalyst RuHCl(CO)(PCy$_3$)$_2$ (**1**) at room temperature and is only marginally more active than **1** at 100 °C. We were surprised by this finding, as we had anticipated that the enhanced donor ability and effectively two-dimensional steric demand of the NHC ligand should promote olefin binding and activation via **2**, relative to **1**.[18] Given the dissociative pathway established for hydrogenation via **1**,[15b,16b] we speculated that the poor performance of **2** might reflect a decrease in the lability of PCy$_3$ trans to an NHC group, vs a second PCy$_3$ ligand. Such a decrease is noted in olefin metathesis via RuCl$_2$(L)(PCy$_3$)(CHPh), for L = IMes vs L = PCy$_3$.[19] We now report the synthesis of ruthenium hydride complexes (**4**) containing both an NHC ligand and a *labile* phosphine donor, the improved catalytic activity of which confirms that the activating effect of the NHC group is masked in **2** by the low lability of the

Chart 1

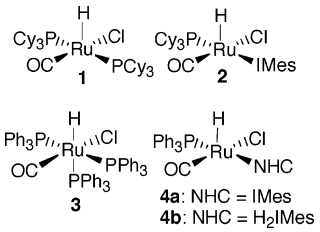

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Table 1. Hydrogenation of Selected Internal Olefins[a]

catalyst	substrate	TOF[b]	time (min)	conversn[c]
1	cyclooctene (COE)	138	10	69[d]
2		164[e]	10	100
4a		164[e]	10	100
1	cyclododecene (CDE)	740	60	33
2		235	60	8
4a		3,228	60	96[d]
4b		3,280	60	97[d]

[a] Conditions: 0.05 mol % of Ru, 50 psi of H_2 (COE); 140 psi of H_2 (CDE), 80 °C; toluene. [b] Turnover frequency calculated at 10 min (COE) and 30 min (CDE). Values are in units of min^{-1} for COE and h^{-1} for CDE. [c] Conversions determined by GC; ±3% in replicate runs. The thermal equilibration period was 7 min for 80 °C (t_0). [d] The conversion was 100% within 30 min (COE) and 2 h (CDE). [e] TOF corrected for ROMP contribution (18%).

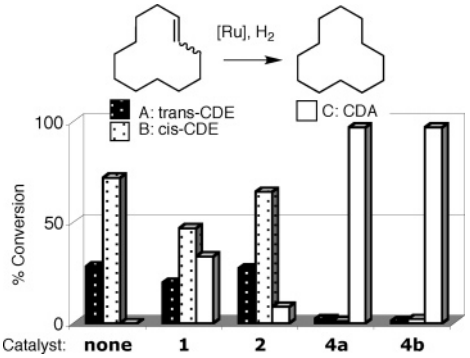

Figure 1. Product distribution at 1 h for reduction of cyclododecene (for conditions see Table 1).

phosphine donor. The new complexes exhibit activity for hydrogenation of unactivated olefins more than triple that of **1** and an order of magnitude greater than that of **2**. Also evident is a broader spectrum of catalytic activity, including isomerization of terminal olefins and polymerization of strained cycloolefins.

Complexes **4** are conveniently accessible by the room-temperature reaction of $RuHCl(CO)(PPh_3)_3$ (**3**) with 1 equiv of the appropriate NHC ligand. The mild reaction conditions, enabled by the lability of the PPh_3 ligands in **3**, result in clean, high-yield formation of NHC derivatives without activation of the mesityl group, in contrast with the thermolytic reactions of $RuHCl(PPh_3)_3$[20] and $RuH_2(CO)(PPh_3)_3$.[21] Quantitative conversion to the target compounds occurs within 3 h. Product identity is established on the basis of MALDI-MS, NMR, and elemental analysis. Particularly diagnostic in the NMR data are the upfield location of the hydride doublet (ca. −24 ppm, $^2J_{HP} = 24$ Hz), which indicates that the hydride ligand is trans to a vacant site, and observation of $^{13}C\{^1H\}$ NMR doublets for the CO and carbene carbons, consistent with retention of a single phosphine ligand. Other signals for the NHC ligand show the expected multiplicities and integration values.[22]

As the high hydrogenation activity of **1** is well established,[15−17] we chose as our targets for comparative catalytic studies internal, unactivated olefins, a class of substrates for which few catalysts are effective.[23] Hydrogenation was carried out at low catalyst loadings (0.05 mol % Ru), to which the Ir systems are not generally amenable.[24] Unexpectedly, in light of the earlier findings, reduction of cyclooctene (COE) suggests the trend **4a** ≈ **2** > **1** (Table 1), with the NHC catalysts effecting complete consumption of substrate within 10 min at 50 psi and 80 °C (GC analysis). The integrated intensity of the cyclooctane signal is low relative to the internal standard, however, and closer examination reveals that both **4a** and **2** trigger competing polymerization of cyclooctene. Nearly 20% polymer was isolated by removal of solvent and cyclooctane product under vacuum. While this material proved too insoluble for NMR or GPC analysis, IR characterization indicates complete hydrogenation of the unsaturated polymer (a notoriously challenging substrate)[25] by catalyst **4a**. Ruthenium hydrides have previously been found to be effective ROMP catalysts, typically for highly strained, bicyclic monomers.[26,27]

The implied balance between the hydrogenation and ROMP activities of **4** suggests that these catalysts may have the broadest applicability in hydrogenation of low-strain cycloolefins or acyclic olefins. Of particular interest in the former category are macrocyclic rings, with potential relevance to the synthesis of saturated odiferous or organoleptic compounds[28] by tandem RCM-hydrogenation.[29,30] We undertook reduction of cyclododecene (CDE) as a representative substrate with a slightly lower degree of ring strain than COE.[31] CDE and other macrocyclic substrates pose a twofold challenge for hydrogenation: not only is reduction more difficult with increasing ring size but also macrocycles frequently exist as mixtures of the cis and the sterically encumbered trans internal olefins. The resistance of *trans*-CDE to hydrogenation is illustrated by the product distributions shown in Figure 1: for catalysts **1** and **2**, the proportion of the trans isomer at 1 h is little changed from that in the starting material. Catalysts **4a** and **4b**, in contrast, efficiently reduce both cis and trans olefins, effecting conversion to cyclododecane (CDA) more than 10 times faster than **2** and 3−4 times faster than **1**.[32] Essentially identical activity is found for the IMes (**4a**) and H_2IMes (**4b**) catalysts; no polymerization is observed in either case.

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Table 2. Reduction vs Isomerization of Allylbenzene[a]

catalyst	$p(H_2)$ (psi)	propylbenzene (%)	PhCHCHMe (%) cis	PhCHCHMe (%) trans	TOF (h^{-1})[b]
1	50	72	0	9	2880 (360)
	140	86	0	9	3440 (360)
2	50	51	1	6	2040 (280)
	140	94	0	6	3760 (240)
4a	50	60	0	40	2400 (1600)
	140	89[c]	0	11	3560 (440)
4b	140	49	10	37	1960 (1880)

[a] Conditions: 0.05 mol % of Ru, 2.00 mmol of allylbenzene in toluene, 80 °C; 30 min reaction time following "t_0". Conversions were determined by GC; ±3% in replicate runs. [b] Turnover frequency for hydrogenation; TOF values for isomerization are given in parentheses. [c] 100% at 2 h.

Electron-rich Ru alkylidene complexes containing NHC ligands frequently promote olefin isomerization, for which metal hydrides are proposed as the catalytically relevant species.[33] Such behavior has important implications for hydrogenation of *terminal* olefins by catalysts of type **4**, if conversion to internal olefins occurs over the time scale of hydrogenation. To quantify the reduction, vs isomerization, capabilities of the well-defined hydride complexes **1**,[34] **2**, and **4**, we employed allylbenzene, which affords a sensitive probe of isomerization capabilities. Catalyst **1** effects ca. 70% reduction of allylbenzene within 30 min under 50 psi of H_2 at 80 °C, accompanied by 9% isomerization (Table 2). Comparable isomerization activity is found for **2**, though the hydrogenation efficiency is ~20% lower. While conversion profiles indicate that both catalysts reduce *cis*-propenylbenzene at appreciable rates,[32] neither is effective for reduction of the trans olefin under these conditions. Indeed, the olefin remaining after 2 h is almost entirely *trans*-propenylbenzene, which is reduced very slowly, even on raising the hydrogen pressure to 140 psi. Consistent with the earlier report on reduction of 1-hexene,[14] the NHC catalyst **2** outperforms **1** under the more forcing conditions. More surprisingly, use of **4a** offers no improvement. The higher hydrogenation activity of **4a** is clearly offset, for this α-olefin substrate, by its potent isomerization activity: at "t_0", nearly 20% internal olefin is already present, and this increases to 40% within 30 min *under 50 psi of H_2*. Reduction of the trans olefin is effected, albeit slowly, at 50 psi; it can be efficiently reduced at 140 psi. Interestingly, catalyst **4b** proves significantly more active for isomerization, even at 140 psi, and is thus less effective for reduction of allylbenzene.

The foregoing expands the range of Ru−NHC complexes to include five-coordinate ruthenium hydrido carbonyl complexes containing a labile PPh_3 ligand. The new complexes are effective catalysts for the challenging problem of hydrogenating sterically hindered trans-internal olefins: both caveats and opportunities are implicit in their additional activity for isomerization of terminal olefins and polymerization of strained cycloolefins. The poorer performance of the PCy_3 analogue **2** is notable: the presence of a labile phosphine donor in the precatalyst is clearly fundamental to the activity of the NHC complexes, consistent with a dissociative mechanism involving phosphine loss prior to olefin binding. Indeed, this synergy between an activating N-heterocyclic carbene (NHC) ligand and a labile PPh_3 donor is likewise responsible for the exceptionally high metathesis activity of "mixed ligand" catalysts $RuCl_2(NHC)(PPh_3)(=CHR)$.[3,35] A clear parallel thus exists between the requirements for maximum activity in metathesis, isomerization, and hydrogenation catalysis, and the application of these findings to tandem metathesis−isomerization and metathesis−hydrogenation chemistry is now in progress.

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Supporting Information Available: Text giving synthetic and spectroscopic details for **4a** and **4b** and the general hydrogenation protocol, and figures giving representative composition profiles. This material is available free of charge via the Internet at http://pubs.acs.org.

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