Carbonyl-Amplified Catalyst Performance: Balancing Stability against Activity for Five-Coordinate Ruthenium Hydride and Hydridocarbonyl Catalysts

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The activity of $RuHCl(H_2)(PCy_3)(L)$ **2a/b** and $RuHCl(CO)(PCy_3)(L)$ **3a/b** (**a**: L = PCy_3; **b**: L = IMes; IMes = 1,3-dimesitylimidazol-2-ylidene) was assessed in hydrogenation of a range of molecular and polymeric olefins and in hydrogenation and isomerization of allylbenzene. Elevated temperatures and/or high H_2 pressures are required for efficient hydrogenation. Under these conditions, **3a/b** outperform their dihydrogen analogues in both total productivity and turnover frequencies, despite theoretical and experimental evidence that the π-acid CO ligand should be deactivating. A thermolysis study reveals that the CO complexes are much less susceptible to deactivation under conditions relevant to catalysis (also, the IMes derivative **2b** is shorter-lived than **2a**). We attribute the superior performance of **3a/b** to their greater stability, which maintains higher concentrations of active catalyst than that possible for their H_2 analogues over the time scale of hydrogenation.

Introduction

The high volume of waste characteristic of fine chemicals and pharmaceutical manufacturing[1,2] is coming under closer scrutiny in an increasingly stringent economic climate that underscores the correspondence between process costs and the proportion of waste generated per ton of product. Tandem catalysis is of interest for its potential to improve process efficiencies by eliminating unnecessary workup stages and solvent use, two major contributors to waste in pharmaceutical manufacturing.[1,3] Improved efficiencies in catalyst consumption confer added advantages in reducing direct costs, as well as indirect costs associated with purification of the organic products.

As part of a program of study focusing on tandem catalysis,[4−6] we have developed efficient[7] methodologies for tandem ROMP−hydrogenation (ROMP = ring-opening metathesis polymerization).[8−11] Hydrogenation is important in extending the range of applications for unsaturated ROMP polymers, by reducing their susceptibility to oxidative, thermal, and chemical degradation.[12] Tandem metathesis−hydrogenation methodologies typically rest on the accessibility of five-coordinate Ru hydrides from Grubbs catalysts of type **1** (Scheme 1). We earlier showed[10] that the hydrido-dihydrogen complex **2a** is formed cleanly by hydrogenolysis of **1a** in the presence of base: the corresponding hydridocarbonyl complexes **3** are formed from both **2**[8] and the alkylidene complexes **1**[13−15] by reaction with methanol or other primary alcohols, via established[16−19] alcohol decarbonylation pathways.[20] In related work, we found that use of small amounts of methanol as cosolvent dramatically increased hydrogenation efficiency in tandem ROMP−hydrogenation via **1a**, leading us to speculate that formation of **3a**—by

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(7) Reduction of ROMP polyoctenes was achieved via tandem catalysis at 50−60 °C and as little as 1 atm of H_2: see ref 8. Hydrogenation of polynorbornenes, particularly those bearing bulky substituents, is considerably more demanding; see ref 9. Hydrogen pressures of up to 1000 psi can be required for efficient reduction at these moderate temperatures: the high pressures are preferable to use of higher temperatures, which can trigger competitive thermal cross-linking of the unsaturated polymers. Less satisfactory results have been reported using a range of other catalysts (e.g., Wilkinson's catalyst, $RhCl(PPh_3)_3$; the Crabtree catalyst, $[Ir(COD)(PCy_3)(py)]PF_6$, and various supported palladium catalysts), despite their often outstanding performance in reduction of molecular olefins at relatively low H_2 pressures. See, for example, ref 9 and: (a) Lee, L.-B. W.; Register, R. A. *Macromolecules* **2005**, *38*, 1216–1222. (b) Dettmer, C. M.; Gray, M. K.; Torkelson, J. M.; Nguyen, S. T. *Macromolecules* **2004**, *37*, 5504–5512. (c) Lee, B. S.; Mahajan, S.; Clapham, B.; Janda, K. D. *J. Org. Chem.* **2004**, *69*, 3319–3329. (d) Sohn, B. H.; Gratt, J. A.; Lee, J. K.; Cohen, R. E. *J. Appl. Polym. Sci.* **1995**, *58*, 1041. (e) Vargas, J.; Santiago, A. A.; Tlenkopatchev, M. A.; Gavino, R.; Laguna, M. F.; Lopez-Gonzalez, M.; Riande, E. *Macromolecules* **2007**, *40*, 563–570.

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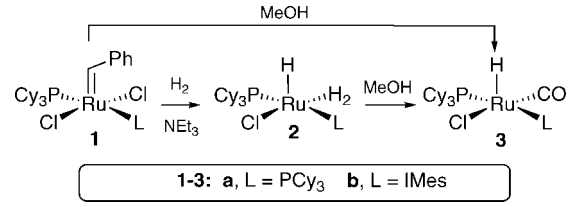
inference, a more reactive catalyst than **2a**—could be an important contributing factor.[8,21]

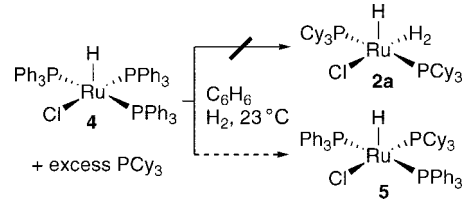
While ample precedents exist for hydrogenation via **3a**,[13,22−27] catalysis via **2a** has gone less studied,[28] and no direct comparison of the hydrogenation activity of the two complexes has been reported. We were intrigued by the possibility that **3a** is the more active, given that much evidence correlates higher hydrogenation activity with a more electron-rich Ru center. Thus, Ru catalysts containing strongly σ-donating alkylphosphine ligands outperform those containing arylphosphines, and incorporation of a CO ligand is known to *decrease* hydrogenation activity in arylphosphine complexes of Ru, Rh, and Ir.[26,29−31] The latter behavior is consistent with the inhibiting effect of the π-acid ligand on both phosphine loss (a required step in olefin hydrogenation via **3a**[22,27] and related polyphosphine[31] catalysts) and oxidative addition of dihydrogen. Further, in a computational study designed to probe the effect of a σ-donor, versus a π-acid, ancillary ligand in $RuHCl(L)(P^iPr_3)_2$ model systems (L = CO, PH_3), we found a systematically more stable reaction profile for the PH_3 species.[32] That is, this study revealed no electronic basis for increased hydrogenation activity on the part of the CO complex.

The apparent contradiction between these findings and the tandem catalysis data in the presence of methanol prompted us to undertake a systematic experimental comparison of the hydrogenation activity of the isolated, well-defined dihydrogen and carbonyl complexes. The complexes examined are those accessible from the first- and second-generation Grubbs catalysts, viz., $RuHCl(H_2)(L)(PCy_3)$ (**2a/b**) and $RuHCl(CO)(L)(PCy_3)$ (**3a/b**). Here we describe synthesis of the previously unreported **2b**, we demonstrate that the carbonyl derivatives are more efficient hydrogenation catalysts than their dihydrogen analogues, and we show that this effect originates in the greater robustness of the CO complexes, which limits their susceptibility to the deactivation pathways from which their H_2 analogues suffer.

Scheme 1. Hydride Complexes Formed from First- and Second-Generation Grubbs Metathesis Catalysts



Scheme 2. Attempted Synthesis of 2a[a]



[a] Dashed arrow indicates incomplete reaction: for details, see text.

Results and Discussion

Synthesis of $RuHCl(H_2)LL'$ Complexes 2a/b. We recently reported a clean, high-yield route to the hydridocarbonyl complexes **3a/b**, in which $RuHCl(CO)(PPh_3)_3$ is warmed with PCy_3 in benzene.[33] The success of this approach led us to attempt synthesis of **2a** by the analogous reaction of $RuHCl(PPh_3)_3$ **4**. These efforts were thwarted, however, by the poor solubility of **4** in aromatic solvents, which resulted in only partial conversion to $RuHCl(PCy_3)(PPh_3)_2$ **5** (30% of the soluble portion and an undetermined amount of the suspended material; Scheme 2) over 24 h at room temperature. Complete conversion, moreover, was hindered by the onset of product decomposition on longer reaction, while use of methylene chloride, in which **4** is soluble, is precluded by the susceptibility of the basic alkylphosphine to chlorination by this solvent. We therefore prepared **2a** by established methods, involving hydrogenolysis of **1a**[10] or ligand exchange[34] of $[RuCl_2(COD)]_n$ with PCy_3 (in the latter synthesis, we used 2-propanol as a convenient alternative to the original *sec*-butanol solvent,[34] and higher pressures of H_2). The identity of **2a** was confirmed by comparison to the reported[35,36] NMR data, Table 1.

Leitner and co-workers have successfully prepared the dihydride complex $RuH_2(H_2)_2(IMes)(PCy_3)$ by ligand exchange of $RuH_2(H_2)_2(PCy_3)_2$ with IMes at 55 °C under H_2, the room-temperature reaction failing to yield product.[37] We obtained

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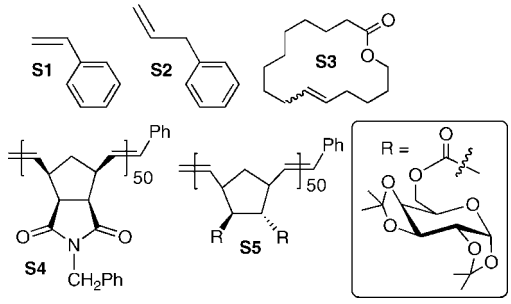
Table 1. Key NMR Data for Ruthenium Hydride Complexes Relevant to This Work (Ar, 298 K)

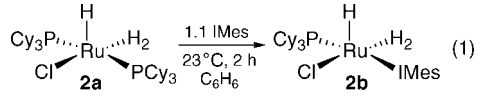
complex	solvent	δ_P (ppm)	δ_H (ppm)	ref
$RuHCl(H_2)(PCy_3)_2$, **2a**[a]	C_6D_6	54.2 (s)	−16.3 (br s)[b]	10,35
	CD_2Cl_2	52.8 (s)	−16.93 (br s)[b,c]	this work
$RuHCl(N_2)(PCy_3)_2$, **6a**	C_6D_6	43.7 (s)	−27.26 (t, $^2J_{PH}$ = 18.3 Hz)	52
$RuHCl(H_2)(IMes)(PCy_3)$, **2b**	C_6D_6	56.3 (s)	−16.44 (br s)[b]	this work
$RuHCl(N_2)(IMes)(PCy_3)$, **6b**	C_6D_6	45.0 (s)	−27.63 (d, $^2J_{HP}$ = 21.4 Hz)	this work
$RuHCl(CO)(PCy_3)_2$, **3a**	C_6D_6	46.9 (s)	−24.21 (t, $^2J_{HP}$ = 18.1 Hz)	33
$RuHCl(CO)(IMes)(PCy_3)$, **3b**	C_6D_6	47.8 (s)	−24.82 (d, $^2J_{HP}$ = 21.2 Hz)	33
$RuH_2Cl_2(PCy_3)_2$, **7**	C_6D_6[a]	91.3 (s)	−12.0 (t, $^2J_{HP}$ = 31.5 Hz)	10
	CD_2Cl_2	91.3 (s)	−12.39 (t, $^2J_{HP}$ = 31.6 Hz).	10,54

[a] In C_6D_6, the $^{31}P\{^1H\}$ NMR singlet for $RuCl_2(H_2)(PCy_3)_2$ **8** is coincident with that for **2a**, but is accompanied by a singlet for the Ru(IV) tautomer **7** (ratio 1:2).[10] The corresponding hydride signals appear at −16.2 ppm (br s, **8**) and −12.0 ppm (t, 31.5 Hz, **7**). In CD_2Cl_2, only **7** is present. [b] The hydride and dihydrogen signals for **2a/b** appear as a single broad peak integrating to 3H. [c] A chemical shift of −16.8 (br t, J_{HP} = 11 Hz) was originally reported for **2a** in CD_2Cl_2 (250 MHz).[35] The difference may reflect the presence of H_2 in the literature report.

Chart 1. Substrates Employed in Hydrogenation Studies



$RuHCl(H_2)(IMes)(PCy_3)$ **2b** by the corresponding reaction of **2a** under argon: in this case, reaction was complete within 2 h at 23 °C (eq 1). No products other than **2b** and free PCy_3 were evident by NMR analysis, and the 1:1 ratio between the signals for free and bound PCy_3 confirmed clean formation of **2b** (i.e., free of paramagnetic byproducts; see below). Extraction of the free phosphine with hexanes enabled isolation of clean **2b** in ca. 70% yield. Its identity is supported by spectroscopic and elemental analysis.



The NMR features for **2b** correspond well with those for **2a** (Table 1). Thus, a $^{31}P\{^1H\}$ NMR singlet appears at 56.3 ppm, and the broad singlet due to the hydride/dihydrogen ligands at −16.44 ppm. The $T_{1(min)}$ value for the latter signal, 36.6 ms in C_7D_8 (253 K, 300 MHz), corresponds to a H−H distance of 1.03 Å.[38] Both the breadth of this signal and its comparatively long relaxation time are characteristic of η^2-H_2 perturbed by interaction with *cis*-hydride.[38] In comparison, a value of ca. 30 ms was reported for **2a** at 243 K and 250 MHz.[35] Averaging of the classical and nonclassical hydrides in **2b** causes their NMR signal to appear ca. 11 ppm downfield from the doublet due to the unperturbed hydride in the corresponding dinitrogen complex **6b**. (The latter complex is discussed in greater detail below.) Well-resolved singlets appear for the IMes methyl, aromatic, and =C*H*N groups for **2b**, integration of which against the H/H_2 singlet is consistent with the proposed structure.

Catalytic Activity. Hydrogenation studies focused on the substrates shown in Chart 1. In a preliminary assessment of the relative hydrogenation activity of catalysts **2** and **3**, we established their baseline activity toward styrene, **S1**, at 23 °C. The duration of these experiments was normalized to that required for quantitative formation of ethylbenzene by the most reactive catalyst, **3a** (Figure 1a). The lower activity of the IMes derivative **3b** at room temperature, versus its "first-generation" analogue **3a**, has precedent;[39] the data for **2a/b** indicate that this trend is retained for the H_2 complexes. We attribute the drop in activity to the low lability of PR_3 *trans* to an NHC ligand,[40,41] originally described by the Grubbs group in a seminal paper on olefin metathesis.[40] Within both the bis(PCy_3) and the IMes-PCy_3 series, the activity of the CO complexes **3** is consistently greater than that of their dihydrogen analogues **2** at the high H_2 pressures required for complete hydrogenation within <24 h.[42] The implications in terms of process efficiency are manifested most explicitly in the time profile for complete hydrogenation of styrene at a catalyst loading of 0.1 mol % (Figure 1b). Reduction by **3a** under the conditions specified is complete at 1.5 h, while quantitative reduction via **2a** requires 12 h.

We also evaluated the tendency of the more reactive catalysts **2a/3a** to promote competing isomerization, using allylbenzene **S2** as substrate. Hydridocarbonyl **3a** proves considerably more reactive than its H_2 analogue **2a** in both reduction and isomerization (Figure 1a). Of note, hydrogenation is ca. 30 times faster than isomerization for **2a**, but only 15 times faster for **3a**, suggesting that the higher activity of the latter may come at the price of reduced discrimination.

To assess the generality of the trends indicated in Figure 1, we turned to hydrogenation of several additional substrates of broader interest, which present successively greater challenges to reduction (Chart 1; Table 2). Reduction of lactone **S3** affords the musk-odored perfume Exaltolide, while the reduced ROMP polymers are of interest for, respectively, their relevance to well-defined polymer platforms for further functionalization (**S4**)[43] or for tissue engineering (**S5**).[44] Other hydrogenated ROMP polynorbornenes find applications as engineering thermo-

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(42) Catalyst **2a** exhibits a complex dependence on H_2 concentration, possibly reflecting the lower activity of its bis(H_2) derivative, as reported for related dihydride catalysts: see ref 35. Borowski, A. F.; Sabo-Etienne, S.; Chaudret, B. *J. Mol. Catal. A* **2001**, *174*, 69–79. Hydrogenation is slow at low H_2 pressures, however, and use of elevated temperatures to accelerate reaction causes decomposition. This behavior is discussed in more detail in the following sections.

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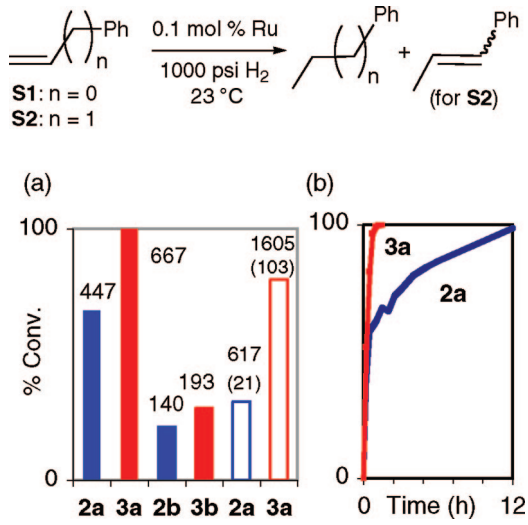

Figure 1. (a) Relative catalyst performance in hydrogenation of styrene (**S1**, 1.5 h, filled bars) and allylbenzene (**S2**, 0.5 h, unfilled), showing turnover frequencies (TOF; mol product·mol catalyst^{-1} h^{-1}), with isomerization TOF in parentheses. (b) Time for complete hydrogenation of styrene by **2a** vs **3a**. All reactions carried out in benzene at 23 °C under 1000 psi H_2, using 0.1 mol % Ru and 1.0 M styrene or 0.7 M allylbenzene. Average of three trials (±3%).

Table 2. Relative Efficiency of Dihydrogen and Carbonyl Catalysts in Hydrogenation of Various Olefinic Substrates[a]

substrate	mol % Ru	time (h)	cat.	TOF (h^{-1})	conv (%)
S1	0.1	0.5	**2a**	1260	63
			3a	1840	92
			2b	540	27
			3b	1520	76
S3	0.1	1	**2a**	830	83
			3a	960	96
			2b	530	53
			3b	810	81
S4	0.1	1	**2a**	310	31
			3a	660	66
			2b	310	31
			3b	510	51
S5	0.5[b]	6	**2a**	3	10
			3a	7	21
			2b	7	20
			3b	17	50

[a] Conditions: 1000 psi H_2, refluxing CH_2Cl_2 (except for **S1**: 23 °C); conversions measured by GC-FID or ^{1}H NMR analysis. [b] Conversions <10% at 0.1 mol % Ru.

plastics[12,45] and fluoropolymers,[46] as polymer supports in synthetic applications,[7c,47] as nanoporous materials,[48] and as gradient polymers with potentially programmable thermal properties.[7b] We recently described tandem ROMP−hydrogenation of **S5** via first-, second-, and third-generation Grubbs catalysts, using protocols that generate **2a/b** and, in the presence of methanol, **3a/b**.[9]

Reduction of these substrates in CH_2Cl_2 follows the trend established above, with the CO complexes **3** outperforming their H_2 analogues **2** in all cases. Also, the "first-generation" catalysts (**2a**, **3a**) generally outperform the second-generation catalysts (**2b**, **3b**) in reduction of all substrates, with the exception of neoglycopolymer **S5**. The challenging nature of **S5** is illustrated by the low turnover numbers found even at 0.5 mol % Ru (i.e., a catalyst loading 5 times higher than that used for **S1**−**S4**). While the CO catalysts remain more effective than their H_2 analogues for reduction of this substrate, maximum conversions are found for the IMes derivative **3b**, rather than the bis-PCy_3 complex **3a**. We attribute this to the significant steric bulk present in **S5**, arising from its polymeric nature, the *endo/exo* disubstitution of the repeat unit, the bulk of the galactose groups, and the additional steric pressure exerted by the acetal protecting groups. The unexpectedly higher activity of the IMes catalyst **2b** may reflect the essentially two-dimensional steric bulk of the N-heterocyclic carbene, relative to PCy_3; we presume that one phosphine ligand is replaced by olefin during the hydrogenation cycle as for **2a**; vide supra.

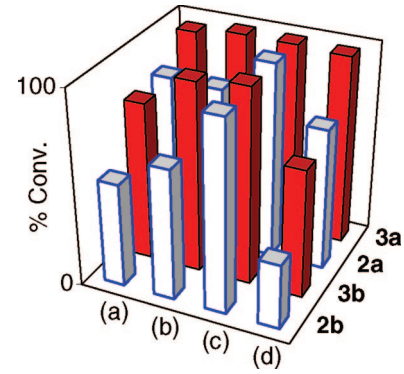

Figure 2. Effect of solvent and additives on hydrogenation of lactone **S3** via catalysts **2** and **3**: (a) CH_2Cl_2 solvent without additives (Table 2); (b) in CH_2Cl_2 with 3 equiv of NEt_3; (c) in 20% MeOH−CH_2Cl_2 with 3 equiv of NEt_3; (d) in C_6H_6 without additives. Conditions: 1000 psi H_2, 0.1 mol % Ru, bath temperature 55 °C, 1 h reaction time.

A more detailed study focused on the effect of solvent and additives on hydrogenation of lactone **S3** (Figure 2; for tabulated numerical data, see Supporting Information). Consistently higher conversions are found for reduction in methylene chloride, relative to benzene: the reactivity trends in both solvents follow the norm established above. Addition of base to the reactions in CH_2Cl_2 improves activity slightly, particularly for the IMes derivatives, suggesting some competing chlorination of the hydride catalyst by the chlorocarbon solvent (see later). Finally, the difference in activity between the H_2 and CO series of catalysts is minimized in the presence of MeOH, in which the dihydrogen catalysts undergo carbonylation, as discussed above.

Relative Stability of 2 and 3. The data above demonstrate that the carbonyl complexes **3** are more effective hydrogenation catalysts than their dihydrogen analogues **2**. Given the similarly low bulk of the CO and H_2 ligands, we discount a steric origin for this higher activity. However, the DFT study described in the Introduction, which predicts a higher-energy reaction profile for hydrogenation via $RuHCl(L)(PR_3)_2$ species in which L is CO, versus the σ-donor PH_3, implies that the π-acidity of the CO ligand should be detrimental to hydrogenation activity.[32] We speculated that the higher hydrogenation efficiency of **3a/b**, particularly at elevated temperatures, might be largely due to their greater stability relative to **2a/b**, and hence higher

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concentrations of the catalytically active species over the time scale of hydrogenation.

This hypothesis stemmed in part from the high reactivity characteristic of the related, classic H_2 complex $RuH_2(H_2)_2(PCy_3)_2$ **9**, a function of the electron-rich character of the metal and the lability of the dihydrogen ligand(s).[36] In **9** and cyclohexylphosphine complexes, this reactivity is manifested in C−H bond activation even at ambient temperatures.[36,49−51] Of interest, Leitner and co-workers have reported that $RuH_2(H_2)_2(IMes)(PCy_3)$ is more reactive than **9** in C−H activation chemistry.[37] While this was of value in enabling intermolecular C−H bond activation at room temperature, it may also signify a greater susceptibility to deactivation via *intra*molecular bond activation.

The ease of H_2-N_2 exchange can afford a preliminary indicator of such lability.[38a] The relative robustness of the $Ru-H_2$ interaction in **2a** is suggested by the early comment that this complex resists exchange with 1 atm of N_2 at room temperature.[35] We find that exchange does occur to afford **6a**, but slowly (5−15% after 24 h; **6a** identified on the basis of the reported chemical shifts[52] of −27.26 and 43.7 ppm for the hydride and ^{31}P nuclei, respectively; Table 1). The higher lability of the dihydrogen ligand in **2b** is suggested by observation of ca. 70% conversion to $RuHCl(N_2)(IMes)(PCy_3)$ **6b** after 24 h under N_2. Complex **6b** is identified from its well-resolved hydride doublet at −27.63 ppm (ca. 11 ppm upfield of the averaged hydride/dihydrogen signal for **2b**), which correlates in HMBC experiments with a new $^{31}P\{^1H\}$ NMR singlet at 45.0 ppm. These chemical shifts agree well with the values for **6a** above.

In related cyclohexylphosphine complexes, loss of a stabilizing H_2 or N_2 ligand is often the entry point to extensive intramolecular bond activation, as noted above.[36,49−51,53] Under argon at 23 °C, neither **2a/b** or **3a/b** shows evidence of bond activation in C_6D_6 after 24 h, as judged by integration of their $^{31}P\{^1H\}$ NMR signals against an internal standard. (Use of an internal standard in these experiments is important, as the potential paramagnetism of the product(s), and the consequent absence of an NMR "marker", means that losses can otherwise easily go unnoticed.) In CH_2Cl_2, however, **2a** undergoes partial conversion to the known[54] Ru(IV) complex $RuH_2Cl_2(PCy_3)_2$ **7**, with a ca. 1:1 ratio of **2a**:**7** after 16 h. We earlier described the low catalytic activity of coordinatively saturated **7**.[8] Its assignment was confirmed in the present experiment by HMBC correlation of the $^{31}P\{^1H\}$ NMR singlet at 91.3 ppm with the expected hydride triplet for **7** at −12.39 (t, $^2J_{PH}$ = 31.6 Hz; CD_2Cl_2). Chlorination of **2a** is consistent with earlier findings from the Toulouse group, which described the successive conversion of $RuH_2(H_2)_2(PCy_3)_2$) **9** to **2a** and **7** in Freons (mixtures of $CDCl_3$, $CDFCl_2$, and CDF_2Cl) and in neat $CDCl_3$.[54] In sharp contrast, **2b** undergoes complete decomposition to paramagnetic products in CH_2Cl_2 over 16 h, while **3a/b** is wholly unaffected.

In a more direct probe of the relative susceptibility of **2a/b** and **3a/b** to deactivation under conditions related to catalysis, we subjected all four complexes to thermolysis in benzene and methylene chloride under 1 atm of H_2. Again, the high stability of the carbonyl complexes is notable, little to no change being evident in either solvent. The dihydrogen complexes are less robust: after just 1 h at 55 °C in benzene, the concentration of **2a** has decreased by ca. 30% (Figure 3a). Free PCy_3 is present, accompanied by minor amounts of an unidentified species at ca. δ_P 63 ppm (6%), but the balance of material is either paramagnetic or devoid of ^{31}P nuclei. For **2b**, ca. 60% decomposition occurs over this time, and no new signals are apparent.

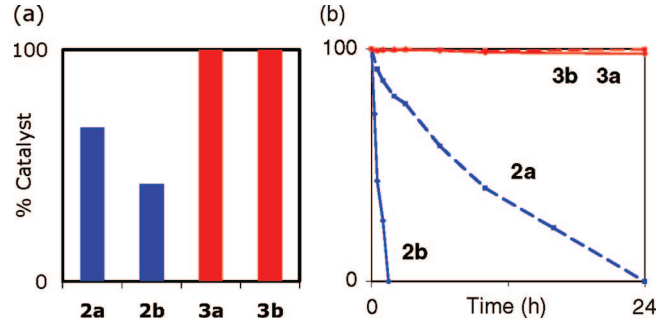

Figure 3. Thermolytic stability of **2** and **3** under 1 atm of H_2, as indicated by $^{31}P\{^1H\}$ NMR integration against $O{=}PPh_3$ as internal standard: (a) after 1 h in C_6D_6 at 55 °C; (b) in refluxing CH_2Cl_2. Dashed lines, L = PCy_3; solid lines, L = IMes.

In refluxing CH_2Cl_2, **2a** is completely consumed after 24 h (Figure 3b), and **7** is the only ^{31}P-containing product observed (70%). The coordinative saturation of **7**, while detrimental to catalytic activity (see above), appears to confer some protection against more extensive decomposition. When formation of **7** is suppressed by repeating this reaction in the presence of NEt_3, the only species observed by $^{31}P\{^1H\}$ NMR is an unidentified product of singlet multiplicity at 36 ppm, which integrates to ca. 40%.

Consistent with the generally greater vulnerability described above, **2b** undergoes near-total conversion to paramagnetic species within 2.5 h in refluxing CH_2Cl_2 (Figure 3b). Unexpectedly, however, a small signal for **2a** is observed within 15 min, which disappears over the next 2 h. A very small signal at 91 ppm (<5% integration) is observable after this time (see Supporting Information). Formation of **2a** from **2b** signifies that the latter undergoes some disproportionation under these conditions, as also reported by the Mol group for thermolysis of a second-generation Ru benzylidene complexes in MeOH at 80 °C.[14] Immediate scavenging of any dissociated IMes by the chlorinated solvent is anticipated, based on Arduengo's findings;[55] this, as well as competing chlorination of dissociated PCy_3, will adversely affect ligand recapture and regeneration of catalytically active Ru complexes.

Conclusions

The foregoing describes a clean, high-yield synthetic route to $RuHCl(H_2)(IMes)(PCy_3)$ **2b** by ligand exchange reactions of $RuHCl(H_2)(PCy_3)_2$ **2a**, although attempts to develop a route to **2a** itself from $RuHCl(PPh_3)_3$ **4** were unsuccessful. Comparison of the olefin hydrogenation activity of **2a/b** with the corresponding carbonyl complexes **3a/b** demonstrates that

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replacing the H_2 ligand by CO improves hydrogenation efficiency, particularly at elevated temperatures. Independent thermolysis experiments suggest that this reflects a positive influence on catalyst lifetime associated with the low lability of the CO ligand, as complexes **3a/b** are much more stable than their dihydrogen analogues **2a/b**. The π-acidity of the carbonyl group may also play a part: while this will have detrimental effects on catalyst initiation via ligand loss, as well as oxidative addition of H_2, it offers the advantage of decreasing the susceptibility of the complex to nucleophilic attack. The significantly greater robustness of the CO complexes appears to compensate for their lower activity, by maintaining higher concentrations of active catalyst over the time scale of hydrogenation.

Experimental Section

General Procedures. Reactions were carried out at room temperature (23 °C) under argon, using standard Schlenk or glovebox techniques, unless otherwise stated. Dry, oxygen-free solvents were obtained using a Glass Contour solvent purification system and stored over Linde 4 Å molecular sieves. $CDCl_3$ and C_6D_6 were degassed by consecutive freeze/pump/thaw cycles and dried over activated sieves (Linde 4 Å). $[RuCl_2(COD)]_n$,[56] $RuHCl(PPh_3)_3$,[57] $RuHCl(CO)(PCy_3)$ **3a**,[33] $RuHCl(CO)(IMes)(PCy_3)$ **3b**,[33] IMes,[58] and substrates **S3**,[59] **S4**,[9] and **S5**[9] were prepared according to literature methods. H_2 (UHP grade) was obtained from BOC Gases and used as received. Styrene and allylbenzene (Aldrich) were distilled from CaH_2 under vacuum and stored at −35 °C under Ar in the dark. Tetrahydronaphthalene was distilled from Na metal, freeze−pump−thaw degassed, and stored over Linde 4 Å molecular sieves under Ar. Ethylbenzene (Aldrich) and PCy_3 (Strem) were used as received. NMR spectra were recorded on a Bruker Avance 300 or Avance-500 spectrometer at 298 K, unless otherwise specified. ^1H and ^{13}C NMR spectra were referenced to the residual proton and carbon signals of the deuterated solvent. Peaks are reported in ppm, relative to TMS (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P) at 0 ppm. IR spectra were measured on a Bomem MB100 IR spectrometer. Microanalysis was carried out by Guelph Chemical Laboratories Ltd., Guelph, Ontario.

Synthesis of $RuHCl(H_2)(PCy_3)_2$ (2a). In a modification of a literature method,[34] a suspension consisting of $[RuCl_2(COD)]_n$ (400 mg, 1.43 mmol), PCy_3 (850 mg, 3.0 mmol), NEt_3 (199 μL, 1.43 mmol), and 2-propanol (20 mL) was stirred at 200 psi H_2 and 80 °C for 40 h. The resulting orange precipitate was filtered off, washed with EtOH (3 × 3 mL) and then cold hexanes (5 × 4 mL), and dissolved in 15 mL of CH_2Cl_2 under H_2. A bright orange solid was obtained by filtering through Celite to remove a dark, insoluble impurity, concentrating to 0.2 mL, and adding 5 mL of cold hexanes under 1 atm of H_2. The precipitate was filtered off, washed with hexanes (3 × 3 mL), and reprecipitated from a minimum volume of toluene by adding hexanes under H_2 and chilling at −35 °C for 1 h, and then dried under vacuum. Yield: 0.511 g (73%). $^{31}P\{^1H\}$ NMR (C_6D_6, Ar): 54.2 (s). ^1H NMR (C_6D_6, Ar): 2.3−0.9 (m, 66 H, Cy), −16.3 (br s, 3H, Ru*H*(H_2). Under N_2, ca. 10% $RuHCl(N_2)(PCy_3)_2$ is observed: δ_P 43.7 (s);[52] δ_H −27.26 (t, 1 H, Ru*H*, $^2J_{PH}$ = 18.3 Hz).

Synthesis of $RuHCl(H_2)(IMes)(PCy_3)$ (2b). Solid IMes (46 mg, 0.15 mmol) was added to orange $RuHCl(H_2)(PCy_3)_2$ **2a** (100 mg, 0.142 mmol) in 5 mL of benzene. No color change is apparent, but $^{31}P\{^1H\}$ NMR monitoring indicated complete reaction at 1.5 h at 23 °C: only signals for free phosphine and **2b** (integration 1:1) were observed in an aliquot removed at this time. The solvent was stripped off, and hexanes (2 mL) added. An orange powder was obtained on cooling to −35 °C overnight. This was filtered off, washed with cold hexanes (3 × 3 mL), and dried under vacuum. Yield: 73 mg (71%; limited by partial solubility in hexanes). $^{31}P\{^1H\}$ NMR (C_6D_6, Ar): 56.3 (s, PCy_3). ^1H NMR: 6.82 (s, 4H, Mes *m*-CH), 6.16 (s, 2H, NCH=C*H*N), 2.37 (s, 12H, *o*-CH_3), 2.14 (s, 6H, *p*-CH_3), 1.88−1.10 (m, 33H, PCy_3), −16.44 (s, 3H, Ru*H*(H_2)). Hydride $T_{1(min)}$: 36.6 ms (C_7D_8, 253 K, 300 MHz; corresponds to a H−H distance of 1.03 Å). $^{13}C\{^1H\}$ NMR: 196.0 (d, $^2J_{PC}$ = 100 Hz, N*C*N), 138.1 (s, Mes *p*-C), 137.1 (s, Mes C_i), 136.5 (s, Mes *o*-C), 129.1 (s, Mes *m*-CH), 121.4 (s, NC=*C*N), 35.3 (d, $^2J_{PC}$ = 17 Hz, Cy), 30.6 (d, $^2J_{PC}$ = 2 Hz, Cy), 28.0 (d, $^2J_{PC}$ = 10 Hz, Cy), 26.9 (s, Cy), 21.1 (s, *p*-CH_3), 19.0 (s, *o*-CH_3). IR (Nujol): ν(Ru−H) 2047 cm^{-1}. Anal. Calcd for $C_{39}H_{60}ClN_2PRu$: C, 64.66; H, 8.35; N, 3.87. Found: C, 64.63; H, 7.98; N, 3.70. NMR spectra under N_2 (24 h) show ca. 70% $RuHCl(N_2)(IMes)(PCy_3)$ **6b**: δ_P 45.0 (s, PCy_3); δ_H −27.63 ppm (d, Ru*H*, $^2J_{HP}$ = 21.4 Hz).

Attempted Synthesis of $RuHCl(H_2)(PCy_3)_2$ 2a from $RuHCl(PPh_3)_3$ 4: Partial Formation of $RuHCl(PCy_3)(PPh_3)_2$ 5. Solid PCy_3 (31 mg, 0.11 mmol) was added to purple **4** (50 mg, 0.054 mmol) in 10 mL of C_6H_6, and H_2 was bubbled through the suspension. No color change was observed after 3 h, but integration of the ^1H NMR signals against the quartet for **4** at −17.5 ppm indicates 70% unreacted **4** in the soluble portion. Complete conversion was hampered by competing decomposition of the product over a further 20 h reaction. $^{31}P\{^1H\}$ NMR for **5** (C_6D_6): 73.3 (d, $^2J_{PP}$ = 118 Hz, 2P, PPh_3), 29.1 (t, $^2J_{PP}$ = 118 Hz, 1P, PCy_3). Key ^1H NMR for **5** (C_6D_6): −18.1 (td, $^2J_{HP}$ = 29 and 18 Hz). $^1H-^{31}P$ HMBC correlations between the $^{31}P\{^1H\}$ NMR doublet and the aromatic ^1H NMR signals support identification of **5** as a bis(PPh_3) complex.

Hydrogenation Reactions. (a) Representative procedure for hydrogenation of molecular substrates. Solid $RuHCl(H_2)(PCy_3)_2$ **2a** (14 mg, 0.0198 mmol) was added to a glass-lined Parr autoclave containing a solution of styrene (2.083 g, 0.020 mol, 1.0 M) with tetrahydronaphthalene as internal standard (1.322 g, 0.010 mol) in 20 mL of C_6H_6 in the glovebox. The autoclave was sealed, removed from the drybox, purged with H_2, and pressurized to 1000 psi H_2 at 23 °C. Samples were analyzed by GC-FID. Kinetic runs on **S1** were monitored by removing 1 mL samples at set time intervals using the sampler tube. The first 0.5 mL was discarded; from the second half, a 5 μL aliquot was removed, diluted to 1.00 mL with CH_2Cl_2, and analyzed (GC). Reactions of other substrates were carried out at a bath temperature of 55 °C. Reactions of **S3** were analyzed by GC-FID; of **S2**, by ^1H NMR.

(b) Representative procedure for hydrogenation of polymer substrates. A solution of **S4** (183 mg, 0.722 mmol, 1.0 M in CH_2Cl_2) with 1,3,5-trimethoxybenzene (51 mg, 0.30 mmol, 0.2 M in CH_2Cl_2) as internal standard was subjected to hydrogenation as above (1000 psi H_2, 55 °C). Following reaction, volatiles were removed under reduced pressure and the residues were dissolved in $CDCl_3$ for ^1H NMR analysis. Conversions were determined through comparison of integrals between olefinic signals (**S4**: br m, 5.58 ppm) and the methoxy singlet of trimethoxybenzene (3.77 ppm). For **S5**, conversions were quantified by comparing the olefinic/galactopyranose C*H* signal at 5.60−5.30 ppm with the galactopyranose C^5 C*H* multiplet at 4.59 ppm.

Thermolysis of 2 and 3. In a representative procedure, a solution of **2a** (8 mg, 0.011 mmol) and O=PPh_3 (4 mg, 0.014 mmol) was dissolved in CH_2Cl_2 (0.75 mL, with a 50 μL spike of C_6D_6 as deuterium lock for shimming) in a J. Young NMR tube. An initial

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$^{31}P\{^{1}H\}$ spectrum was measured to establish the **2a**:$Ph_3P{=}O$ integration ratio at t_o. The NMR sample was then freeze−pump−thaw degassed, backfilled with 1 atm of H_2, and heated.

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Supporting Information Available: NMR spectra for **2b** and thermolysis experiments in CH_2Cl_2; numerical data for Figure 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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