Degradation of the Second-Generation Grubbs Metathesis Catalyst with Primary Alcohols and Oxygen − Isomerization and Hydrogenation Activities of Monocarbonyl Complexes

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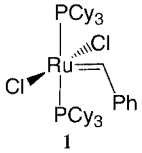
Reaction of the second-generation Grubbs metathesis catalyst [$RuCl_2$(=CHPh)(H_2IMes)(PCy_3)] (**2**) (H_2IMes = 1,3-dimethyl-4,5-dihydroimidazol-2-ylidene) with primary alcohols in the presence of a base produced the complexes [RuClH(CO)(PCy_3)$_2$] (**3**) and [RuClH(CO)(H_2IMes)(PCy_3)] (**5**). When benzyl alcohol was used, the ruthenium phenyl complexes [RuClPh(CO)(PCy_3)$_2$] (**4**) and [RuClPh(CO)(H_2IMes)(PCy_3)] (**7**) were formed in addition to **3** and **5**. Complex **7**, characterised by an X-ray structure analysis, was also formed on exposure of **2** to oxygen. The isomerization and hydrogenation activity of **7** was determined and compared with that of **3** and **4**.

Introduction

With the advent of the Grubbs metathesis catalysts [$RuCl_2$(=CHPh)(PCy_3)$_2$] (**1**) and [$RuCl_2$(=CHPh)(H_2IMes)(PCy_3)] (**2**) olefin metathesis has become an increasingly useful tool for organic transformations.[1] Moreover, these metathesis catalysts can catalyse a number of other reactions,[2] and can also be transformed in situ into various catalytically active species. Single-component tandem catalysis in the presence of **1** and **2** has, so far, included metathesis followed by hydrogenation,[3] dehydrogenation,[3c] and, most recently, isomerization.[4] Relatively little effort, however, has been made to identify the active species responsible for the secondary reaction(s), although various hydride species are thought to be involved.



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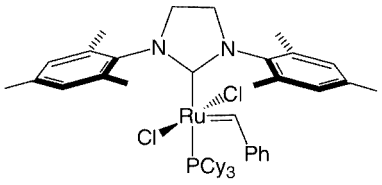

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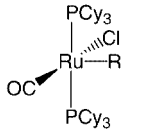
Recently, we[5] and others,[3a−3c,6,7] described how the transformation of the first-generation Grubbs catalyst [$RuCl_2$(=CHPh)(PCy_3)$_2$] (**1**) to the hydride species [RuClH(CO)(PCy_3)$_2$] (**3**) could be affected by aliphatic primary alcohols, and we established that the addition of a suitable base greatly facilitates this reaction. Additionally, if benzyl alcohol is used in place of the aliphatic alcohol, the phenyl complex [RuClPh(CO)(PCy_3)$_2$] (**4**) is produced in good yields. The reactions occur via an alcohol dehydrogenation pathway, with toluene and an alkane being the major organic products. Complex **4** was of particular interest because it was also formed when **1** was treated with oxygen, this reaction being especially effective in the solid state, where the undesirable oxidation of the phosphane ligands is suppressed.

Complexes **3** and **4** proved to be excellent α-olefin isomerization catalysts, producing the β-olefin with high (95%) selectivity. Extending the first-generation research to the important second-generation metathesis catalyst **2** was a natural step. The results of these studies are described here.



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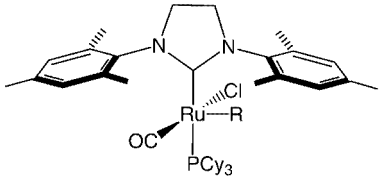
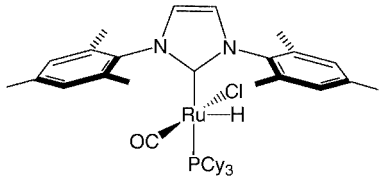
4 R = Ph



5 R = H
7 R = Ph



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Results and Discussion

Reaction of 2 with Primary Aliphatic Alcohols

When the second-generation catalyst **2** was treated with methanol in the presence of triethylamine, the initially dark brown solution slowly became dark orange. Catalyst **2** was more active than the first-generation system **1**, and the reactions proceeded readily at lower temperatures than used previously for **1** (60 vs. 80 °C).[5] However, ^{1}H and ^{31}P NMR spectroscopy revealed an unexpectedly complex reaction in which three different hydrides were produced, in marked contrast to **1** where only one hydride species was formed.[5] Two of these hydride complexes were identified spectroscopically.

The major reaction product (≈30−40% yield by NMR spectroscopy), showing a doublet at δ = −27.8 ppm in the ^{1}H NMR spectrum, was assigned as the expected mixed-ligand hydride species [RuClH(CO)(H_2IMes)(PCy_3)] (**5**). The formation of **5** was verified by comparison of ^{1}H and ^{31}P NMR spectra with those obtained from the model reaction of **3** with H_2IMes. Unfortunately, repeated attempts to isolate complex **5** from either synthetic route were unsuccessful due to the product's extremely high solubility in all common organic solvents, ranging from pentane to methanol. The surprisingly high solubility of **5** — the very closely related complex [RuClH(CO)(IMes)(PCy_3)] (**6**) was reported to be insoluble in methanol[8] — may be because it is not a solid at room temperature. Complex **5** could be precipitated from pentane solutions at −78 °C, but subsequent removal of the supernatant by syringe, followed by warming of the solid to room temperature, gave only a highly air-sensitive, oily residue.

A second hydride (about 25−30% yield by NMR spectroscopy) shows δ = −24.2 ppm as a triplet, and was determined to be complex **3** by comparison with the spectrum of an authentic sample.[5] The formation of complex **3** from **2** is especially noteworthy since it could only have originated from an unexpected H_2IMes ligand exchange with PCy_3. *N*-Heterocyclic carbene (NHC) ligands in ruthenium systems generally show stronger covalent bonds (more exothermic reaction enthalpies) than phosphanes, and so tend not to readily dissociate.[9] We were unable to unambiguously identify the reaction by-products, but the observed ligand exchange must consume the starting material (or products), and should lead to RuCl(H_2IMes) and free H_2IMes fragments which could subsequently combine to produce bis-H_2IMes complex(es). While free H_2IMes displaced PCy_3 in separate reactions (vide infra), in this case any released H_2IMes might also react with the excess alcohol, thereby limiting its immediate availability for further reaction. Reaction of the ligand with alcohol is not available for PCy_3, and so the degradation becomes considerably more complicated than that observed for **1**.

Surprisingly, the addition of an NHC ligand has virtually no effect on the ^{31}P NMR spectrum of the complexes, rendering ^{31}P NMR of less use than usual in monitoring the reaction outcomes; **3**, **5** and **6** show chemical shifts of 47.6,[5] 46.9, and 47.5[8] ppm, respectively.

The third detected hydride species shows a doublet at δ = −7.43 ppm in the ^{1}H NMR spectrum, and was only a minor product (about 10%). While the large downfield shift relative to **3** and **5** suggested a ligand *trans* to the hydride group, the $^2J_{P,H}$ coupling constant of 50.4 Hz is both too high for a phosphorus *cis* and too low for a phosphorus *trans* to the hydride moiety, indicating a distorted coordination environment. The associated phosphorus resonance appears at δ = 47.5 ppm in the ^{31}P NMR spectrum, and so was not separated from those of **3** and **5**.

A fourth, unidentified complex that was definitely not a hydride species shows a phosphorus resonance at δ = 51.2 ppm in the ^{31}P NMR spectrum, and represented about 20−25% of the total phosphorus content of the crude reaction mixture. This peak appeared in a similar location as that found for the reaction of **1** with water,[5] and might arise from the reaction of **2** with adventitious water in the reagents/solvents used.

Ethanol, 1-propanol and 1-nonanol also gave the hydrides **3** and **5** as the dominant products, but with much smaller amounts (<5%) of the unknown hydride. Interestingly, 1-propanol and 1-nonanol gave significantly higher relative yields of **5**; **3**:**5** was 15:85 for these two alcohols, compared with 40:60 and 35:65 for methanol and ethanol, respectively. Ethanol, 1-propanol and 1-nonanol also produced the unknown complex with a ^{31}P NMR peak at δ = 51 ppm, and in approximately the same quantities. Such a significant side-product was never observed in otherwise identical reactions of **1**, further highlighting the quite different behaviour of **1** and **2** in the alcoholic degradation experiments.

The volatile components of the 1-nonanol reaction were analysed by GCMS and showed that, as with **1**, toluene and octane were the major constituents, indicative of an alcohol dehydrogenation/decarboxylation mechanism.[5] Reaction with 1-^{13}C enriched ethanol ($CH_3{}^{13}CH_2OH$) confirmed that the hydride complexes were formed by this pathway. Most of the ^{13}C label was incorporated as the carbonyl groups in **3** and **5**, and the associated hydride signals clearly showed additional coupling due to an adjacent spin-active carbon isotope. A third ^{13}C-labeled carbonyl group, which showed no splitting from phosphorus (singlet), appeared at δ = 204.7 ppm; this complex may possibly be a bis-NHC complex. Interestingly, the third, unidentified, hydride species (δ = −7.43 ppm) showed no additional splitting (remaining a simple doublet), indicating that it does not contain a carbonyl group and, therefore, probably does not form from an alcohol dehydrogenation pathway.

Reaction of 2 with Benzyl Alcohol

As with aliphatic alcohols, when complex **2** was reacted with an excess of benzyl alcohol, in the presence of triethylamine, several products were observed by ^{31}P NMR spectroscopy. This was in sharp contrast to the reaction of **1** with benzyl alcohol under the same conditions, which cleanly generated the phenylruthenium complex **4** in good yield.[5] Again, the main reason for the relatively unsatisfactory reaction is the apparently significant lability of the

H_2IMes ligand under the conditions used, which readily scrambled with the phosphane. Additionally, whereas no hydride complexes formed with **1**, catalyst **2** also produced hydride complexes. Complexes **3** and **5** represented about 25% and 10% of the total phosphorus-containing complexes, respectively, while **4** and the desired product, [RuClPh(CO)(H_2IMes)(PCy_3)] (**7**), were formed in 5% and 30% yield, respectively. The remaining about 30% was due to an unknown species that shows a ^{31}P NMR signal at δ = 51.9 ppm. This chemical shift is very similar to that of the complex(es) formed with aliphatic alcohols, although the about 0.7 ppm difference implies that it may possibly be a slightly different species.

The ^{1}H NMR spectrum revealed that a third hydride species had again formed, in addition to **3** and **5**, but this species was distinct from that present in the aliphatic alcohol reactions, showing a sharp singlet at $\delta = -6.59$ ppm that indicates the complete absence of phosphorus ligands and a substituent *trans* to the hydride atom. This complex might be the bis-carbene [RuClH(CO)(H_2IMes)$_2$], although this could not be confirmed synthetically; complex **3**, with excess H_2IMes, even at 100 °C, gave only the mono-substituted complex **5**. However, this does not rule out a bis-NHC complex; the failure of bis-phosphanes to fully substitute with NHCs can be attributed to the lowered lability of the remaining phosphane after mono-substitution.[6] To gain further insight we analysed the crude reaction mixture by FAB/MS. Unfortunately, this yielded little new information since only **4** and **7** (and their fragmentation products) were detected.

Reaction of 2 with Oxygen

Like complex **1**,[5] complex **2** also reacted with oxygen. However, the reactions were much lower yielding. Thus, **2** reacted with dry air at room temperature in toluene to give, mainly, tricyclohexylphosphane oxide, and only very low amounts of **7**. Furthermore, the diphosphane product **5** was also produced. Higher temperatures gave O=PCy_3 as the only phosphorus-containing species according to ^{31}P NMR spectroscopy.

In the solid state, the reaction of **2** with oxygen (5 bar) was cleaner. Nonetheless, only about 30% of **2** had reacted after 48 h, and, of that, only about 30% was complex **7**. The major product peak in the ^{31}P NMR spectrum appears at δ = 48 ppm, possibly due to O=PCy_3, although the lability of phosphane in the solid state should be relatively low, disfavouring the formation of this product. At higher pressures (50 bar) and 60 °C the complete reaction of **2** was achieved over three days to give, after workup, a 29% yield of the air-stable, bright pink **7**. The fate of the remaining **2** could not be determined; a phosphorus-containing material gave a ^{31}P NMR peak at δ = 54.4 ppm, but could not be isolated. The lower reactivity of **2** compared with **1** towards oxygen is foretold by its superior air tolerance; it can even be purified by chromatography using non-degassed solvents.[10] Nonetheless, the NHC ligand, being a better σ-donor than phosphanes, should render the ruthenium more electron-rich, thereby increasing the nucleophilicity of the benzylidene group toward an electrophile.[11]

Unsurprisingly, complex **7** was more easily prepared, and in better yield, by reaction of **4** with H_2IMes in toluene at 100 °C.

Crystal Structure of 7

Red blocks of **7** suitable for X-ray diffraction were grown by the slow evaporation of a CH_2Cl_2/MeOH solution in air. Figure 1 shows the structure of **7**, with selected bond lengths and angles in the caption.

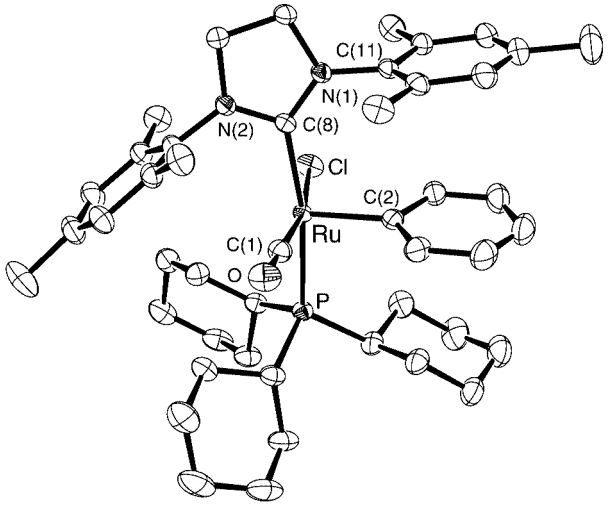

Figure 1. ORTEP representation of complex **7** with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and angles (°): Ru−Cl 2.4542(8), Ru−P 2.4499(7), Ru−C(1) 1.805(3), Ru−C(2) 2.039(3), Ru−C(8) 2.118(3), O−C(1) 1.142(4), N(1)−C(8) 1.335(3), N(2)−C(8) 1.345(4); P−Ru−Cl 89.76(3), Cl−Ru−C(1) 168.6(1), Cl−Ru−C(2) 102.7(1), Cl−Ru−C(8) 86.05(7), P−Ru−C(1) 89.6(1), P−Ru−C(2) 94.25(8), P−Ru−C(8) 168.81(7), C(1)−Ru−C(2) 88.7(1), C(1)−Ru−C(8) 92.5(1), C(2)−Ru−C(8) 96.8(1), Ru−O−C(1) 179.2(3)

The ruthenium occupies a typical distorted square-pyramidal coordination geometry. As in related structures, the halogen is *trans* to the carbonyl moiety, so that the phosphorus is *trans* to the other neutral ligand (in this case H_2IMes). Somewhat surprisingly, few structures of complexes of the type [RuArCl(L)$_2$(CO)] (Ar = aromatic, L = phosphane) have been described,[12] and **7** is the first example containing an NHC ligand.

Overall, the structure most closely resembles that of the hydride complex **6** determined by Nolan,[8] with the phenyl group in **7** residing at the position of the hydride at the apex of the pyramid. The main distortions from an ideal square-pyramidal geometry are the P−Ru−C(8) and Cl−Ru−C(1) angles (both about 169°), which compare with analogous angles of 173.4 and 175.9°, respectively, in **6**. The increased distortion is most likely due to the higher steric influence of the phenyl group in **7** relative to the hydrogen in **6**. Surprisingly, the Ru−C(8) and Ru−P distances in **7** are significantly longer (0.035 and 0.083 Å, respectively) than in **6**; typically, these bond lengths are not greatly affected when

saturated (H_2IMes) or unsaturated (IMes) NHC ligands are present. Conversely, the Ru−CO bond length in **7** is longer (0.021 Å) than in **6**, concomitant with a shortening (0.038 Å) of the C≡O distance. The different electronic influences of the unsaturated (in **6**) and saturated (in **7**) NHC ligands are probably not responsible for these discrepancies. The increased steric demands of the phenyl group are probably the dominant influence, since the pushing back of the neutral ligands may result in less-ideal orbital overlaps with the metal center. The phenyl ring and one of the mesityl groups are in close contact, and almost perfectly eclipse one another. Because the two rings are not quite co-planar, forming a butterfly angle of 10.0(2)°, C(2)···C(11) represents the minimum distance between the rings at 3.259 Å.

Isomerization Activity of Complexes 3, 4 and 7

Previously we reported that complexes **3** and **4**, while totally metathesis inactive, were potent C=C bond isomerization catalysts for α-olefins.[5] Wagener et al. have recently made a detailed study of the double-bond isomerization activity of the first- and second-generation Grubbs catalysts **1** and **2**, and compared that with the Mo-based Schrock metathesis catalyst.[13] Double-bond isomerization is highly relevant in metathesis chemistry because it is the primary cause of secondary metathesis products; this is generally considered to be a major limitation of olefin metathesis. Nonetheless, double-bond isomerization has also recently been deliberately exploited in a tandem metathesis-isomerization reaction for the synthesis of cyclic enol ethers[4] in which the metathesis catalysts **1** or **2** were converted by hydrogen, after metathesis had ceased, into uncharacterised isomerization catalysts. We decided to determine the isomerization activity of complex **7** towards 1-octene, and compare this with the first-generation systems **3** and **4**.

As we recently reported for metathesis catalysed by **1** and **2**,[14] additional solvents were unnecessary in the isomerization reactions. Because solvents are a major hurdle in the development of "green" chemistry, any reactions where they are not required are particularly relevant to this increasingly timely area.[15] Figure 2 summarises the 1-octene isomerization activity of **7** over a range of temperatures. In each case, the reactions were allowed to proceed to maximal conversion, and, for comparison, the results for **3** and **4** under the same conditions are included.

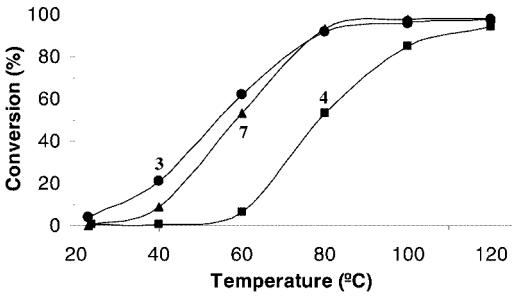

Figure 2. Double-bond isomerization of neat 1-octene (100,000 equivalents) in the presence of catalysts **3**, **4** and **7** as a function of reaction temperature; all reactions were allowed to proceed until 1-octene was no longer consumed

From Figure 2, the hydride complex **3** remains the most active catalyst with respect to turnover number. At lower temperatures, the phenyl-substituted analogue of **3**, complex **4**, displayed considerably lower activity, and was essentially inactive below 50 °C, possibly because the active species has to be generated in situ − for both **3** and **4** this active species is likely to be [RuClH(CO)(PCy_3)].[16] The NHC-substituted analogue **7** was almost as active as the hydride **3**. The loss in activity associated with substituting the hydride moiety (in **3**) for a phenyl group (in **4**) is at least partially offset by the increase in activity associated with replacing one of the tricyclohexylphosphane ligands with H_2IMes (in **7**). Unfortunately, as mentioned above, the H_2IMes-substituted hydride **5** could not be obtained in a sufficiently pure form for comparison.

Interestingly, at higher temperatures, and especially after prolonged reaction times, metathesis products (predominantly tridecene and dodecene, from the cross-metathesis of 1-octene with 2-octene and the self-metathesis of 2-octene, respectively) were detected in the reactions involving catalyst **7**. While these longer chain olefins represented only about 3−5% of the reaction products, it is noteworthy that only the NHC-containing compound initiated only metathesis, i.e. metathesis products have never been observed in reactions involving **3** and **4**.

Figure 3 depicts the relative reaction rates and selectivity over time for the isomerization of 1-octene into 2-octene at 100 °C. Catalyst **7** is clearly much more active than either **3** or **4**. Again, the presumed loss of activity due to the exchange of a hydride for a phenyl group is more than compensated for by the addition of the NHC ligand. Indeed, 97% conversion of 100,000 equivalents of 1-octene in the presence of **7** was achieved in less than 5 minutes, with 95% selectivity for 2-octene. For each catalyst, the selectivity for 2-octene formation rapidly decreased once all of the 1-octene had been consumed. Thus, the selectivity after 8 h was highest for catalyst **4**, followed by **3** and finally **7**, coinciding with their relative activities. We had previously determined that catalyst **4** could not isomerise 2-octene, and so the decrease in selectivity is primarily due to decomposition of the active catalyst into unknown ruthenium complexes that

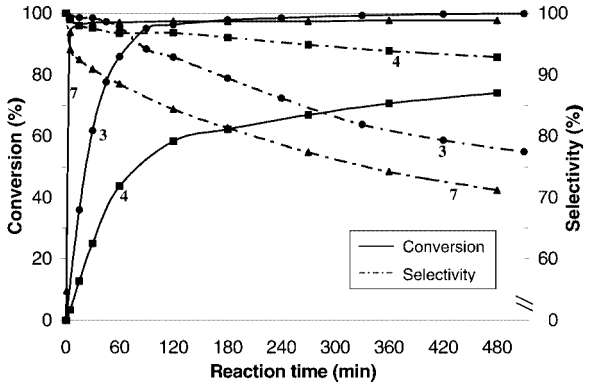

Figure 3. Double-bond isomerization of neat 1-octene (100,000 equivalents) into 2-octene at 100 °C in the presence of catalysts **3**, **4** and **7** as a function of reaction time

Table 1. Hydrogenation of 1-octene in the presence of catalysts **3**, **4** and **7**, under various reaction conditions

T (°C)	$P(H_2)$ (bar)	Cat.	Equiv. of 1-octene[a]	Reaction time (h)	Conversion (%)	Selectivity (%)[b]	Isomerization products (%)[c]
23	4	3	100,000	18	99.9	100	0
23	4	4	100,000	18	1.6	100	0
23	4	7	100,000	18	0.4	100	0
100	4	3	100,000	3	98.7	100	0
100	4	4	100,000	3	98.5	100	0
100	4	7	100,000	3	99.3	100	0
100	4	3	350,000	2	98.3	84.1	15.6
100	4	4	350,000	2	98.5	90.2	9.7
100	4	7	350,000	2	99.1	58.9	40.7
100	1	3	250,000	3	98.5	95.3	3.2
100	1	4	250,000	3	99.6	77.8	22.1
100	1	7	250,000	3	99.1	81.4	18.4

[a] Mol of 1-octene per mol of catalyst. [b] Selectivity towards the formation of octane. [c] Isomerization products: 2-, 3-, and 4-octene.

are also catalytically active toward olefin isomerization but lack the selectivity (and activity) of the parent catalyst.[5] The *cis* to *trans* ratio of the 2-octene produced for each catalyst was approximately 30:70.

Hydrogenation Activity of 3, 4 and 7

Hydrogenation of alkenes is an important organic transformation, and can be facilitated by traditional homogeneous catalysts such as $[RhCl(PPh_3)_3]$ (Wilkinson catalyst), $[RuClH(PPh_3)_3]$ and $[RuH(CO)(PPh_3)_3]$.[17] More recently, catalyst **3** has been found to be an excellent olefin hydrogenation catalyst,[8,16,18] and has also been exploited for the hydrogenation of polybutadiene rubber.[19] Furthermore, the second-generation analogue **6** has recently been tested for hydrogenation activity, and displayed activity similar to **3** at higher temperatures.[8] Due to the current interest in single-component tandem metathesis-hydrogenation reactions,[3] we tested the efficacy of catalysts **4** and **7** for the hydrogenation of 1-octene, and compared the results with those of **3** (Table 1). Various reaction conditions were tested, and, again, the reaction proceeds very well in neat substrate, i.e. no additional solvents were required for good conversions and reaction rates.

From the data in Table 1 catalyst **3** is clearly the most active catalyst for the hydrogenation of 1-octene. Indeed, only **3** shows appreciable hydrogenation activity at room temperature. At 100 °C, **4** and **7** were "activated", and also became good hydrogenation catalysts, comparable in activity to **3**, and gave complete conversion into octane when 100,000 equivalents (mol) of 1-octene were reacted.

To better test the limits of the catalysts, reactions with lower catalyst loadings were examined. Thus, 350,000 equivalents (mol) of 1-octene were hydrogenated in the presence of **3**, **4** or **7** at 100 °C. All the catalysts consumed the 1-octene completely, but none gave selective conversion into octane. Catalysts **3** and **4** showed comparable activity and selectivity, whereas **7** produced lower amounts of octane, with isomerization clearly competing with the hydrogenation. This result is perhaps not surprising given the very high activity of **7** with regard to isomerization (vide supra), while the hydrogenation activity of **7** towards 2-octene is clearly lower.

Remarkably, the absence of solvent may benefit these reactions. Whereas Nolan reported turnover rates for the hydrogenation [$P(H_2)$ = 4 bar) of 1-hexene in benzene at 100 °C of 21,500 and 24,000 (mol product)(mol catalyst)$^{-1}h^{-1}$ for **3** and **6**, respectively,[8] we attained turnover frequencies of well over 100,000 h^{-1} for all the systems tested at 100 °C, even at only $P(H_2)$ = 1 bar.

Conclusions

The chemistry previously developed for the first-generation ruthenium metathesis catalyst **1**,[5] could be extended to include the second-generation catalyst **2**. However, the reactions were complicated by an unanticipated exchange involving the NHC ligand, even at relatively low temperatures (60 °C). The lability of the NHC ligand allowed not only the formation of the desired mixed-ligand systems, but also the corresponding diphosphane complexes. In theory these complexes could hinder olefin metathesis reactions that employ **2** in alcoholic solvents, but the higher temperatures and relatively long time needed for their formation limits their role in potential side-reactions.

Complex **7**, a fully air-stable solid, is a highly active isomerization catalyst − considerably more active than either of the first-generation systems **3** and **4**. We tentatively suggest that the higher σ-donation of the NHC ligand (relative to phosphanes), which ultimately renders the second-generation metathesis catalysts more active than their first-generation congeners, may also explain their (or their decomposition products') efficacy as isomerization catalysts. We also found that complexes **4** and **7** are efficient hydrogenation catalysts at higher temperatures, which may aid in the development of single-component tandem metathesis-hydrogenation of olefins[3a,3b] when employing the second-generation metathesis catalysts.

Experimental Section

Unless otherwise stated, all manipulations were performed under a nitrogen atmosphere on a vacuum line using standard Schlenk techniques. Complex **1** (Fluka), potassium *tert*-pentoxide solution (1.7 M in toluene, Fluka), and 1-octene (98%, Aldrich) were obtained from commercial sources. 1,3-Dimesityl-4,5-dihydroimidazolinium chloride[20] and the complexes **2**,[21] **3**,[22] and **4**[5] were prepared by the literature procedures. NMR spectra were recorded on a Varian Mercury 300 spectrometer, at 300.14, 75.48 and 121.50 MHz for the proton, carbon and phosphorus channels, respectively. Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Germany.

[RuClH(CO)(H_2IMes)(PCy_3)] (5): Potassium *tert*-pentoxide solution (1.7 M in toluene, 260 μL, 0.442 mmol) was added to a suspension of 1,3-dimesityl-4,5-dihydroimidazolinium chloride (0.150 g, 0.437) in toluene (5 mL) and stirred for 10 min. The resulting solution was transferred, via a steel cannula fitted with a filter, to a second flask containing a toluene (2 mL) solution of **3** (0.100 g, 0.138 mmol). The mixture was then heated to 100 °C for 3 h. No colour change was observed. The solvent was removed under reduced pressure, leaving an oily residue that was miscible with all common organic solvents at room temperature. Cooling a concentrated pentane solution to −78 °C produced a yellow solid. The mother liquor was then carefully removed by syringe and the solid allowed to warm to room temperature, during which time it slowly melted. The resultant highly air-sensitive oil was spectroscopically characterised as complex **5** (≈75% purity). IR (toluene): $\tilde{\nu}$ = 1896 cm^{-1} (vs, C≡O). ^1H NMR (CD_2Cl_2): δ = 25.37 (d, J_{HP} = 21.3 Hz, 1 H, Ru-*H*), 2.5−1.1 (multiple peaks, 51 H, H-aliphatic), 3.17 (br. s, 2 H, CH_2CH_2), 3.78 (br. s, 2 H, CH_2CH_2), 6.80 (br. s, 2 H, $C_6Me_3H_2$), 6.99 (br. s, 2 H, $C_6Me_3H_2$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 46.7 ppm.

[RuClPh(CO)(H_2IMes)(PCy_3)] (7), Method A: Potassium *tert*-pentoxide solution (1.7 M in toluene, 220 μL, 0.374 mmol) was added to a suspension of 1,3-dimesityl-4,5-dihydroimidazolinium chloride (0.130 g, 0.379) in toluene (4 mL) and stirred for 10 min. The resulting solution was then transferred, via a steel cannula fitted with a filter, to a second flask containing a toluene (2 mL) solution of **4** (0.100 g, 0.125 mmol). The mixture was heated to 100 °C for 3 h, during which time the solution became a brighter orange/red. The solvent was then removed under reduced pressure, and methanol subsequently added to the residue. Rapid stirring (1 h) produced a bright pink precipitate, which was collected by filtration and then washed with methanol (4 × 10 mL) and pentane (2 × 5 mL) to give complex **7** as a crimson powder (0.072 g, 70%).

Method B: Finely powdered **2** (0.050 g, 0.059 mmol) was deposited as a solid in an autoclave that was subsequently pressurised with oxygen (50 bar) and then heated in an oil bath to 60 °C for 3 days. After releasing the pressure, workup in the same manner as Method A gave complex **7** (0.014 g, 29%). IR (KBr): $\tilde{\nu}$ = 1901 cm^{-1} (vs, C≡O). ^1H NMR (CD_2Cl_2): δ = 1.07 [m, 11 H, $P(C_6H_{11})_3$], 1.24 [m, 4 H, $P(C_6H_{11})_3$], 1.54 (s, 3 H, *p*-Me $C_6Me_3H_2$), 1.62 [br. s, 14 H, $P(C_6H_{11})_3$], 1.88 [m, 4 H, $P(C_6H_{11})_3$], 2.20 (s, 9 H, *o*-Me/*p*-Me $C_6Me_3H_2$), 2.63 (s, 6 H, *o*-Me $C_6Me_3H_2$), 3.85 (br. s, 4 H, CH_2CH_2), 5.89 (d, $^3J_{H,H}$ = 7.50 Hz, 1 H, *m*-H C_6H_5), 6.24 (d, $^3J_{H,H}$ = 7.20 Hz, 1 H, *p*-H C_6H_5), 6.30 (d, $^3J_{H,H}$ = 7.50 Hz, 1 H, *m*-H C_6H_5), 6.46 (br. s, 2 H, $C_6Me_3H_2$), 6.83 (d, $^3J_{H,H}$ = 7.80 Hz, 1 H, *o*-H C_6H_5), 6.88 (s, 2 H, $C_6Me_3H_2$), 7.14 (d, $^3J_{H,H}$ = 7.20 Hz, 1 H, *o*-H C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 19.3, 19.4 (*o*-Me/*p*-Me $C_6Me_3H_2$), 21.2 (*o*-Me $C_6Me_3H_2$), 26.9 [s, $P(C_6H_{11})_3$], 28.4 [d, $J_{C,P}$ = 8.5 Hz, $P(C_6H_{11})_3$], 29.6 [d, $J_{C,P}$ = 16.6 Hz, $P(C_6H_{11})_3$], 34.5 [d, $J_{C,P}$ = 16.2 Hz, $P(C_6H_{11})_3$], 118.5, 124.3, 125.6, 129.6, 130.0, 136.2, 136.8, 137.1, 138.2, 139.1, 140.5 (C-Ar), 155.9 (d, $^2J_{C,P}$ = 12.0 Hz, *i*-C C_6H_5), 205.6 (d, $^2J_{C,P}$ = 13.7 Hz, Ru-*C*O), 210.8 [d, $^2J_{C,P}$ = 94.9 Hz, Ru-*C*$(N)_2$] ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 22.2 ppm. $C_{46}H_{64}ClN_2OPRu$: calcd. C 66.69, H 7.79, N 3.38; found C 66.78, H 7.72, N 3.31.

Isomerization Reactions: Immediately before use, the 1-octene was passed through a column (20 cm × 1.5 cm) of neutral alumina (Acros, 50-200 μm), containing 15 g of alumina per 100 mL of octene, into a Schlenk flask. The 1-octene was then deoxygenated by a series of degassings (by evacuation of the flask), followed by refilling with nitrogen. For each reaction, 20 mL (127 mmol) of 1-octene was used. The reaction vessel was immersed in an oil bath and allowed to equilibrate to the desired temperature. An appropriate quantity (six-figure analytical balance) of the catalyst under investigation was then added to the 1-octene. No additional solvents were used. All reactions were thoroughly stirred, by way of a magnetic stirrer bar, and were allowed to proceed to completion, i.e. the reported results are those obtained when 1-octene consumption had ceased. The product distribution of the isomerization reactions was measured by GC/FID (Carlo Erba 8000 Top) using a ZB-5 (5% phenyl polysiloxane) column (Zebron).

Hydrogenation Reactions: 1-Octene was prepared in the manner described above for the isomerization reactions. A small quantity of the catalyst under investigation was introduced into an autoclave fitted with a glass liner, and the autoclave was subsequently evacuated and flushed with hydrogen. 1-Octene (10 mL) was introduced by syringe, and the autoclave pressurised with the desired level of hydrogen; this pressure was maintained throughout the experiment. The autoclave was heated, where appropriate, by way of an oil bath. After completion of the reaction, the hydrogen was vented off, and the solution analysed as for the isomerization reactions.

Crystal Structure Determination of 7: Red blocks of **7** suitable for X-ray diffraction were grown by the slow evaporation of a CH_2Cl_2/MeOH solution. Intensity data were collected on an Enraf−Nonius CAD-4 diffractometer, using a crystal of dimensions 0.50 × 0.45 × 0.125 mm, with graphite-monochromated Mo-K_α X-rays (λ = 0.71069) and ω-2θ scan. A total of 7461 unique reflections in the range 1.6° < 2θ < 25° were collected at room temperature, and these were subsequently corrected for Lorentz effects, polarization effects, and for linear absorption by a Ψ-scan method. Crystal data: $C_{46}H_{64}ClN_2OPRu$, FW = 828.48, crystal class monoclinic, space group $P2_1/c$, a = 12.2573(8), b = 15.6707(12), c = 22.358(4) Å, β = 94.686(10)°, V_c = 4280.2(9) $Å^3$, D_c = 1.286 g cm^{-3}, Z = 4, $F(000)$ = 1752, μ(Mo-K_α) = 0.502 mm^{-1}.

The structure of **7** was solved using the direct methods option of SHELXS-97[23] and subsequently refined using SHELXL-97.[24] All non-hydrogen atoms were assigned anisotropic temperature factors and all hydrogen atom positions were determined by calculation. For the methyl groups of the mesityl substituents, where the location of the hydrogen atoms was uncertain, the AFIX 137 card was used to allow the hydrogen atoms to rotate to the maximum area of residual density, while fixing their geometry. The refinement converged with R_1 = 0.0422 for 6751 data with $I \geq 2\sigma(I)$, 0.0466 for all data; wR_2 = 0.1146 $\{w = 1/[\sigma^2(F_o^2) + (0.0752P)^2 + 2.3804P]$ where $P = (F_o^2 + 2F_c^2)/3\}$, and GoF = 1.046. No parameter shifted in the final cycle. The final difference map showed no peaks or troughs of electron density greater than +1.29 and −1.02 e·$Å^{-3}$ respectively, both near Ru.

CCDC-199892 contains the supplementary crystallographic data for complex **7**. These data can be obtained free of charge at

www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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