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Degradation of the First-Generation Grubbs Metathesis Catalyst with Primary Alcohols, Water, and Oxygen. Formation and Catalytic Activity of Ruthenium(II) Monocarbonyl Species

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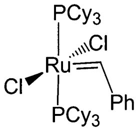
The first-generation Grubbs metathesis catalyst $(PCy_3)_2Ru({=}CHPh)(Cl)_2$ (**1**) was reacted with primary alcohols at 70 °C to give the monohydride species $(PCy_3)_2(CO)Ru(Cl)(H)$ (**4**) in ∼20% yield. Addition of either an inorganic or organic base greatly facilitated the formation of the hydride, and **4** could be isolated in >70% yield in the case of 1-propanol and triethylamine. Analysis of the reaction products and labeling experiments revealed that **4** was formed via a noncatalytic alcohol dehydrogenation pathway. When benzyl alcohol was used, $(PCy_3)_2(CO)Ru(Cl)(Ph)$ (**5**) was formed, this also being one of the products of the decomposition of **1** by oxygen in both solid and solution states. Complexes **4** and **5** were found to be active and selective alkene double-bond isomerization catalysts.

Introduction

The olefin metathesis catalyst systems **1** and **2a** have attracted considerable attention over the past few years, largely as a consequence of their excellent functional group tolerance, ease of use, and relatively high catalytic activity.[1] Metathesis in the presence of hybrids of **1** and **2a** bearing solubilizing functional groups can even be carried out in protic media, such as alcohols and water.[2]



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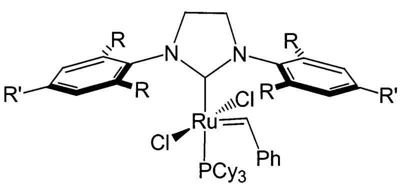

2a R = R' = Me

2b R = Pr^i, R' = H

Recently, we prepared and characterized the second-generation ruthenium complex **2b**, studied its olefin metathesis activity, and compared this with that of **1** and **2a**.[3] Complex **2b** had also been published by Fürstner, but its isolation was reported to be hindered, owing to the formation of a byproduct.[4] Although experimental and spectroscopic details for this byproduct were not reported, its crystal structure was determined and assigned as the Ru(IV) dihydride $(PCy_3)_2Ru(Cl)_2(H)_2$ ("**3**"). The ruthenium appeared to occupy an octahedral coordination environment, with the chlorine, phosphine, and hydride pairs all mutually trans to their counterparts. The structure was especially remarkable in light of a previously characterized analogue of "**3**", $(PPr^i)_2Ru(Cl)_2(H)_2$, which was found to have a distorted-square-antiprismatic geometry.[5]

We were intrigued by the formation of complex "**3**" during the synthesis of **2b**, since we have not observed such a species in any of several preparations of **2b**, despite using very similar reaction protocols.[3] Additionally, we wondered if this material, as proposed by Fürstner,[4] was indeed a candidate for the hitherto unknown compound(s) responsible for the double-bond isomerization seen in some of the reactions using ruthenium metathesis catalysts.[3,6] While various hydride complexes have been prepared by reaction of **1** with dihydrogen,[7] "**3**" had clearly formed without dihydrogen as a reagent. Grubbs has recently described the formation of the square-pyramidal monohydride complex $(PCy_3)_2(CO)Ru(Cl)(H)$ (**4**) from the thermal decomposition of $(PCy_3)_2Ru({=}CHOEt)(Cl)_2$ (eq 1),[8] and we wondered if there was more than a merely superficial resemblance of this reaction and the byproduct "**3**".

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(1) (a) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29. (b) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413−4450.

(2) (a) Connon, S. J.; Blechert, S. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 1873−1876. (b) Rölle, T.; Grubbs, R. H. *Chem. Commun.* **2002**, 1070−1071. (c) Lynn, D. M.; Mohr, B.; Grubbs, R. H.; Henling, L. M.; Day, M. W. *J. Am. Chem. Soc.* **2000**, *122*, 6601−6609.

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(4) Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem. Eur. J.* **2001**, *7*, 3236−3253.

(5) Grünwald, C.; Gevert, O.; Wolf, J.; González-Herrero, P.; Werner, H. *Organometallics* **1996**, *15*, 1960−1962.

(6) (a) Bourgeois, D.; Pancrazi, A.; Nolan, S. P.; Prunet, J. *J. Organomet. Chem.* **2002**, *643*−*644*, 247−252. (b) Fürstner, A.; Thiel, O. R.; Ackermann, L.; Schanz, H.-J.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 2204−2207.

(7) (a) Fogg, D. E.; Amoroso, D.; Drouin, S. D.; Snelgrove, J.; Conrad, J.; Zamanian, F. *J. Mol. Catal. A: Chem.* **2002**, *190*, 177−184. (b) Drouin, S. D.; Zamanian, F.; Fogg, D. E. *Organometallics* **2001**, *20*, 5495−5497. (c) Drouin, S. D.; Yap, G. P. A.; Fogg, D. E. *Inorg. Chem.* **2000**, *39*, 5412−5414. (d) Oliván, M.; Caulton, K. G. *Inorg. Chem.* **1999**, *38*, 566−570. (e) Sutton, A. E.; Seigal, B. A.; Finnegan, D. F.; Snapper, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 13390−13391.

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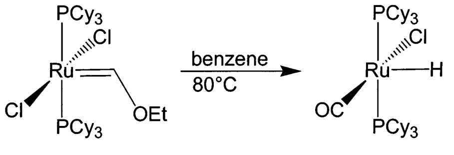

(1)

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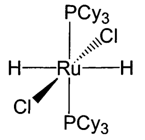
We decided to investigate these curious results further and have discovered that **4** can also be synthesized by reaction of **1** with primary alcohols in the absence of dihydrogen. We now report the results of these studies.



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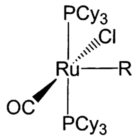
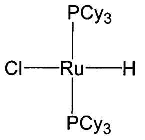


4 R = H
5 R = Ph



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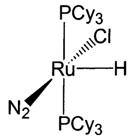

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Results and Discussion

When catalyst **1** was reacted with an excess of methanol in toluene at 70 °C for 2 days, the initially purple-red solution gradually became clear dark orange. The progress of the reaction was monitored by ^{31}P NMR, which showed the slow disappearance of the signal at 37.3 ppm from **1** concomitant with the emergence of a new peak at 47.5 ppm, among others.[9] Similarly, in the ^{1}H NMR, the benzylidene resonance from **1** at 20.6 ppm was gradually replaced by a hydride signal at -24.3 ppm. Whereas ethanol and 1-propanol were also found to readily generate the hydride, 2-propanol and water (vide infra) were found to be ineffective and only other, unknown, products were observed in the ^{31}P and ^{1}H NMR spectra.

Addition of a suitable base (organic or inorganic) was found to greatly facilitate the hydride-forming reaction, in terms of both rate of formation and yield. When 1 equiv of sodium methoxide or sodium hydroxide or $^1/_2$ equiv of potassium carbonate, dissolved in methanol, was added to a toluene solution of **1** at 70 °C, the reaction was complete in 15 min, giving an ~50% yield of the hydride by ^{31}P NMR (35% isolated). The use of an organic base also stimulated hydride formation, and ~85% yield by ^{31}P NMR (73% isolated) of the hydrido species was obtained when using 1-propanol together with triethylamine. In this case, however, the reaction rate was significantly lower, with ~24 h needed for the complete consumption of **1**. Interestingly, in the presence of triethylamine, water could be used in lieu of a primary alcohol, although only a modest amount (~30%) of hydride was formed in this case. 2-Propanol remained essentially unreactive with regard to hydride formation even with the added bases; the very low yields of hydride detected are possibly attributable to adventitious water in the reagents. In all instances, the heating of the reaction proved beneficial for both the high conversion of **1** and moderate yields of the hydride, although when bases were used the hydride was generated even at room temperature.

The isolated hydride complex was a bright yellow powder and was air stable in the solid state for a few hours before noticeable decomposition occurred; solid samples could be easily handled in air. Solutions of the hydride under nitrogen were thermally stable, but exposure to air, even at room temperature, resulted in their rapid decomposition.

While full spectroscopic data for the dihydride complex "**3**" have not been published, the hydride peak in the ^{1}H NMR was reported to appear at -24.38 ppm.[4] We had therefore initially assigned our ruthenium hydride species as the dihydride complex "**3**". However, certain aspects of this designation were found to be inconsistent. The integration of the ^{1}H NMR spectrum of our complex clearly showed a hydride to tricyclohexylphosphine ratio of 1:2, as opposed to the 1:1 expected for "**3**". Furthermore, the elemental analysis (EA) data for our complex did not fit those required for $(PCy_3)_2$-$Ru(Cl)_2(H)_2$ ("**3**"), giving a carbon percentage that was too high. Finally, IR data strongly indicated the presence of a carbonyl group. The NMR, EA, and IR data together suggested the formula of our hydrido species was in fact that of the *monohydride monochloride* $(PCy_3)_2(CO)Ru(Cl)(H)$ (**4**).

Fogg et al. have recently suggested that complex **4** might be formed as a byproduct from the stoichiometric hydrogenolysis of **1** with methanol/dichloromethane in the presence of triethylamine, although it was not isolated.[7a,b] Our results verify this observation, but it is noteworthy that hydrogen is in fact not necessary for the formation of **4**. The species **4** is a relatively well-known system that has been previously reported and crystallographically characterized by both Grubbs[8] and Nolan[10] and can be readily synthesized from the reaction of $[(cod)Ru(Cl)_2]$ (cod = 1,5-cyclooctadiene), PCy_3, and ethanol.[11] The reported spectroscopic properties of **4**[8,11] were indistinguishable from those obtained from our samples generated by the degradation of **1**.

Mechanism for the Formation of 4. Notwithstanding that a number of aspects regarding the decomposition of catalyst **1** have been studied in some detail,[12] the identity of the approximately eight inorganic phosphorus-containing species observed in the ^{31}P NMR have not yet been elucidated. Therefore, the mechanism for the reaction of **1** with an alcohol to form **4** is of interest, since it may shed some light on a possible decomposition pathway for **1**, particularly when primary alcohols and/or water are present.

We wondered what the actual source of the hydride atom was: the alcohol group, the benzylidene moiety, and alcohol dehydrogenation[13] were all considered.

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(9) Other significant resonances in the ^{31}P NMR spectrum were two single peaks at 36.1 and 25.9 ppm, together with multiple peaks around 73 ppm. Some free PCy_3 (10.5 ppm) was also evident. The NMR yield of **4** was ~30%.

(10) Lee, H.-M.; Smith, D. C.; He, Z.; Stevens, E. D.; Yi, C. S.; Nolan, S. P. *Organometallics* **2001**, *20*, 794−797.

(11) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043−2045.

(12) Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202−7207.

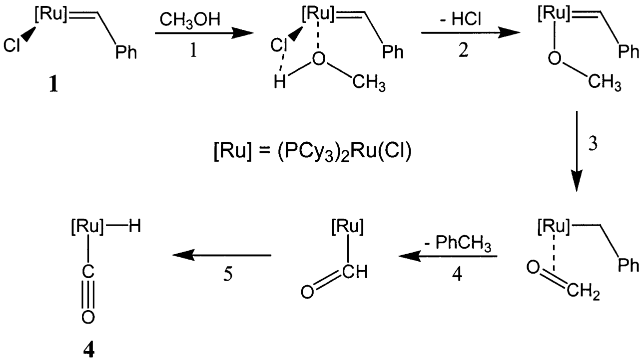
Initially we postulated that the alcohol group might add to the benzylidene in **1**, eliminating benzene, among other products. The resulting intermediate species could then eliminate RCl, in a fashion similar to that recently described by Grubbs for the decomposition of ruthenium Fischer-type carbene complexes of the type $(PCy_3)_2Ru({=}CHOR)(Cl)_2$.[8,14] However, Fischer-type carbene complexes show good stability;[8] still, we had not observed this intermediate species in the NMR spectra of the decomposition reaction mixtures. Furthermore, GC analysis of the reaction mixture when 1-nonanol was used as an alcohol source revealed that no chlorononane was formed. In fact, octane was detected, this strongly suggesting that alcohol dehydrogenation, possibly by partially decomposed **1**, was the primary source of the hydride moiety in **4**. The dehydrogenation of alcohols provides a source of aldehydes, which can react with ruthenium species via decarboxylation to give carbonyl and hydride moieties.[13] The continuing presence of the relatively small excess of alcohol (5−10 equiv), even after prolonged reaction times, showed that the dehydrogenation was noncatalytic. To add further insight into the mechanism for the reaction of **1** with alcohols, a number of additional experiments were carried out.

To trace the origin of the hydride group in **4**, this being most likely from the CH_2 group adjacent to the alcohol moiety,[13a,b] we reacted **1** with CH_3CH_2OD. As predicted, predominantly nondeuterated **4** formed, although some deuterated material, $(PCy_3)_2(CO)Ru(Cl)(D)$ (**4-*d***), was also present. The formation of some **4-*d*** could be explained by the observation that the hydride moiety in isolated samples of **4** readily underwent deuterium exchange (to give **4-*d***) when treated with excess CH_3CH_2OD under the reaction conditions used for the generation of **4** from **1**.

We also analyzed the organic byproducts of the various degradation experiments by NMR and GC/MS. The composition of the *nonvolatile* reaction residues was found to be very complex, due to the presence (and decomposition) of unknown ruthenium compounds, and the only product that could be unambiguously identified (by comparison of its spectral data with that of authentic samples) was *cis*- and *trans*-stilbene (ratio ~90:10). While stilbene was also found to be a thermal decomposition product of **1** by Grubbs,[12] we were not wholly convinced that this was the only fate of the benzylidene group. Therefore, the deuterated analogue of the Grubbs catalyst, $(PCy_3)Ru({=}CDPh)(Cl)_2$ (**1-α-*d***), was synthesized and reacted with methanol (10 equiv) in the presence of triethylamine (10 equiv), and the reaction products were subsequently analyzed with ^2H NMR spectroscopy.

Confirming that H_α from the benzylidene is not a source for the hydride in **4**, we observed no detectable amounts of **4-*d*** when reacting **1-α-*d*** with methanol. Noteworthy is the fact that we did observe small amounts (~12% of total D) of CH_3OD in the ^2H NMR spectrum, indicating that some exchange had taken place. This was later verified in a ^1H NMR experiment, where we clearly observed gradual loss in the deuterium enrichment of the H_α.[15] However, exchange with the alcohol was not the main fate of the deuterium label.

Scheme 1



The dominant feature of the ^2H NMR spectrum was a resonance at 7.2 ppm (~25%). We assigned this signal predominantly to C_6H_5D and possibly some *trans*-styrene-d_2 (7.1 ppm), although the cis form (6.6 ppm) was not detected. Interestingly, the remainder of the deuterium atoms (~60%) were present in a number of products showing chemical shifts ranging from 2.2 to 0.9 ppm, with a peak at 2.1 ppm being especially prominent. GC of the crude reaction mixture showed that toluene was a major reaction product; therefore, we assigned the identity of this latter signal as $PhCH_2D$. GC also verified the formation of benzene as one of the reaction products.

The beneficial role of added bases was clarified by fractional crystallization of the reaction residue, which resulted in colorless crystals of triethylamine hydrochloride (characterized by NMR). The formation of triethylamine hydrochloride also identifies the fate of the "lost" chlorine.

Additional proof that alcohol dehydrogenation was responsible for the formation of **4** was provided by using 1-^{13}C-labeled ethanol. Thus, when **1** was reacted with $CH_3{}^{13}CH_2OH$ in the usual way, ^{13}*C*-carbonyl-labeled **4** ($(PCy_3)(^{13}CO)Ru(Cl)(H)$) resulted. This was determined by ^{13}C NMR, which showed in a very short period of time only a triplet attributable to the carbonyl group. Moreover, the ^1H NMR showed the hydride moiety as a complicated multiplet (as opposed to a simple triplet), confirming the presence of the ^{13}C label adjacent to the hydride.

Unfortunately, from these results, the mechanism by which **4** forms from **1** could still not be unambiguously elucidated. Particularly, the role of the benzylidene group is not fully clear. Scheme 1 shows a proposed mechanism that is consistent with the observations for the degradation of **1** by methanol.

The mechanism presented in Scheme 1 cannot, however, be immediately extended to include the longer chain alcohols that were found to be equally effective at forming **4**. Scheme 1 would predict that longer chain alcohols should give either an alkyl benzene in steps 3 and 4 or, alternatively, an alkyl complex (step 5) as

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(13) (a) Chen, Y.-Z.; Chan, W. C.; Lau, C. P.; Chu, H. S.; Lee, H. L. *Organometallics* **1997**, *16*, 1241−1246. (b) Portnoy, M.; Frolow, F.; Milstein, D. *Organometallics* **1991**, *10*, 3960−3962. (c) Shinoda, S.; Itagaki, H.; Saito, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 860−861. (d) Jung, C. W.; Garoou, P. E. *Organometallics* **1982**, *1*, 658−666. (e) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221−231.

(14) Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *177*, 5503−5511.

(15) Lynn, D. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 3187−3193.

opposed to a hydride. However, regardless of the alkyl alcohol used, the benzylidene group was still found to be fully hydrogenated to toluene and neither substituted benzenes (e.g. such as ethyl benzene when ethanol was reacted) nor alkyl complexes were formed.

Furthermore, Scheme 1 also does not explain the modest success of using water as a source of hydride atoms. In this case, we speculated that the water reacts with the benzylidene group to form a primary alcohol in situ, which in turn reacts with the ruthenium fragment to produce **4**. It seemed to us that the most likely alcohol to form from the reaction of **1** with water is benzyl alcohol. To test this idea, **1** was reacted directly with benzyl alcohol in the presence of triethylamine. However, instead of forming the hydride **4**, the new complex $(PCy_3)_2(CO)Ru(Cl)(Ph)$ (**5**) was produced in 54% isolated yield. This result was slightly surprising, since the longer chain alkyl alcohols clearly had not resulted in alkyl complexes. Nevertheless, in the benzyl alcohol case at least, the moiety on the α-carbon of the alcohol is transferred to the metal center (step 5, Scheme 1) and not to the benzylidene group.

Species closely related to **5** have been synthesized previously; bis-$PBu^t{}_2Me$[16] and various bis-PPh_3[17] analogues are known. Unsurprisingly, we found that complex **5** can be readily synthesized in 75% yield following the literature methodology used for the synthesis of the related compounds,[16] by reaction of complex **4** with diphenylmercury. In contrast to **4**, solid **5** was completely air stable, and even exposed solutions decomposed only very slowly.

Of particular interest is that complex **5** gives its ^{31}P NMR resonance at 25.9 ppm. We immediately recalled that this is *exactly* the same chemical shift observed for a species in decomposed samples of **1** and, indeed, is present in many of the crude reaction mixtures when **1** is involved, including metathesis.[18] We wondered if complex **5** is in fact also a decomposition product of complex **1**. To verify this, we measured the IR spectra of a number of different reaction residues showing a peak at 25.9 ppm and, as expected, a strong band at 1894 cm^{-1} was observed, the same location as for **5**. Careful comparison of the aromatic region of the ^1H NMR lent additional evidence, by way of the presence of two triplets at 6.65 and 6.59 ppm, the same positions seen in **5**. While we were unable to isolate the complex from the other reaction products, the ^{31}P NMR, ^1H NMR, and IR data taken together provide very strong evidence that one of the major decomposition products of **1** could be **5**.

We presumed that the source of the oxygen required for formation of the carbonyl group in **5** arises from either adventitious water or oxygen present in the glassware, solvents, and/or reagents. To ascertain which of these two oxygen sources was responsible, we reacted **1** dissolved in toluene with both water and dry air at 80 °C. While the reaction of **1** with water was relatively slow, after 3 days a single phosphorus-containing species, showing a ^{31}P NMR peak at 49.2 ppm, had formed. The identity of this compound has not yet been determined, but it showed no hydride or carbene resonances in the ^1H NMR. Conversely, when a small portion of dry air was introduced to a solution of **1**, the solution rapidly became dark brown. ^{31}P NMR of the crude mixture showed a broad peak at 46.8 ppm (possibly due to $O{=}PCy_3$) and a sharp peak at 25.9 ppm, assigned to complex **5**. Fortuitously, while **5** is insoluble in methanol, all of the other reaction products dissolved, this allowing the isolation of **5** from the reaction (6% yield) and thereby confirming its formation. When excess triethylamine was added, higher yields of **5** (~15%) were observed.

Remarkably, the reaction of oxygen with **1** also occurred for solid samples. In fact, the reaction is much more efficient, due to the suppression of decomposition from the oxidation of the phosphine ligands which are labile in solutions of **1** but not in solid samples. Thus, a sample that was stored at 4 °C in air for a prolonged period of time (over 4 years) slowly developed a peak at 25.9 ppm in the ^{31}P NMR spectrum (24% conversion). Complete conversion of **1** to **5** can be achieved overnight when **1** is pressurized (40 bar) with pure oxygen at 60 °C, in 75% yield.[19] Whereas addition reactions of electron-rich Schrock-type carbenes with the other chalcogens (sulfur, selenium, and tellurium) are known,[20] to the best of our knowledge, reaction with oxygen as the electrophile is unprecedented. While the mechanistic details of the reaction of **1** with oxygen are not yet clear, we presume the carbene ligand in **1** is first "oxygenated" concomitant with the loss of HCl to initially give the benzoyl complex $(PCy_3)_2(Cl)RuC(O)Ph$. This intermediate species could then deinsert CO to give **5**.[21]

Analysis of the Formation of "3". While we could not duplicate the reaction conditions required to produce the hydride "**3**" *as reported* by Fürstner,[22] we did discover that "**3**" and **4** likely have more in common than first appears. While examining the crystal structure data for Fürstner's reported *dihydride* species "**3**"[4] together with that of other crystallographically characterized hydride species, we noticed that the structure of "**3**" bore a remarkable resemblance to those of the monohydride complexes **4**[8,10] and $(PCy_3)_2Ru(H)(Cl)$ ("**6**").[23]

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[16] Huang, D.; Streib, W. E.; Bollinger, J. C.; Caulton, K. G.; Winter, R. F.; Scheiring, T. *J. Am. Chem. Soc.* **1999**, *121*, 8087−8097.

[17] Rickard, C. E. F.; Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1990**, *389*, 375−388.

[18] After metathesis of excess 1-hexene with **1** (i.e. sufficient 1-hexene was used to ensure complete decomposition of **1**) at 60 °C and subsequent vacuum distillation of the product 6-dodecene, ^{31}P NMR (C_6D_6) of the residue revealed only five phosphorus-containing species: δ 50.8 (4%), 46.9 (19%, possibly $O{=}PCy_3$), 35.0 (19%), 25.9 (12%), and 10.9 (46%, PCy_3). ^1H NMR showed no hydride- or metal−carbene-containing compounds.

[19] A second, unidentified product that shows a very broad peak at 50.4 ppm accounts for ~25% of the total phosphorus content in the ^{31}P NMR spectrum of the crude sample.

[20] (a) Werner, H.; Schwab, P.; Bleuel, E.; Mahr, N.; Windmüller, B.; Wolf, J. *Chem. Eur. J.* **2000**, *6*, 4461−4470. (b) Wolf, J.; Zolk, R.; Schubert, U.; Werner, H. *J. Organomet. Chem.* **1988**, *340*, 161−178. (c) Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939−5940.

[21] (a) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1979**, *182*, C46−C48. (b) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1−C6.

[22] We have reacted catalyst **1** with most of the reagents (and combinations thereof) used in the synthesis of **2b**, including some of the possible impurities that can be present in these starting materials. For example, acetone, *tert*-butyl alcohol, benzaldehyde, and 1,3-bis-(2,6-diisopropylphenyl)-4,5-dihydroimidazolinium chloride all failed to react with **1**, under the conditions used for the synthesis of **2b**, to produce hydride complexes. Interestingly, triethyl orthoformate, particularly in the presence of a base, produced modest amounts of complex **4**.

[23] van der Schaaf, P. A.; Kolly, R.; Hafner, A. *Chem. Commun.* **2000**, 1045−1046, including Supplementary Information.

Therefore, the crystal structure data for complexes "**3**",[24] **4**, and "**6**" were more carefully examined.

The original structure of "**6**" showed a 14-electron mononuclear complex in which the ruthenium occupies a square-planar coordination environment, with the two phosphines trans to one another.[23] However, a later reevaluation of the structure showed that the compound had actually formed as the 16-electron dinitrogen adduct $(PCy_3)_2(N_2)Ru(H)(Cl)$ (**7**).[25] The structure of **4** is very similar to that of **7**, with the carbonyl group simply occupying the position of the dinitrogen molecule in **7**. A cursory examination of the unit cell parameters of the Van der Schaaf structure of **7**, the Nolan and Grubbs structures of **4**, and the Fürstner structure of "**3**" reveals that there is a very close similarity in the values. Indeed, closer scrutiny of the three hydride structures showed that all of the corresponding atomic coordinates are in each case virtually identical: i.e., "**3**", **4**, and **7** appear to be *isostructural*. The disparity of the structural data for "**3**" seems to lie solely in the modeling of the chlorine atom(s). Like "**3**", the structures of **7** and **4** are centrosymmetric with only one unique phosphine and chlorine in the asymmetric unit. The chlorine atom and dinitrogen (for **7**) and carbonyl (for **4**) molecules are disordered, each with the required site occupancy of 50%.[10,23,25] Examination of the structure of "**3**" revealed that the temperature factors for the full-occupancy unique chlorine (in the asymmetric unit) are disproportionately large relative to the rest of the atoms. The incorrect modeling of the chlorine atom as full occupancy in "**3**" and the absence of the dinitrogen/carbonyl molecule was made more successful than would normally have been the case, due to the very similar additional electron density resulting from their superposition.

From this information it is our contention that the crystal structure reported by Fürstner for "**3**" may have been incorrectly assigned, and the complex's real identity is that of either **4** or **7**. Of the two, we believe that **4** is the more probable, given the identical chemical shifts of the hydride in the ^{1}H NMR spectrum,[26] together with its likely origins of formation revealed in the present article.

Isomerization Activity of 4. Fürstner suggested that hydrides such as **4** (or **7**) might be responsible, at least in part, for the carbon−carbon double-bond isomerization sometimes seen as byproducts of metathesis reactions.[4] This proposition is not unfounded; a number of ruthenium complexes, particularly hydrides, have been found to exhibit catalytic double-bond isomerization activity toward olefins.[7e,27] It should be noted that **4** and its bis-PPr^i_3 analogue are extremely versatile reagents; **4** has been recently receiving increasing attention, since it was shown to be a potent catalyst for the hydrogenation of alkenes[10,28] and polybutadiene rubber,[29] while the bis-PPr^i_3 system has been exploited in a wide range of mostly stoichiometric reactions.[30] However, small-alkene isomerization reactions using **4** or its analogues have, to the best of our knowledge, not previously been specifically examined.

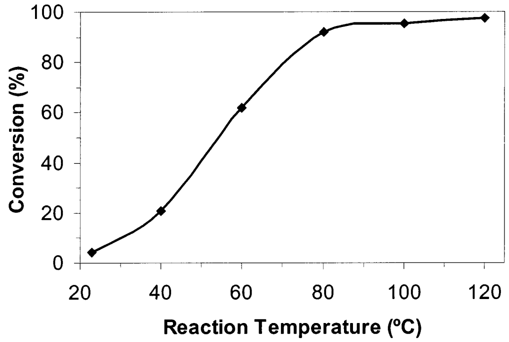

Figure 1. Conversion as a function of reaction temperature for the isomerization of neat 1-octene (88 000 mol equiv) in the presence of catalyst **4**.

We therefore decided to determine the efficacy of **4** in the double-bond isomerization of 1-octene at various temperatures. We found that the use of an additional solvent was unnecessary and that surprisingly low catalyst loadings could be used. Figure 1 graphically depicts the results of this study.

It is clear that complex **4** is a capable double-bond isomerization catalyst. No metathesis products were detected in any of the reactions using **4**. Furthermore, the catalyst showed a high degree of selectivity toward the formation of 2-octene, even when high conversions had been attained. Reaction of 88 000 mol equiv of 1-octene with **4** at 100 °C gave 97% conversion with 92% selectivity for 2-octene after 3 h. At 120 °C, selectivity was compromised, decreasing to only 56% after 3 h. The cis:trans ratio of the 2-octene formed was found to be independent of the reaction temperature, consistently being 30:70.

We wished to examine the selectivity as a function of reaction time for **4**, since we noticed that the selectivity was significantly reduced after long reaction times, particularly at higher temperatures. Figure 2 shows the conversion and selectivity for 2-octene as a function of time at 100 °C.

To further test the selectivity of **4**, we investigated the double-bond isomerization of *trans*-2-octene at high temperatures. Using 20 000 mol equiv relative to catalyst, we saw only 1% conversion to 3-octene at 80 °C after 24 h. At higher temperatures more isomerization was observed: viz. 6% and 33% for 100 and 120 °C, respectively. The relatively low 3-octene formation implies that 2-octene does not easily decompose the

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[24] Cambridge Crystallographic Data Centre, Supplementary Publication No. CCDC-154 932.

[25] van der Schaaf, P. A.; Kolly, R.; Hafner, A. *Chem. Commun.* **2001**, 940. For the web edition, see the "Corrections/Additions" amendment for ref 19.

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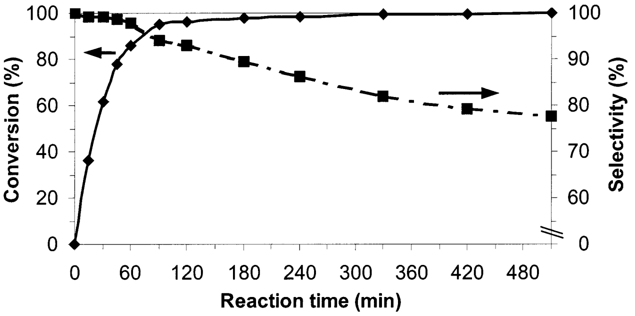

Figure 2. Conversion and selectivity for 2-octene as functions of reaction time for the isomerization of neat 1-octene (88 000 mol equiv) by **4** at 100 °C.

catalyst, probably because it reacts only poorly with this substrate. In no instance was 1-octene observed; thus, the isomerization reaction with **4** appears to be effectively irreversible.

From the data, we conclude that the decrease in selectivity over time is largely attributable to the decomposition of the active catalyst. NMR analysis of the spent catalyst revealed a single broad peak in the ^{31}P NMR spectrum at 47.2 ppm, with a shoulder at 47.5 ppm, while the ^{1}H NMR showed the absence of any hydrido species. Interestingly, the peak(s) in the ^{31}P NMR spectrum of decomposed **4** are also prominent in the spectrum of exhausted **1** that we recorded after activity in the metathesis of 1-octene had ceased.[31] Whether the decomposition products are indeed the same for **1** and **4** remains presently unknown. In any case, they are most likely poorly defined ruthenium complexes, possibly polymeric, that can also isomerize 1-octene but lack the activity and selectivity of **4**.

We also tested the isomerization activity of complex **5** and found it to be a good precatalyst for this reaction, although the activity was lower than for **4**. We tentatively suggest that the likely active catalytic species, $(PCy_3)(CO)Ru(Cl)(H)$,[28a] is also formed in situ when **5** is reacted with a terminal alkene.

Conclusions

The reaction of the first-generation Grubbs catalyst **1** with primary alcohols gave, in part, the ruthenium hydride **4**[23] in modest to good yields. The reaction pathway was determined to be alcohol dehydrogenation followed by decarbonylation. Both inorganic and organic bases were found to facilitate the reaction. When benzyl alcohol was used in place of an aliphatic alcohol, the analogous reaction took place to produce the phenyl-substituted complex **5**. Compounds **4** and **5** were found to be good double-bond isomerization catalysts; in fact, **4** isomerized 1-octene more effectively than **1** is capable of metathesizing it.[3] It is, however, not conclusive if any hydride species can also form during olefin metathesis initiated by **1**; certainly the carbonyl species **4** could never form if substrates devoid of an oxygen-containing functionality are used. The present results indicate that the use of primary alcohols or water in the synthesis or reactions of catalyst **1** could potentially lead to the formation of **4**, especially at elevated temperatures and in the presence of a base (or basic groups). It is highly likely that this reaction led to the formation of the hydride that was inadvertently isolated by Fürstner in the synthesis of **2b**, quite possibly during the methanolic workup.[4]

We have also shown that complex **5** is formed from **1** in the presence of oxygen (air), and this could also have repercussions with regard to isomerization side reactions. Because **5** was also found to be a capable isomerization catalyst, secondary metathesis products, which form as a result of isomerization, might be anticipated in metathesis reactions that are not completely free of oxygen, particularly when higher temperatures are used.

We are currently investigating the reaction of the "second-generation" Grubbs catalyst **2a** with alcohols. Preliminary results indicate that **2a** also readily forms hydride(s), with the expected mixed-ligand system.

Experimental Section

Unless otherwise stated, all manipulations were carried out under a nitrogen atmosphere on a vacuum line using standard Schlenk techniques. All solvents used were dried and distilled under nitrogen. $(PCy_3)_2Ru(=CHPh)(Cl)_2$ (**1**; Fluka), diphenylmercury (Merck), 2-octene (Acros), and 1-octene (98%, Aldrich) were obtained from commercial sources. Styrene-α-*d* was prepared by the literature procedure.[32] NMR spectra of the complexes 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 determined at H. Kolbe Mikroanalytiches Laboratorium.

$(PCy_3)_2Ru(=CDPh)(Cl)_2$ (1-α-d). Styrene-α-*d* (0.75 mL, 6.5 mmol) was added to a solution of **1** (0.50 g, 0.608 mmol) in CH_2Cl_2 (5 mL), and the resulting mixture was stirred for 1 h at room temperature. Most of the CH_2Cl_2 was removed under vacuum, and methanol (20 mL) was then added, producing a purple solid. After the mixture was stirred for several minutes, the solid was filtered in air and washed with methanol (10 mL), followed by pentane (5 mL). The product thus obtained was subjected a second time to the above procedure to give **1**-α-*d* (95% atom D (^{1}H NMR); yield 0.31 g, 62%).

$^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 37.5. ^{1}H NMR (C_6D_6): δ 8.69 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H, *o*-H C_6H_5), 7.23 (m, 3H, C_6H_5), 2.85 (s, br, 6H, $P(C_6H_{11})_3$), 1.93 (d, J = 11.1 Hz, 12H, $P(C_6H_{11})_3$), 1.67−1.52 (m, 30H, $P(C_6H_{11})_3$), 1.26−1.19 (m, 18H, $P(C_6H_{11})_3$). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 152.9 (*i*-C C_6H_5), 131.2, 129.2 (C_6H_5), 32.4 (vt, $J_{C,P}$ = 8.5 Hz, $P(C_6H_{11})_3$), 30.1 (s, $P(C_6H_{11})_3$), 28.1 (vt, $J_{C,P}$ = 4.3 Hz, $P(C_6H_{11})_3$), 26.9 (s, $P(C_6H_{11})_3$), Ru=*C*D not resolved after 3 days' acquisition.

$(PCy_3)_2(CO)Ru(Cl)(H)$ (4). 1-Propanol (0.1 mL, 1.34 mmol) and triethylamine (0.17 mL, 0.121 mmol) were added to a toluene solution (4 mL) of **1** (0.200 g, 0.243 mmol), and the resulting mixture was heated at 75 °C overnight. During this time the solution changed from dark purple-red to clear dark orange-yellow. After the mixture was cooled to room temperature, methanol (10 mL) was added, resulting in the rapid formation of a yellow precipitate. After this mixture was stirred for 1 h, the solid was collected by filtration, washed with methanol (2 × 5 mL) followed by hexanes (5 mL), and dried under vacuum to give **4** as a bright yellow powder (0.128 g, 73%). The same procedure, but using a methanolic solution (0.122 M) of K_2CO_3, NaOH, or NaOMe (0.5 mL, 0.061 mmol) instead of Et_3N, also produced **4** (0.030 g, 35%). Spectra of the isolated product are indistinguishable from those of an authentic sample.[11]

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IR (KBr, cm^{-1}): 1906 (ν(CO)), 1445 (ν(RuH)). IR (toluene, cm^{-1}): 1902 (ν(CO)). ^{31}P{^{1}H} NMR (C_6D_6): δ 47.55. ^{1}H NMR (C_6D_6): δ 2.52 (br, 6H, P(C_6H_{11})$_3$), 2.22 (d, J = 10.5 Hz, 6H, P(C_6H_{11})$_3$), 2.02 (d, J = 10.5 Hz, 6H, P(C_6H_{11})$_3$), 1.68 (m, 28H, P(C_6H_{11})$_3$), 1.23 (18H, m, P(C_6H_{11})$_3$), −24.25 (t, $J_{H,P}$ = 18.3 Hz, 1H, RuH). ^{13}C{^{1}H} NMR (C_6D_6): δ 34.9 (vt, $J_{C,P}$ = 8.6 Hz, P(C_6H_{11})$_3$), 31.2 (s, P(C_6H_{11})$_3$), 30.4 (s, P(C_6H_{11})$_3$), 28.0 (br s, P(C_6H_{11})$_3$), 26.9 (s, P(C_6H_{11})$_3$), Ru−CO not resolved.

(PCy$_3$)$_2$(CO)Ru(Cl)(Ph) (5). Method A. Benzyl alcohol (0.6 mL, 5.80 mmol) and triethylamine (0.2 mL, 1.42 mmol) were added to a toluene (3 mL) solution of **1**, and the subsequent mixture was heated to 80 °C for ~24 h. The course of the reaction was followed by unlocked ^{31}P NMR. When **1** was completely consumed, the solvent was removed under reduced pressure to leave a dark orange oil. Without further precaution to preclude air, nondegassed ethanol (30 mL) was added to the residue, and the mixture was vigorously stirred for 2 h. The resulting pale orange solid was filtered and washed with ethanol (2 × 10 mL) and pentane (2 mL) to give pure **5** (0.145 g, 60%).

Method B. Diphenylmercury (0.20 g, 0.564 mmol) was added to a toluene (5 mL) solution of **4** (0.20 g, 0.275 mmol). The reaction mixture was refluxed for 12 h, during which the time the solution became dark orange. Without further efforts to preclude air, the solution was filtered through a plug of Celite to remove elemental mercury. The reaction was worked up in the same way as for Method A, to give **5** as a pale orange powder (0.221 g, 75%).

Method C. A toluene (5 mL) solution of **1** (0.20 g, 0.564 mmol) was stirred at 60 °C in the presence of dry air for 4 h. During this time, the solution became dark brown-green. ^{31}P NMR of the reaction mixture showed two signals: a very broad peak at 46.8 ppm and a sharp singlet at 25.9 ppm. The solvent was completely removed under vacuum, and methanol (10 mL) was introduced. The mixture was vigorously stirred for 6 h. Filtration, followed by washing with methanol (4 × 5 mL), gave **5** (0.012 g, 6%).

Method D. Finely powdered **1** (0.050 g, 0.061 mmol) was deposited in an autoclave which was subsequently pressurized with oxygen (40 bar). The autoclave was heated at 60 °C for 18 h. After the oxygen was vented off, the resulting brownish solid was collected and thoroughly washed with methanol and pentane to give pure **5** (0.036 g, 74%).

IR (KBr, cm^{-1}): 1894 (ν(C)O). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 25.4. ^{1}H NMR (CD_2Cl_2): δ 7.54 (v br, 2H, o-H C_6H_5), 6.65 (t, 2H, J = 7.20 Hz, m-H C_6H_5), 6.59 (t, 1H, J = 6.60 Hz, p-H C_6H_5), 2.42 (br, 5H, P(C_6H_{11})$_3$), 2.00 (d, J = 12.0 Hz, 5H, P(C_6H_{11})$_3$), 1.68 (m, 23H, P(C_6H_{11})$_3$), 1.51−1.18 (m, 33H, P(C_6H_{11})$_3$). The peak at 7.54 ppm resolves to a doublet at ~80 °C. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 205.8 (t, $J_{C,P}$ = 13.9 Hz, Ru−CO), 156.1 (t, $J_{C,P}$ = 10.0 Hz, i-C C_6H_5), 139.7 (v br, o-C C_6H_5), 128.9, 127.3 (s, o-C C_6H_5), 125.9 (br s, m-C C_6H_5), 120.8 (s, p-C C_6H_5), 35.3 (vt, $J_{C,P}$ = 9.2 Hz, P(C_6H_{11})$_3$), 30.5, 30.1 (s, P(C_6H_{11})$_3$), 28.3 (m, P(C_6H_{11})$_3$), 27.1 (s, P(C_6H_{11})$_3$). Anal. Calcd for $C_{43}H_{71}OP_2ClRu$: C, 64.36; H, 8.92. Found: C, 64.39; H, 8.84.

Isomerization Reactions. Immediately prior to use, the octene was passed through a column (20 cm × 1.5 cm) of neutral alumina (Acros, 50−200 μm), using 15 g of alumina per 100 mL of octene, into a Schlenk flask. The octene was then deoxygenated by a series of degassing (by evacuation of the flask), followed by refilling with nitrogen. For each reaction, 20 mL (127 mmol) of octene was used. The reaction vessel was immersed in an oil bath and allowed to equilibrate to the desired temperature. To the octene, 1.05 mg (six-figure analytical balance) of catalyst was then added. No additional solvents were used. All reactions were thoroughly stirred by way of a magnetic stirrer bar. All reactions were allowed to proceed to completion; i.e., the reported results are those obtained when substrate 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).

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