Stabilization of (Trialkylphosphine)ruthenium Alkylidene Metathesis Catalysts using Phosphine Exchange

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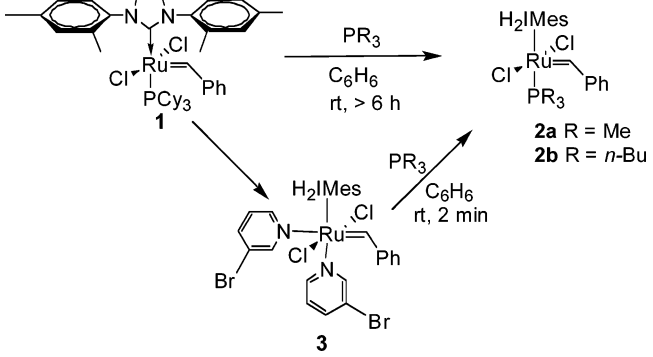
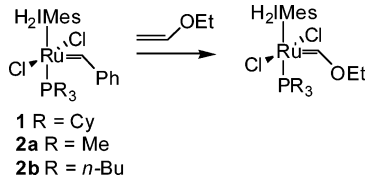
Summary: The second-generation Grubbs analogues $(H_2IMes)RuCl_2(=CHPh)(PR_3)$ *(R = Me, Bu) were essentially metathesis-inactive and air-stable at room temperature but exhibited first-order metathesis with ethyl vinyl ether at elevated temperature. The* PMe_3 *complex underwent second-order ligand exchange with* PBu_3*, indicating different coordination mechanisms (dissociative vs associative) in the two reactions.*

In efforts to prepare conjugated diruthenium alkylidenes as potential molecular wires through stoichiometric metathesis (alternatively called olefin metathesis for metal incorporation or OMMI),[1] we have had needs for both fast-initiating, reactive precursor complexes and methods for eliminating the metathesis reactivity and forming stable complexes when the reaction is done. While the former has been well studied[2,3] and much progress has been made in synthetic applications,[4] there have been limited reports regarding the latter.[5] Deactivation of metathesis catalysts in a way that produces stable ruthenium products might also be useful for isolation and identification of catalyst products from catalytic processes. This report concerns the deactivation and stabilization of ruthenium alkylidene complexes through the coordination of trimethylphosphine (PMe_3) and tributylphosphine (PBu_3). While PMe_3 analogues of ruthenium metathesis catalysts have been studied computationally,[6] experimental reports have not yet appeared. A PBu_3 complex has been reported as part of a larger study.[7] In the course of this study, we discovered a PMe_3 complex that undergoes metathesis and PBu_3 substitution by dissociative and associative processes, respectively.

Scheme 1



Scheme 2



Treatment of the Grubbs second-generation catalyst $(H_2IMes)RuCl_2(=CHPh)(PCy_3)$ (**1**)[8] with PMe_3 or PBu_3, either 1 equiv or excess, cleanly produced the phosphine-exchanged complexes **2a**,**b** (Scheme 1). Though both phosphines are much smaller (Tolman cone angles of 118 and 132°, respectively, compared to 170° for PCy_3),[9] coordination of a second PMe_3 or PBu_3 to the 16-electron ruthenium center was not observed, even in the presence of excess ligand.

Since complex **1** is slow to lose PCy_3, the substitution reaction of this complex requires more than 6 h to reach completion. Complexes **2a**,**b** were prepared much more quickly through the bromopyridine complex **3**. As reported, complex **3** can be formed very quickly from **1**,[10] and in turn, the reaction between **3** and PMe_3 or PBu_3 is essentially instantaneous at ambient temperature.

Complexes **2a**,**b** were unreactive with respect to OMMI at room temperature (Scheme 2). While **1** showed complete reaction with ethyl vinyl ether (EVE) to give the Fischer carbene complex in 10 h (a time scale characteristic of PCy_3 loss),[11] the reaction of 1 equiv of EVE with complexes **2a**,**b** gave only 10% conversion to the analogous Fischer carbene after 1 and 5 days, respectively.[12] The reactions were no faster in the presence of excess EVE. Compound **2a** showed first-order kinetics when

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Table 1. Relative Rates for OMMI with EVE, Cone Angles, and pK_a Values

	PR_3[a]	k_{rel} at 80 °C	θ (deg)[b]	pK_a[c]
1	PCy_3	1.0	170	9.70
2a	PMe_3	0.0055	118	8.65
2b	PBu_3	0.0062	132	8.43

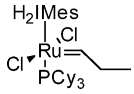
[a] Bound phosphine in reactant. [b] Cone angle of PR_3.[9] [c] pK_a of protonated PR_3.[13]

treated with EVE between 20 and 80 °C, and the rates were independent of the olefin concentration. Eyring analysis of the reaction between **2a** and EVE gave $\Delta H^{\ddagger} = 30.4 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = 13 \pm 3$ cal/(mol K). The reported values for the first-order reaction of **2b** and EVE are $\Delta H^{\ddagger} = 27.6$ kcal/mol and $\Delta S^{\ddagger} = 5$ cal/(mol K),[7] and our 80 °C rate constant, 8.06×10^{-4} s^{-1}, matched the expected value. These results are consistent with the usual mechanism for Grubbs type metathesis catalysts: rate-determining, unimolecular dissociation of phosphine from the ruthenium complex.[7]

The relative rates for **2a**,**b** (Table 1) are more than 2 orders of magnitude lower than the rate for **1**, as expected, due to the tighter binding of the smaller and more strongly donating phosphines. The rate constants for **2a**,**b** are essentially the same; the small differences in cone angle and pK_a favor tighter binding for PMe_3 (reflected perhaps in the 3 kcal/mol difference in $\Delta H^{\ddagger}$), but this is balanced by an entropy effect that apparently favors dissociation of PMe_3.

Similarly, reaction of **2a**,**b** and 1-octene gave no observable stoichiometric reaction, as the ^{1}H NMR signals for these compounds persisted and no new H_α peaks were observed. Nonetheless, catalytic conversion of 1-octene to the homodimer (7-tetradecene) was observed, requiring approximately 3 days. The same reaction catalyzed by **1** required less than 12 h, and complex **3** catalyzed the reaction within minutes. The dissociation of PR_3, though very slow from **2a**,**b**, gives an active catalyst identical with that of **1**. This species apparently catalyzed the reaction with high enough turnover that the catalytic reaction was finished before any stoichiometric reaction was observable. To rule out the possibility that this catalysis is due to traces of remaining **3**, a control experiment was performed. A slight excess of EVE was added prior to the addition of octene to convert traces of **3** into the analogous Fischer carbene (a reaction done in seconds[10]), which would render it essentially metathesis inactive. The homodimer was still formed, but at a slightly slower rate. The reduction in rate is most likely due to the competition between octene and EVE; the Fischer carbene was observed in the ^{1}H NMR in the usual days time scale.

We recently reported that alkylidene analogues of benzylidene **1**, such as propylidene **4**, undergo PCy_3 loss 10 or more times faster than **1**.[3] We therefore prepared the PMe_3 complex **6** in



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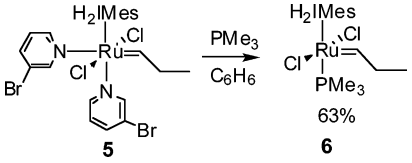
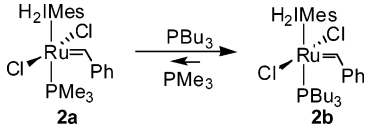
order to determine whether dissociation of PMe_3 occurs faster from this complex than from **2a**. Addition of PMe_3 to the bromopyridine complex **5** gave **6** cleanly (Scheme 3), and this complex was found to be no more reactive than benzylidene **2a**. Thus, **6** and EVE reached 10% reaction in about 3 days at room temperature. At elevated temperatures, **6** was reactive with

Scheme 3



5 **6**

Scheme 4



2a **2b**

EVE at a rate comparable with that for **2a**,**b**, in contrast to the marked room-temperature rate differences of **1** and **4**.[3]

The tighter binding of PMe_3 and PBu_3 also led to increased stability for complexes **2a**,**b**. For example, **2a** was found to be air stable in CD_2Cl_2 solution for 3 days, while complete decomposition of **1** in air was observed within 1 day. The air stability of **2a** in C_6D_6 was similar to that in CD_2Cl_2, with observable decomposition starting after 3 days and completing after 6 days. The stability of the PMe_3 complex was reduced in $CDCl_3$ (under N_2), as observed for other ruthenium alkylidenes.[14] Decomposition of **2a** was observed to start after 1.5 h with complete decomposition after 3 days. Decomposition of **2b** was observed to begin after 2 days in $CDCl_3$, but only 50% decomposition was seen after 1 month.

The addition of excess PBu_3 to **2a** at room temperature gave a 1:1 mixture of **2a** and **2b** after 12 h, and the reaction proceeded completely to **2b** after 3 days (Scheme 4). At 80 °C the reaction of 1 equiv of PBu_3 with **2a** went to completion within 1 h. The reverse phosphine exchange was not observed in 12 h, even with the addition of excess PMe_3 to **2b** at room temperature, but at 80 °C, a mixture of **2a**,**b** was formed, with the ratio dependent on the amount of PMe_3 added. When the mixture was cooled to room temperature, **2b** was again the major product.

It should be noted that the higher vapor pressure of PMe_3 (bp 38 °C) also favors **2b** in the exchange equilibrium, especially at higher temperatures. In a control sample of PMe_3 in C_6D_6, the PMe_3 ^{1}H NMR signal nearly disappeared completely at 80 °C, regaining its full strength upon cooling to room temperature. Thus, the PMe_3 is effectively removed from the solution at 80 °C. While this effect contributes, the higher stability of **2b** is still evident from the room-temperature mixtures with excess PMe_3.

The rate contrast for **2a** between metathesis, taking a day to reach 10% conversion, and phosphine exchange with PBu_3, taking only 12 h to reach 50% conversion, is inconsistent with a dissociative process for both. In fact, if we accept that the metathesis reaction with EVE follows the usual dissociative mechanism, as suggested by the kinetic data above, then any other reaction that starts with the same dissociative step would necessarily proceed at the same rate or slower. Therefore, the phosphine exchange cannot be dissociative. Indeed, the reaction of **2a** with 1 equiv of PBu_3 was found to proceed with second-order kinetics at all temperatures between 25 and 80 °C, and the rate was found to depend linearly on the concentration of PBu_3. Eyring analysis gave $\Delta H^{\ddagger} = 15.8 \pm 0.6$ kcal/mol and

(12) The analogous ^{1}H NMR H_α Fischer carbene peaks for **2a**,**b** are 13.76 ppm ($J = 3.7$ Hz) and 13.72 ppm ($J = 3.9$ Hz), respectively.

(13) Henderson, W. A.; Streuli, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791−5794.

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$\Delta S^{\ddagger} = -18.7 \pm 2$ cal/(mol K). The higher rate (relative to metathesis), second-order kinetics, first-order dependence on [PBu_3], and large, negative $\Delta S^{\ddagger}$ are all consistent with an associative mechanism.

Complex **2a** represents the first example of a monoruthenium Grubbs type catalyst that shows different coordination mechanisms in reactions with olefins and phosphines. For example, phosphine substitution reactions of **1** have been shown to proceed with a dissociative mechanism,[15] as verified in our experiments. Despite the ability of **2a** to undergo associative phosphine substitution, the side-on, weaker π coordination of an olefin undergoing metathesis apparently makes the associative process less competitive with the dissociative mechanism, as signaled by the first-order kinetics, the rate independence with respect to [olefin], and the positive $\Delta S^{\ddagger}$. Ligand size clearly determines whether substitution can occur associatively.

The exchange reaction between **2a** and PMe_3-d_9 was also studied.[16] The reaction was observable within minutes and was complete within a few hours at 25 °C—clearly faster than either metathesis or PBu_3 substitution. The rate was dependent on the concentration of the free phosphine; an increase in phosphine concentration increased the rate. The rate constant of this exchange reaction was determined to be 0.0055 ± 0.003 M^{-1} s^{-1}.[17] The rate constant was larger than that of the phosphine exchange between **2a** and PBu_3 at 25 °C (0.0012 M^{-1} s^{-1}), as expected for an associative process with a smaller ligand.

Interestingly, addition of PMe_3 (or PMe_3-d_9) to **2a** led to decomposition on a hours-to-days time scale, with the decomposition rate increasing with increased [PMe_3]. The decomposition was slower than phosphine exchange, allowing the measurement of the exchange rate constant, but it did result in relatively large error bars on this determination. In contrast, addition of PBu_3 to **2a** or PMe_3 to **2b** caused much slower decomposition. This is consistent with decomposition arising from attack of phosphine on the alkylidene, as reported for related complexes.[18] Larger phosphines in either role (as nucleophile or bound ligand) slow the rate of this process.

In attempts to make coordinatively saturated complexes, **1** and **3** were treated with the bidentate phosphine ligands $Me_2P(CH_2)_nPMe_2$, where $n = 1$ (dmpm), 2 (dmpe). In each of these reactions, the benzylidene fragment was lost, as determined by ^{1}H NMR. A possible explanation is that coordination of the first phosphine brings the second into close proximity, where it reacts with the benzylidene. With monophosphines, the coordinated ligand serves to protect the benzylidene ligand from nucleophilic attack.

While complexes **1** and especially **3** catalyze the polymerization of acetylene,[19] complexes **2a**,**b** and **6** react very sluggishly. While a good yield of polyacetylene was obtained with **3** in CH_2Cl_2 or $CDCl_3$ in minutes, only a trace of polymer was observed after overnight reactions with **2a** or **6** in CH_2Cl_2. In $CDCl_3$, the reaction was marginally faster, with a trace of polymer observed after 1 h with **2a**,**b** or **6**.[20]

In conclusion, coordination of PMe_3 or PBu_3 to an (H_2IMes)$RuCl_2$ alkylidene complex rendered the catalyst unreactive in metathesis reactions at room temperature and led to increases in stability. The kinetic analysis of **2a** indicates that during phosphine exchange with PBu_3 or PMe_3-d_9 this complex does not follow the usual dissociative mechanism for ruthenium alkylidene metathesis catalysts. For these particular exchange reactions, several lines of evidence support associative mechanisms. As demonstrated by this study, the use of phosphine exchange rates as measures of phosphine dissociation kinetics—while valid in many cases—should be done with caution.[21] OMMI reactions followed by stabilization with PMe_3 or PBu_3 might be used to produce stable complexes for electronic or other applications, and we are now pursuing this direction.

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Supporting Information Available: Text, figures, and tables giving experimental procedures, spectroscopic characterization, and kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Magnetization transfer experiments have been used to determine the rates of degenerate phosphine exchange reactions in similar systems.[7,15a] In this specific case, the volatility of PMe_3 and the relatively slow rate make this experiment impractical.

(17) (a) Duffield, R. B., Calvin, C. *J. Am. Chem. Soc.* **1946**, *68*, 557−561. (b) Caravan, P.; Comuzzi, C.; Crooks, W.; McMurray, T. J.; Choppin, G. R.; Woulfe, S. R. *Inorg. Chem.* **2001**, *40*, 2170−2176. A detailed account of our analysis can be found in the Supporting Information.

(18) Hong, S. H.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 7414−7415.

(19) Schuehler, D. E.; Williams, J. E.; Sponsler, M. B. *Macromolecules* **2004**, *37*, 6255−6257.

(20) A trace amount of polymerization that was observed within minutes was prevented by addition of EVE before the acetylene reaction. This apparently removed traces of **3** or other active impurities.

(21) Grubbs and co-workers have been generally careful in this respect.[7,15a]