5696 *Organometallics* **2006,** *25,* 5696−5698

Anionic Ligand Exchange in Hoveyda−Grubbs Ruthenium(II) Benzylidenes

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Received October 5, 2006

Summary: A series of Hoveyda−Grubbs benzylidenes, Ru(X)$_2$(IMesH$_2$)(═CH-2-(2-PrO)C$_6$H$_4$) (X = Cl, Br, CF$_3$CO$_2$, C$_2$F$_5$CO$_2$; IMesH$_2$ = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) were demonstrated to undergo intermolecular anionic ligand exchange when mixed. The implication is that anionic ligand exchange is occurring between identical ruthenium benzylidenes at all times in solution. A mechanism involving bridged dimers is invoked.

The introduction of the well-defined ruthenium benzylidene Ru(Cl)$_2$(PCy$_3$)$_2$(═CHPh), “Grubbs I” (**1**; PCy$_3$ = tricyclohexylphosphine),[1] and representative modified benzylidenes such as Ru(Cl)$_2$(IMesH$_2$)(PCy$_3$)(═CHPh), “Grubbs II” (**2**; IMesH$_2$ = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene),[2] Ru(Cl)$_2$(IMesH$_2$)(═CH-2-(2-PrO)C$_6$H$_4$), “Hoveyda−Grubbs II” (**3**),[3] and Ru(CF$_3$CO$_2$)$_2$(IMesH$_2$)(═CH-2-(2-PrO)C$_6$H$_4$), “Buchmeiser−Hoveyda−Grubbs II” (**4**),[4] with variously improved catalytic activity and stability, has had a tremendous impact on olefin metathesis.[5] The different coordinated ligands around the ruthenium center have provided multiple opportunities for the preparation of immobilized catalysts on solid supports.[6,7] In particular, the ability to replace the ubiquitous anionic chloride ligand with a functionalized perfluoroacetate attached to a solid support has been recently exploited.[4,8] However, we now show in this communication that anionic ligands on Hoveyda−Grubbs ruthenium(II) benzylidenes are subject to degenerate exchange. This has implications for ruthenium benzylidene precatalysts immobilized through the “anionic position” and also for the solution phase chemistry of these benzylidenes in general (vide infra).

Bis(trifluoroacetate) **4** is prepared from Hoveyda−Grubbs **3** by the action of 2 equiv of silver trifluoroactetate in tetrahydrofuran solution.[4] Ru(C$_2$F$_5$CO$_2$)$_2$(IMesH$_2$)(═CH-2-(2-PrO)-C$_6$H$_4$)[8c] can be prepared in similar fashion with silver pentafluoropropanoate. These reactions are complete within 30 min and are driven by the precipitation of silver(I) chloride. We also note that **4** can also be prepared by the action of lead(II) trifluoroacetate on benzylidene **3** in THF or dichloromethane. The reaction is much slower (3 days for 95% conversion), but very clean. Other perfluorocarboxylate salts (K, Na, Li) gave only minimal conversions. Dibromide benzylidene **6** was prepared by the action of excess lithium bromide on dichloride **3**.

An equimolar quantity of bis(trifluoroacetate) benzylidene **4** (δ_H; RuC*H* = 17.51 ppm) and bispentafluoropropanoate ben-

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10.1021/om060913n CCC: $33.50
Publication on Web 10/18/2006

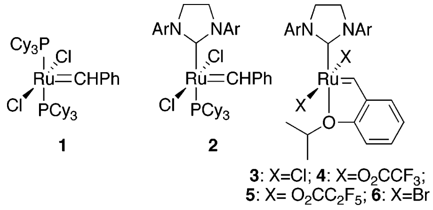


Figure 1. Ruthenium benzylidenes. Ar = mesityl.

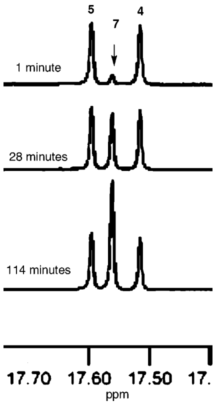
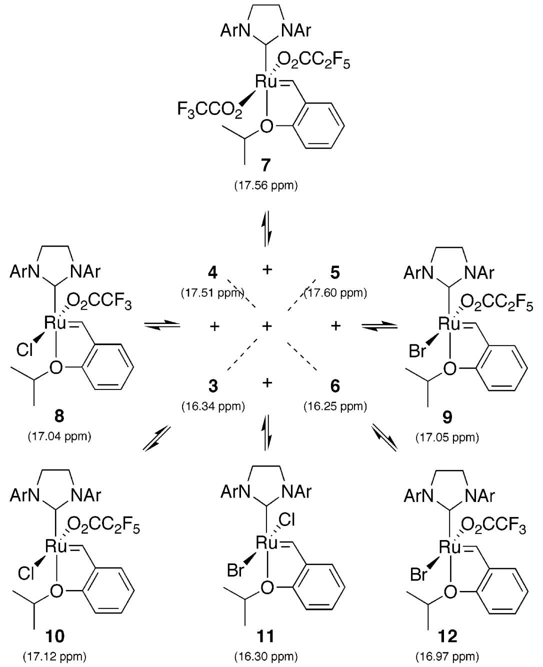


Figure 2. ^1H NMR plots of the benzylidene region for the exchange of perfluorocarboxylates **4** and **5** to give **7**.

Scheme 1. Ligand Exchange in Complexes 4−6



zylidene **5** (δ_H; RuC*H* = 17.60 ppm) were combined in d_8-THF at room temperature (Scheme 1). ^1H NMR analysis revealed the immediate formation of a new benzylidene singlet at 17.56 ppm, which became increasingly intense (Figure 2). After ca. 2 h the relative ratios of the three peaks were 1:2:1, respectively, where the new resonance is the most intense. This ratio was invariant thereafter, showing that the mixture had reached equilibrium. The statistical 1:2:1 ratio of the three resonances is a clear indication of pseudodegenerate ligand exchange (i.e., perfluoroacetate and perfluoropropanoate), and the resonance was assigned to the benzylidene proton of the mixed perfluorocarboxylate species: $Ru(CF_3CO_2)(C_2F_5CO_2)(IMesH_2)({=}CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4)$ (**7**). The new chemical shift at an "average" value of those of the two precursors also lends credence to the assignment. Mass spectrometry of the equilibrium mixture confirmed the identity of the new species with a characteristic isotope pattern centered around 832 Da. It is important to note that isolation of pure **7** is not viable under these conditions, since it will "disproportionate" into **4** and **5** by equilibrium ligand exchange, and compound **7** was analyzed as an equilibrium mixture with **4** and **5**. This is true also for benzylidenes **8**−**10** and **12**. Benzylidene **11** was analyzed by mass spectrometry before the mixture had fully attained equilibrium.

The propensity of a perfluoroacetate benzylidene to exchange with dihalo benzylidenes was examined. All combinations of bistrifluoroacetate **4** and bispentafluoropropanoate **5** with dichlorobenzylidene **3** (δ_H; RuC*H* = 16.34 ppm) and dibromobenzylidene **6** (δ_H; RuC*H* = 16.25 ppm) were studied. In all cases, exchange to give a new mixed benzylidene signal in the ^1H HMR spectrum was observed, viz., **8** (from **3** and **4**), **9** (from **5** and **6**), **10** (from **3** and **5**), and **12** (from **4** and **6**). The chemical shifts of the new benzylidenes are always intermediate between the original values of the starting materials (see Scheme 1). In each case the new species was characterized by mass spectrometry. The equilibrium positions for these exchanges were also 1:2:1 (adjusting for some benzylidene decomposition over these time periods), with the new benzylidene as the major product. The rate at which these reactions equilibrated was significantly slower compared to the exchange between **4** and **5**, but both dihalides (**3**, **6**) exchanged anionic ligands with both pefluorocarboxylates (**4**, **5**) at approximately the same rate (ca. 450 min for 50% of equilibrium conversion).

Finally, the exchange between chloride **3** and bromide **6** was examined (Scheme 1). Again, a new benzylidene peak was observed for the mixed halide species **11**, but this exchange is much slower and only 10% conversion to **11** was observed after 20 h.

Each of these Hoveyda−Grubbs benzylidenes is therefore subject to anionic ligand exchange. The experiments that we have performed show exchange between discrete chemical species. *However, the implication is that anionic ligand exchange is occurring between identical ruthenium benzylidenes at all times in solution.* Moreover, these exchanges were examined at ambient temperature and concentrations (0.067 M) typical of those conditions under which olefin metatheses reactions are conducted, and it is interesting to consider whether these exchange reactions have some role in the metathesis catalytic cycle, or whether this is just an unrelated side-process. In addition, these observations also require that this exchange is taken into account in the design of solid-supported ruthnium(II) benzylidenes immobilized through the anionic position. As to the mechanism of exchange, at this stage we propose bridged dimers. Structural evidence in support of this comes from the work of Hoveyda, who isolated a dichloro-bridged species from a 2-methoxy (rather than isopropoxy) benzylidene.[3b] Grubbs has reported bimetallic, bridged-chloride ruthenium carbenes derived from the reaction of Grubbs I and $[(p\text{-cymene})MCl_2]_2$ (M = Ru, Os, Rh).[9] Mol has also isolated and characterized carboxy-

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late-bridged dimers in the Grubbs I series.[10] It is reasonable to postulate that a dicarboxylate bridged dimer is more accessible on steric grounds than a mixed carboxylate-halide dimer, which is in turn more accessible than a dihalide dimer. This provides a qualitative explanation for the relative rates at which the equilibria are established.

Acknowledgment. We thank BASF for financial support and a studentship (to K.T.).

Supporting Information Available: General experimental procedures. Characterizing data for **6**; NMR traces and mass spectra for exchange experiments generating benzylidenes **7**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060913N

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