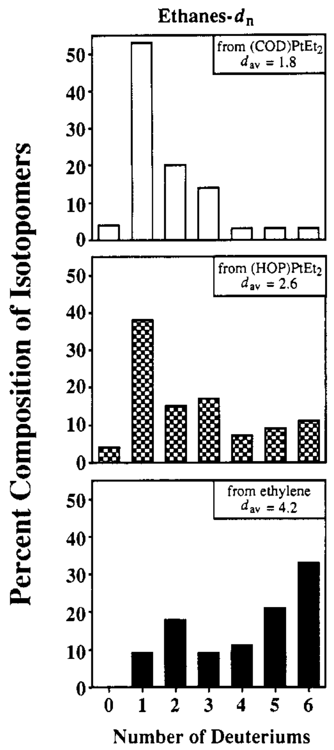

Figure 4. Isotopic distributions of the isotopomers of ethane from the reductions of (COD)PtEt$_2$ (top), (HOP)PtEt$_2$ (middle), and ethylene (bottom) in EtOD under MTL conditions.[11]

have a slower rate of C–H bond activation (relative to the rate of reductive elimination) than those derived from ethylene. This difference is probably largely due to the presence of coadsorbed cyclooctyl* moieties, which readily donate hydrides to the surface of platinum. The excess surface hydrides serve to increase the rate of reductive elimination of the Et* groups from the surface.

The relative rates of exchange and reductive elimination of surface ethyls derived from (HOP)PtEt$_2$ appear intermediate between those derived from ethylene and (COD)PtEt$_2$. The Et* moieties derived from (HOP)PtEt$_2$ more closely model the Et* moieties derived from ethylene than those from (COD)PtEt$_2$, presumably because HOP* is less likely to donate H* to the surface than is COD*. At present, (HOP)PtR$_2$ complexes appear to provide the best precursors for (DO)PtR$_2$-based routes to surface alkyls, and they provide R* most similar to those generated from olefins.

The MTL Regime vs the RRL Regime

In all of the reductions we have studied in ROD, the content of deuterium in the product alkanes was greater under MTL conditions than under RRL conditions.[9,11,29] Since the rate of reduction (and thus of reductive elimination) is of similar magnitude in both regimes (vide supra), this observation suggests that the rate of C–H bond activation of surface alkyls is faster under MTL conditions than under RRL conditions. Reductions under RRL conditions are typically carried out at −20 °C, and those under MTL conditions at 40 °C. This conclusion is therefore consistent with earlier research, which concluded that rates of C–H bond activation increase with temperature.[30]

Concluding Remarks

Our studies of the heterogeneous hydrogenation of (diolefin)dialkylplatinum(II) complexes demonstrate that by using a combination of organometallic chemistry and catalysis, it is possible to generate structurally well-defined surface alkyls under conditions typically used in organic synthesis. These reactions thus provide a new method of studying surface alkyls using standard physical–organic probes: rate–structure profiles, isotopic labeling, and stereochemistry.

It remains to be established whether this approach can be extended to other reactions and metals. Reactions that require high temperatures run the risk of inducing thermal decomposition or homogeneous reaction of the organometallic species and are thus poor candidates for this approach. Reactions that require specific surface structures or complex surfaces are also poor candidates, and those that do not generate surface alkyls (e.g., the reduction of N_2 or NH_3) are unlikely to benefit from this approach. For reactions that involve surface alkyls and relatively simple metal surfaces (e.g., hydrogenation, hydrogenolysis, isomerization, formation of metal films from OMCVD, Ziegler–Natta polymerization, perhaps Fischer–Tropsch and related reactions), this type of study should be applicable and should provide information complementary to that available from kinetics and vacuum-physics approaches. In addition, the ability of this type of chemistry to form surface organometallic groups should also be preparatively useful in technologies requiring such species, e.g., promotion of adhesion and wetting and control of corrosion and friction.

A number of our colleagues have made essential contributions to the research described here. We particularly acknowledge the research of Tim Miller and Tom McCarthy.

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[30] Anderson, J. R.; Kemball, C. *Proc. R. Soc. London, A* **1954**, *226*, 472–489.

Additions and Corrections

Vol. 24, 1991

R. J. Beuhler, G. Friedlander, and L. Friedman*: Fusion Reactions in Dense Hot Atom Assemblies Generated by Cluster Impact.

Page 198. Recent experiments using crude magnetic analyses of cluster beams after ion acceleration have shown that our original estimates of cluster fusion rates have been overestimated by at least 2 orders of magnitude. These experiments provide direct evidence for artifact beam contamination. Details will be presented in a later publication. Experiments are in progress to determine accurate rates or limits of rates of cluster impact fusion. The new experiments should shed light on the extent to which cluster impacts result in a concentration of energy in a small fraction of atoms in the target.