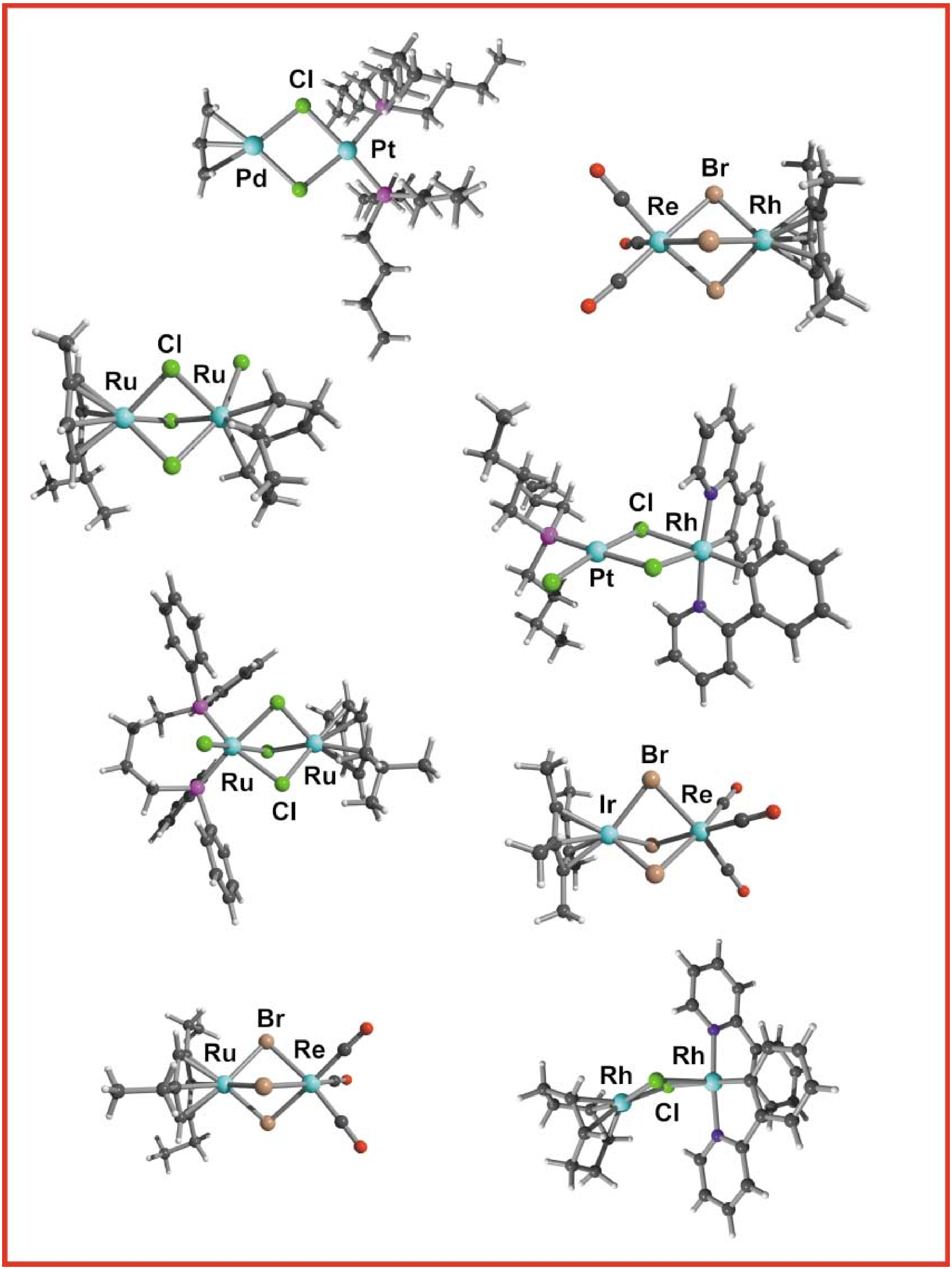
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Asymmetric Halogeno-Bridged Complexes: New Reagents in Organometallic Synthesis and Catalysis

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Abstract: Several methods to synthesize bimetallic complexes in which two different metal fragments are connected by halide bridges are described. Using simple starting materials a large pool of structurally defined bimetallic complexes with unique chemical reactivities can be prepared in short time. Applications in organometallic synthesis and homogeneous catalysis are discussed.

Keywords: bridging ligands · combinatorial chemistry · heterometallic complexes · homogeneous catalysis · organometallic complexes

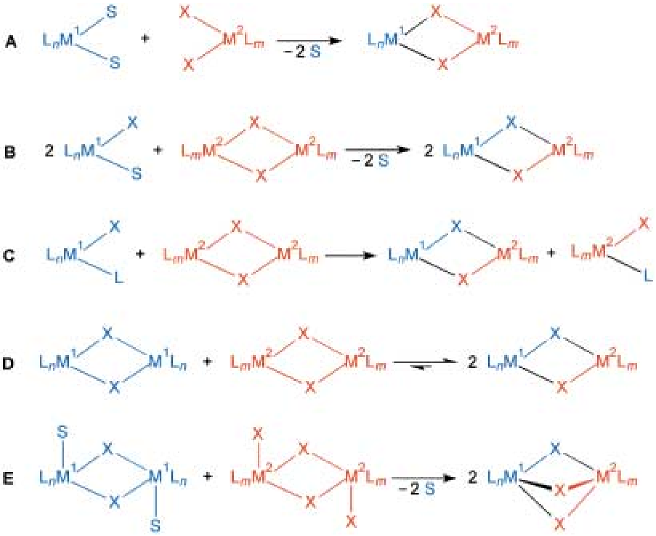
Introduction

During the last decades tremendous efforts have been made to synthesize structurally defined polynuclear complexes, in particular heterobimetallic complexes. The motivation behind these efforts were often potential applications of such compounds as catalysts and reagents in organic synthesis. Although considerable progress has been made in this field,[1] synthetically useful polynuclear complexes are still rare. A major difficulty is the fact that structural and electronic effects have to be controlled very precisely in order to observe cooperative effects. In most cases, our theoretical understanding is not sufficient to design and prepare efficient and selective transition metal catalysts from scratch, let alone heterobimetallic catalysts. Therefore, methods to generate large pools of structurally defined heterobimetallic complexes are highly warranted. The rapidly evolving techniques of combinatorial catalysis[2] could then be applied to identify potentially useful complexes in short time.

In the following we will show that asymmetric, halogeno-bridged complexes of the late transition metals are well suited for the above-mentioned purpose.[3] They can be synthesized from simple starting materials, they show both high reactivity and high structural variability. First applications of these complexes as reagents and catalysts will be described and potential developments will be discussed.

Discussion

Synthesis: Dinuclear complexes in which two identical metal fragments are connected by halogeno bridges are among the most versatile starting materials in organometallic synthesis and catalysis. By contrast, asymmetric complexes in which *two different* metal fragments are joined by halogeno ligands have rarely been described until recently. Now, synthetic strategies have emerged which allow the easy preparation of such complexes in excellent yields. The methods employed are summarized in Scheme 1.



Scheme 1. Methods for the synthesis of asymmetric halogeno-bridged complexes (S: solvent molecule or weakly bound ligand).

Upon reaction of a complex having two weakly coordinating ligands "S" (e.g. PhCN) with another complex having two terminal halogeno ligands the corresponding asymmetric compounds (**1**) are obtained (Scheme 1, method A).[4] Reactions of this kind have first been described in 1986. More recently, a similar strategy was employed to synthesize

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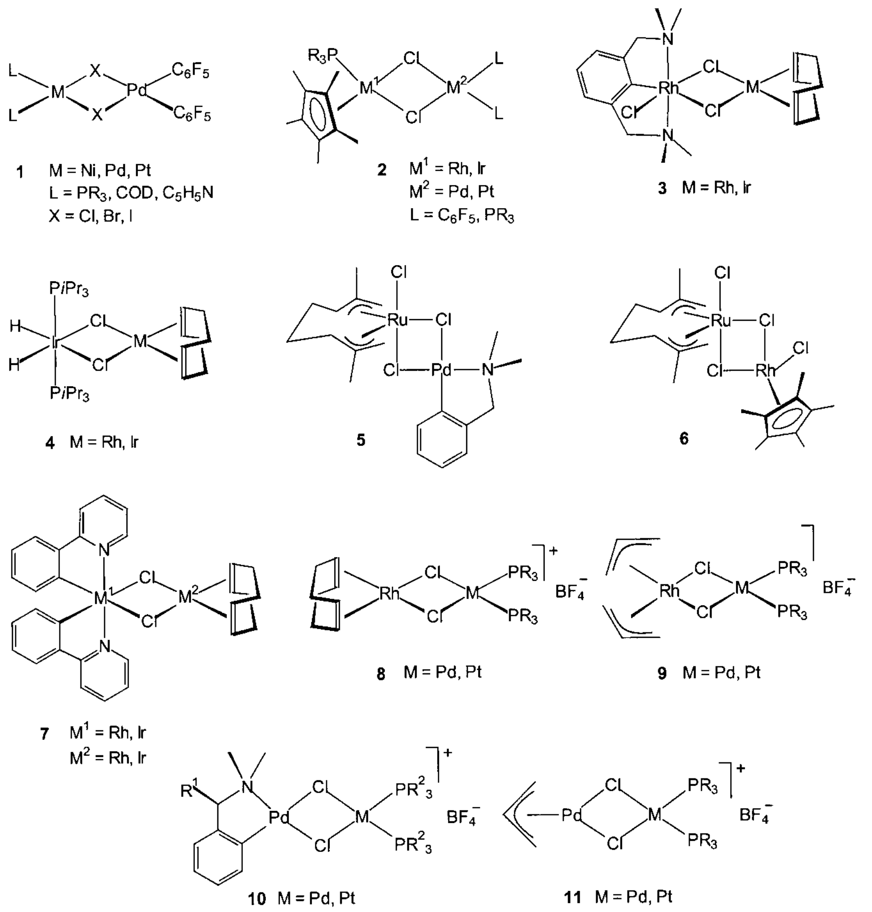


1 M = Ni, Pd, Pt
L = PR_3, COD, C_5H_5N
X = Cl, Br, I

2 M^1 = Rh, Ir
M^2 = Pd, Pt
L = C_6F_5, PR_3

3 M = Rh, Ir

4 M = Rh, Ir

5

6

7 M^1 = Rh, Ir
M^2 = Rh, Ir

8 M = Pd, Pt

9 M = Pd, Pt

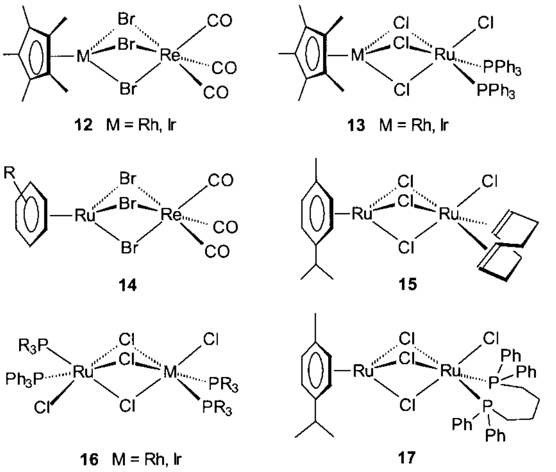
10 M = Pd, Pt

11 M = Pd, Pt

Figure 1. Selected examples of asymmetric complexes with two halogeno bridges.

Cp*Rh^{III} and Cp*Ir^{III} containing complexes such as **2**.[5] For complexes having only one weakly bound ligand the suited reaction partner is a halogeno-bridged complex (method B). Following this methodology asymmetric complexes with orthometalated Rh^{III} fragments have been prepared (**3**).[6] Instead of compounds with one labile ligand, unsaturated 16 e^- complexes such as $[IrH_2Cl(PiPr_3)_2]$ can be employed to give **4**.[7] Method C is based on a ligand transfer reaction and has been used to synthesize the catalyst precursors **19**[8] and **20**.[9] The obvious drawback of this reaction is the fact that one equivalent of an undesired side product, $[L_mM^2XL]$, is produced which has to be separated from the product. Probably the most general and easy way to obtain asymmetric halogeno-bridged complexes is the metathesis reaction D. Reactions of this kind had been described occasionally[10] but detailed investigations highlighting the potential of this method have been published only recently.[11] This method is applicable to a wide range of halogeno-bridged complexes of the late transition metals and just a few selected examples are shown in Figure 1 (**5**–**11**). In most cases it is sufficient to dissolve equimolar amounts of the respective homodimeric complexes in an organic solvent such as chloroform and the asymmetric complexes are formed within seconds. Especially suited starting materials are charged complexes such as $[(R_3P)_2M(\mu\text{-}Cl)_2M(PR_3)_2]^{2+}$ (M = Pd, Pt) (**8**–**11**).[11c] It should be noted, that asymmetric complexes containing the catalytically important[12] $(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Ru^{IV}$ fragment (**5**, **6**) have been obtained not only by the metathesis reaction D[11e] but also by method A.[13]

Metathesis reactions can also be employed to synthesize asymmetric complexes with *three* halogeno bridges (Scheme 1, method E).[14] In this case, one reaction partner needs to have two additional terminal halide ligands and the other reaction partner two weakly bound ligands (**12**–**14**). The advantage of this method is that the reaction is basically irreversible. Alternatively, triple bridged complexes have been prepared using monomeric starting materials such as $[RuCl_2(CH_3CN)_2(cod)]$,[14a] $[RuCl_2(PPh_3)_3]$,[15] and $[RuCl_2(PPh_3)(dppb)]$[14a] (**15**–**17**, Figure 2).



12 M = Rh, Ir

13 M = Rh, Ir

14

15

16 M = Rh, Ir

17

Figure 2. Selected examples of asymmetric complexes with three halogeno bridges.

Reactivity: Halogeno-bridged complex are neither thermodynamically nor kinetically very stable. In terms of potential applications this is mostly advantageous since it ensures a high intrinsic reactivity. On the other hand, the presence of an excess of donor ligands (e.g. phosphines) will most certainly yield the respective monomeric adducts. Under such conditions, cooperative bimetallic reactivity is therefore not expected.

The solubility of asymmetric complexes can be quite different from that of the respective starting materials. $(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Ru^{IV}$ complexes such as **5** and **6**, for example,

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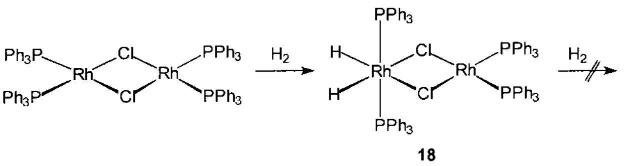
display a good solubility in a variety of organic solvents whereas the homodimeric $[(\eta^3{:}\eta^3\text{-}C_{10}H_{16})RuCl(\mu\text{-}Cl)]_2$ is only sparingly soluble. The utility of the catalyst precursor $[RuCl_2(PPh_3)_3]$ is strongly diminished because of its low solubility. When coordinated to other metal fragments via chloro bridges, $Ru(PPh_3)_x$ complexes are highly soluble (e.g. **13**). These results show that halogeno-complexes can be employed as labile "ligands" to stabilize and solubilize catalytically important metal fragments.

Asymmetric halogeno-bridged complexes also display a unique chemical reactivity. This is evident from the catalytic applications which have been published so far (see below). Supporting theoretical investigations have shown that the electronic situation of asymmetric complexes can differ substantially from that of the respective homodimeric complexes.[11b] The electron density of the allyl ligand in **11**, for example, is significantly reduced when compared with the symmetric complex $[(C_3H_5)Pd(\mu\text{-}Cl)]_2$. This suggests an enhanced reactivity towards nucleophiles.

Apart from catalytic applications asymmetric complexes can be used as starting materials for other heterometallic complexes. The chloro-bridged complexes **2**, for example, have been employed to synthesize defined tetranuclear products in reactions with the alkynylation agents $[M(C{\equiv}CR)]_n$ (M = Cu, Ag).[5]

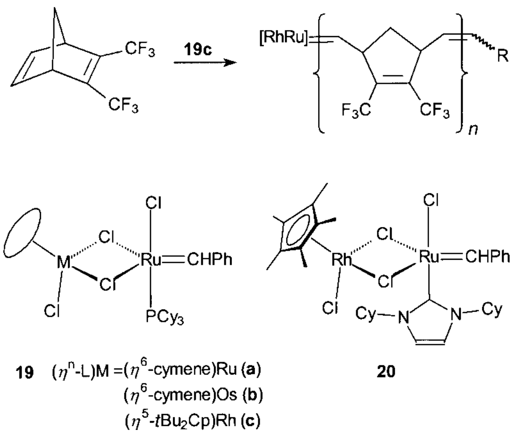
Catalysis: Catalytic hydrogenations using the Wilkinson catalyst, $[RhCl(PPh_3)_3]$, have been investigated intensively since the seminal discovery in 1965.[16] Among other species, the asymmetric mixed-valence Rh^{III}–Rh^{I} complex **18** is formed upon reaction with H_2 (Scheme 2).[17] Interestingly, the oxidative addition of H_2 to the second rhodium atom is not observed, even under high pressure. This indicates that the Rh^{III} fragment modulates the reactivity of the adjacent Rh^{I} fragment, presumably by electronic communication via the chloro bridges.



Scheme 2. Formation of an asymmetric Rh^{III}-Rh^{I} complex in hydrogenation reactions with the Wilkinson catalyst.

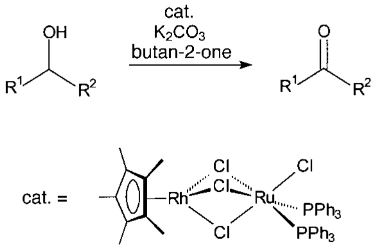
Another asymmetric chloro-bridged complex which was tested as a catalyst in hydrogenation reactions is the heterobimetallic Ru^{II}–Rh^{III} complex $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3RhCl(PPh_3)_2]$.[18] It was found to be of moderate activity.

Convincing evidence that highly active catalysts can be found within this class of compounds was recently provided by Grubbs et al.[8] They have synthesized the homo- and heterobimetallic complexes **19a–c**. In ring-closing and ring-opening olefin metathesis reactions they proved to be significantly more active (up to 80 times) than the well known carbene complex $[(PCy_3)_2Cl_2Ru{=}CHPh]$ (**21**) developed by the same group. With the catalyst precursor **19c**, even hexafluorodimethyl norbornadiene can be polymerized (Scheme 3), a reaction that proved to be difficult with the standard catalyst **21**. Importantly, the reactivity of the bimetallic complexes depends on the second metal fragment indicating some interaction during catalysis. Soon after, the structurally related Rh^{III}–Ru^{II} complex **20** having a *N*-heterocyclic carbene ligand was described by Herrmann.[9] To best of our knowledge, this compound represents one of the most active catalyst precursors for olefin metathesis developed so far.



Scheme 3. Olefin metathesis with homo- and heterobimetallic, chloro-bridged complexes.

We have investigated the catalytic oxidation of secondary alcohols with butan-2-one.[14a] Although various methods are available for the oxidation of alcohols, transition metal catalyzed reactions in which a ketone such as butan-2-one acts as a solvent *and* oxidation reagent are especially appealing—both from an economic as well as environmental point of view. Screening different asymmetric complexes with three chloro bridges we have identified the Rh^{III}–Ru^{II} complex **13a** to be an exceptionally active catalyst precursor with activities surpassing that of known monomeric complexes (Scheme 4).



Scheme 4. Catalytic oxidation of secondary alcohols with an asymmetric Rh^{III}-Ru^{II} complex.

Conclusion

Asymmetric halogeno-bridged complexes show unique chemical and physical characteristics which distinguish them from their homo(bi)metallic counterparts. The examples described above highlight the potential of such complexes as starting materials for new polymetallic compounds and as homogeneous catalysts in organic synthesis. For catalytic applications it is important that a large number of structurally defined complexes can be synthesized within a short time. Metathesis

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reactions are especially suited because several homodimeric starting materials are commercially available and hundreds more have been described in the literature. It should be noted, that if a given pool of *n* homodimeric halogeno-bridged complexes which serve as the starting material is enlarged by only one suitable compound, *n* new potential bimetallic catalysts can be prepared. Thus, it is possible to screen the catalytic behavior of heterobimetallic complexes very efficiently. Given the high reactivity of this class of compounds we expect that several new heterobimetallic catalysts with interesting characteristics will be discovered in the near future.

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