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Synthesis of Group 9 Metal-Olefin Complexes with Identical Ligand Frameworks and Comparison of their Catalytic Activity in [2+2+2] Cycloaddition and other Addition Reactions

Nico Weding,[a] Ralf Jackstell,[a] Haijun Jiao,[a] Anke Spannenberg,[a] and Marko Hapke[a,*]

[a] Leibniz-Institut für Katalyse e.V. (LIKAT) an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany
Fax: (+49)-381-1281-51213; e-mail: marko.hapke@catalysis.de

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Abstract: The preparation and catalytic evaluation of the three group 9 (cyclopentadienyl)metal(trimethylvinylsilane) complexes of the type $C_5H_5M(H_2C{=}CHSiMe_3)_2$ (M = cobalt, rhodium and iridium) are reported. The complexes were investigated in [2+2+2] cycloaddition as well as in hydrogenation, hydroformylation and hydroboration reactions. Despite the identical organic frameworks and structural parameters, the complexes display remarkable reactivity and stability differences.

Keywords: catalysis; cobalt; cyclopentadienyl ligands; cyclotrimerization; iridium; olefins; rhodium

Introduction

The [2+2+2] cycloaddition reaction has nowadays become an established component of the chemists' toolbox for the synthesis of aromatic moieties in complex organic molecules.[1] The recent decades have seen impressive developments in the application of new catalyst systems and in the substrate scope. For many transition metals cycloaddition reactions are known in which at least stoichiometric cyclotrimerizations reactions of alkynes or alkynes and alkenes are mediated. In addition, their application for the synthesis of heterocycles has been substantiated by numerous published examples. The maturing of the methodology is verified by its recent utilization in natural product synthesis, where important key pieces of the molecular structure are assembled in a convergent synthesis by a [2+2+2] cycloaddition reaction.[2] The significant advances in the scope of [2+2+2] cycloaddition reactions as well as their mechanistic background based on theoretical studies of different metal catalysts have been regularly reviewed or reported.[3,4]

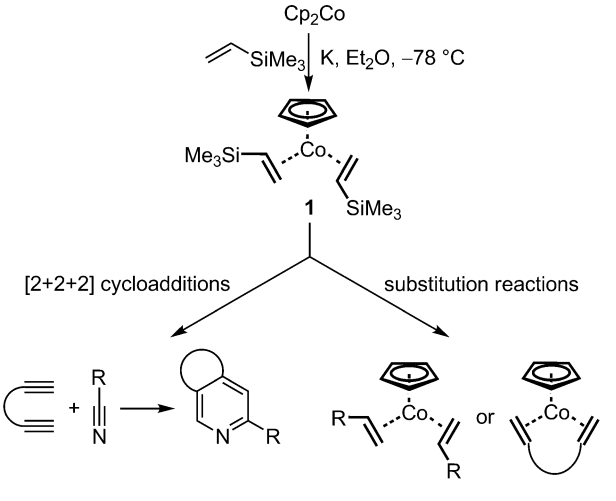
The investigation of catalytic reactions commonly comprises the evaluation of the catalyst system with respect to significant properties like activity, stability and versatility. In most cases these evaluations screen for the most appropriate ligand system (and additional beneficial additives) for a given metal known to catalyze the desired reaction. This has been the case for the [2+2+2] cycloaddition reactions right from the begining of their systematic investigation by Reppe et al. for nickel-catalyzed transformations of acetylene.[5] Their experiments highlighted the eminent role of the ligand by switching between [2+2+2] and [2+2+2+2] cycloaddition just by changing from a phosphine to an oxygen-containing ligand. These initial studies were later complemented by other systematic studies on the influence of the ligand in cyclotrimerizations. Early examples were provided by Bönnemann et al., accessing the role of covalently bound, substituted cyclopentadienyl (Cp) and indenyl (Ind) ligands for the activity of prominent Co(I) complexes for cyclotrimerizations.[6] These studies were amended by examinations of substituted Cp and Ind ligands for Rh-catalyzed [2+2+2] cycloaddition reactions, showing that substitution with electron-donating groups resulted in higher activity at lower temperature for these complexes.[7] Lately Yamamoto et al. undertook a systematic study of the influence of complexes $(Me_nC_5H_{5-n})Ru(COD)Cl$ ($n = 1$–5) for catalytic cycloadditions of diynes.[8] They found, that a Cp ligand containing three methyl groups (1,2,4-$Me_3C_5H_2$) turned out to be the most efficient catalyst, possibly beat balancing the electronic and sterically effects.

The group 9 metals of the periodic table, as was outlined already by the examples above, are providing a large array of catalyst systems for achiral as well as asymmetric cyclotrimerization and cross-cyclotrimerization reactions. However, the catalytic properties of the members cobalt, rhodium and iridium in specific reactions have been rarely compared synoptically.[9] We have recently surveyed the synthesis and application of different group 9 metal-olefin complexes specifically for [2+2+2] cycloaddition reactions, showing the difference between cobalt on one side and the higher congeners rhodium/iridium on the other side.[10]

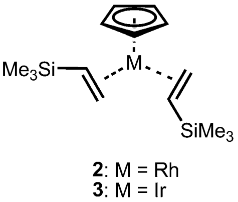
Our research interests are centred around the preparation and catalytic properties of Co(I) olefin complexes as highly reactive catalyst complexes for cyclotrimerization reactions. Very recent studies provided complex **1** as a highly reactive source for the "CpCo" fragment, containing trimethylvinylsilane as an easily displaceable spectator ligand. Complex **1** can act as a highly active catalyst in cycloaddition reactions as well as a precursor for substitution reactions with other mono- and diolefins, providing a wide range of new olefin complexes in excellent yields (Scheme 1).[11]

After having established the synthetic access for the sensitive complex **1**, we were interested in the properties of the complexes containing the same organic ligands, but with rhodium (**2**) or iridium (**3**) as the central metal instead (Scheme 2). Trimethylvinylsilane was rarely used as ligand for these complexes, but should provide insight into the stability of coordination to the metal throughout this group.

The Rh(I) complex **2** was obtained in a study conducted by Perutz and co-workers, where they observed the substitution reaction of the ethylene ligands in CpRh($H_2C{=}CH_2$)$_2$ with trimethylvinylsilane under photochemical conditions.[12] Complex **2** was isolated on a very small scale, but was stable enough to be isolated by chromatography. To the best of our knowledge, the Ir(I) complex **3** had not been prepared so far.



Scheme 1. Synthesis and reactions of the versatile Co(I) olefin complex **1**.



Scheme 2. Formula of the heavier CpRh(I) and CpIr(I) olefin complexes **2** and **3**.

Due to the known higher stability of the CpM-olefin complexes (M = Rh, Ir) we posed the question, how the reactivities of complexes **1–3** differ in cycloaddition and other addition reactions. This would mean an elucidation of the role of different metals from the same group of the periodic table in chemically completely identical environments concerning the organic ligands and framework.

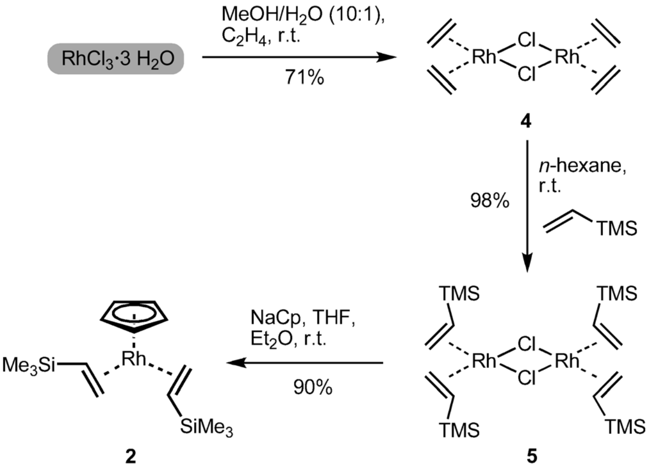
Results and Discussion

Synthesis and Characterization of Complexes 2 and 3

For the synthesis of complexes **2** and **3** the common starting materials are the corresponding metal(III) chlorides. Our initial idea was to adopt the literature procedure for the preparation of dinuclear Rh(I) and Ir(I) tetraethylene complexes for trimethylvinylsilane as olefin.[13] However, basic experiments quickly proved that the direct synthesis under reducing conditions starting from $RhCl_3{\cdot}3H_2O$ or $(NH_4)_3IrCl_6{\cdot}3H_2O$ in the presence of excess trimethylvinylsilane gave either no product or only very small amounts of the desired complexes **5** or **8**.

For the synthesis of **2** we therefore followed the published procedure for the preparation of the tetraolefin complex **5**, which could be prepared by ligand exchange from the tetraethylene complex **4** at room temperature in *n*-hexane and in excellent yield.[14] The reaction was succeeded by subsequent reaction with NaCp, yielding **2** with near quantitative isolated yield for the final step (Scheme 3).

The synthetic access for the iridium congener **3** turned out to be significantly more complicated and less efficient. The tetraethylene complex **7** needed to be prepared *via* the corresponding cyclooctene complex **6**, requiring the substitution from **6** with ethylene to proceed at temperatures as low as –50 °C. The



Scheme 3. Preparation of CpRh(I) olefin complex **2**.

crude substitution product (**7**) was directly reacted with excess trimethylvinylsilane, yielding the isolable complex **8** in 53% yield over two steps. Again the final step is the reaction with NaCp, here yielding the target complex **3** in just 47% yield, which is in strong contrast to the rhodium complex **2** (Scheme 4). However, this synthetic route gave access to sufficient amounts of complex **3**.

The structural characterization of complexes **2** and **3** by X-ray crystallography was attempted, but was successful only for Rh(I) complex **2** (Figure 1).[15] The Ir(I) congener provided only crystals of poor quality from which no valid structural data set could be obtained. Interestingly, the structural parameters for **2** are only slightly different compared to those of Co(I) complex **1**.[11]

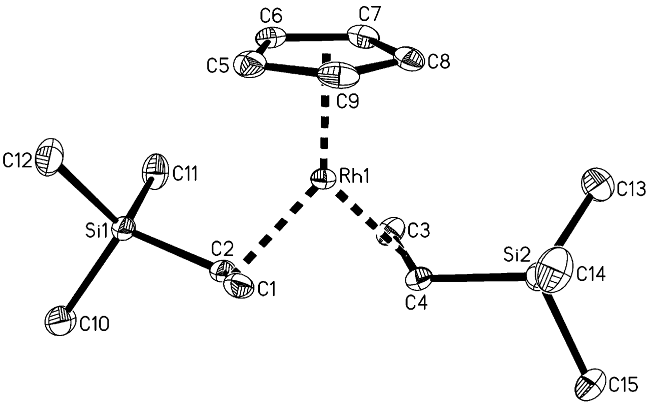
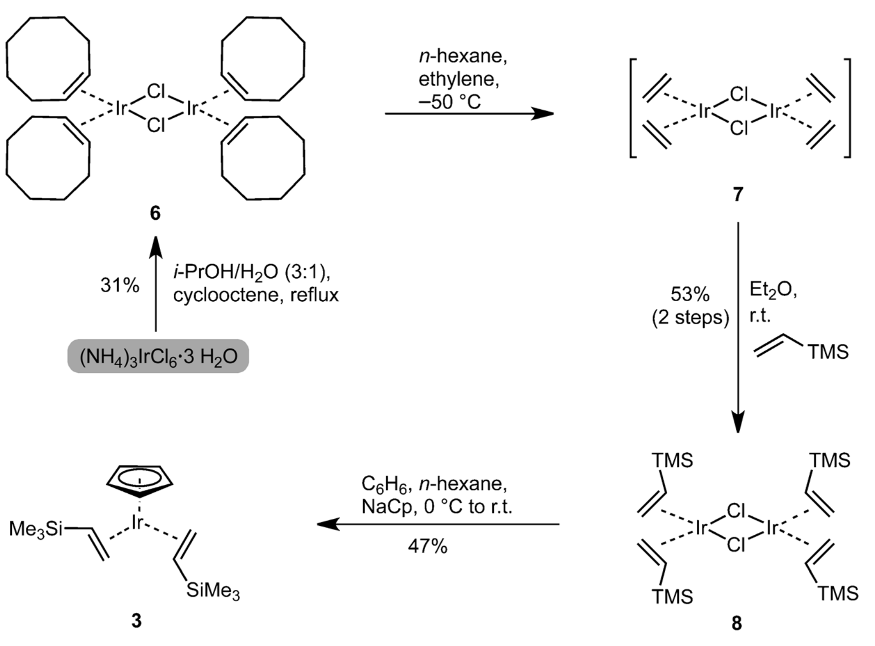


Figure 1. ORTEP drawing of the molecular structure of CpRh($H_2C{=}CHSiMe_3$)$_2$ (**2**) in the crystal. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C1−C2 = 1.406(4), C3−C4 = 1.416(4), C1−Rh1 = 2.129(2), C2−Rh1 = 2.138(2), C3−Rh1 = 2.129(3), C4−Rh1 = 2.144(2), Cp(centroid)−Rh1 = 1.901(2), C4−C3−Rh1 = 71.25(15), C2−C1−Rh1 = 71.14(15), C3−C4−Rh1 = 70.04(14), C1−Rh1−C3 = 108.00(12), C2−Rh1−C4 = 88.22(10).

While the vinylsilane is coordinating to the metal centre, the double bond character of the olefin vanishes [d_{cov}(C=C) = 1.34 Å, in **1**: d(C-1−C-2) = 1.409(3) Å and d(C-3−C-4) = 1.408(2) Å; in **2**: d(C-1−C-2) = 1.406(4) Å and d(C-3−C-4) = 1.416(4) Å], which points to the existence of significant back-bonding. The steric demand of the trimethylsilyl groups required in **1** as well as in **2** a twisted orientation of the olefins [**1** (C-1−C-2−C-3−C-4) = −22.26(15)°, **2** (C-1−C-2−C-3−C4) = 24.1(2)°]. Due to the considerably larger covalent radius of the rhodi-



Scheme 4. Preparation of CpIr(I) olefin complex **3**.

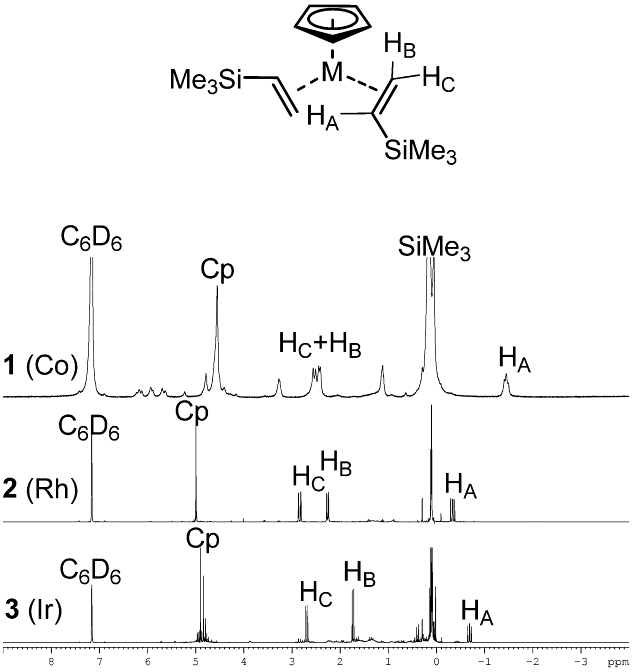
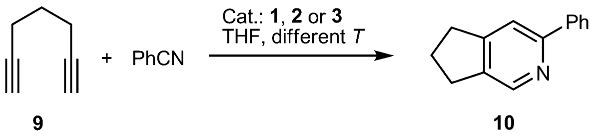


Figure 2. ^{1}H NMR spectra of the complexes **1**, **2** and **3** in correlation.

Table 1. Catalytic screening of intermolecular [2+2+2] cycloaddition reactions.



Entry	Catalyst[a]	T [°C]	Yield of **10** [%][b]
1	**1** (Co)	0	>99
2	**2** (Rh)	100	7[c]
3	**3** (Ir)	100	traces[d]

[a] In each experiment 5 mol% catalyst were used.

[b] 2 equiv. of PhCN per equiv. of **9** were used and the isolated yield is given referring to **9**.

[c] The homocyclized trimer of **9** was isolated in 23%, together with not further characterized higher oligomerization products.

[d] Traces of **10** were detected by ^{1}H NMR.

um atom, the averaged distance to the cyclopentadienyl anion is significantly longer than in **1** {**1**: d[Cp(centroid)–Co] = 1.723(2) Å, **2**: d[Cp(centroid)–Rh] = 1.901(2) Å}. Although the complexes **1** and **2** show many structural similarities, **2** and also **3** are significantly more stable than **1** and can even be handled in air without decomposition.

Figure 2 displays the individual ^{1}H NMR spectra of the group 9 metal-trimethylvinylsilane complexes **1**–**3** referenced against C_6D_6 as solvent. In all complexes, the proton neighboring the silyl group (H_A) is found with the largest high-field shift, compared to the resonances observed for the free olefin. Obviously the resonances in **1** are broad, while **2** and **3** show sharp signals. These complexes show a dynamic behaviour in solution, which depends on the temperature and light irradiation.[12,16]

Catalytic Properties in [2+2+2] Cycloaddition Reactions

CpCo(I)-olefin complexes for cyclotrimerization reactions are by far the most often applied catalyst systems for this class of compounds. There are much less documented examples for the application of CpRh(I)-olefin complexes and to the best of our knowledge no examples for detailed studies on comparable iridium species.[10]

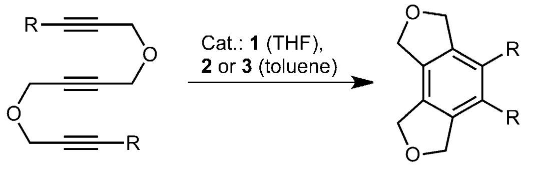
We decided to investigate inter- and intramolecular cyclotrimerizations. Based on our experience with the preparation of pyridines from diynes and nitriles,[11,17] we reacted 1,6-heptadiyne and benzonitrile with the different metal complexes **1**–**3** (Table 1). While for **1** we observed near to quantitative formation of pyridine **10**, the Rh(I) congener **2** gave much lower yields, requiring significantly higher temperature (100 °C). Under the same conditions Ir(I) complex **3** was still nearly inactive and only traces of product were observed. This initial screening experiment already displayed profound differences in reactivity.

To facilitate the cycloaddition process we turned to completely intramolecular cyclotrimerization reactions of triynes and cyanodiynes. These substrates have found use earlier in a number of cases under participation of group 9 metal complexes.[3]

In our first screening experiments we investigated triynes **11** and **12** with terminally unsubstituted as well as arylated diyne moieties, to explore the reactivities with better accessible and sterically more shielded alkyne moieties. The results are presented in Table 2.

For Co(I) complex **1** in both cases the expected products **13** and **14** were isolated. For the phenyl-terminated triyne **12**, however, the isolated yield of benzene **14** was only half of that of **13**, derived from the terminally unsubstituted triyne **11**. The higher reactivity of **11** became evident also for Rh(I) complex **2**, where **13** was isolated in 54% yield, compared to the reaction with **12**, where the expected cycloaddition product **14** was observed with crucially lower yield. However, the yield of **13** and **14** was significantly better at the necessary higher reaction temperatures compared to **1**.[18] Finally for the Ir(I) complex **3** we did not observe the formation of crucial quantities of either **13** or **14** in significant amounts from the respective triynes at all. In both cases the starting materials

Table 2. Reactivities of complexes **1**–**3** in intramolecular cyclotrimerizations with triynes.



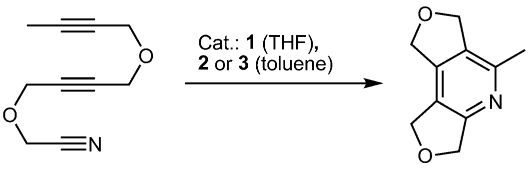
11 (R = H)
12 (R = Ph)

13 (R = H)
14 (R = Ph)

Entry	Catalyst[a]	T [°C]	**13** [%][b]	**14** [%][c]
1	**1** (Co)	0	30	14
2	**2** (Rh)	100	54[d]	39 d)
3	**3** (Ir)	100	traces[e]	–

[a] In each experiment 5 mol% catalyst were used.
[b] Yield, referring to **11**.
[c] Yield, referring to **12**.
[d] After the reaction a red residue was collected and identified as oligomers of either **11** or **12**.
[e] The expected product was identified by the corresponding ^{1}H NMR signals.

Table 3. Reactivities of complexes **1**–**3** in intramolecular cyclotrimerizations with cyanodiyne **15**.



15

16

Entry	Catalyst[a]	T [°C]	Yield of **16** [%][b]
1	**1** (Co)	0	82
2	**2** (Rh)	110	32
3	**3** (Ir)	110	traces[c]

[a] In each experiment 5 mol% catalyst were used.
[b] Isolated yields.
[c] Traces of the product were identified in the ^{1}H NMR spectrum.

were reisolated with at least over 75% of the starting amount. The rather small amount of missing material might have been consumed by side reactions, which we have not further investigated. For **2** and **3** no reactivity with **11** and **12** at all was observed when performing the reaction at 50 °C in THF.

In a final set of experiments we compared the reactivity of complexes **1**–**3** in cycloaddition reactions with cyanodiyne **15**. Cyanodiynes have found use in different cyclotrimerizations and especially in Ru-catalyzed processes good yields at ambient temperature have been reached.[19]

In our experiments an interesting effect was observed (Table 3). While Co(I) complex **1** gave a very good yield of pyridine **16**, again at low reaction temperature, for Rh(I) complex **2** only 32% of **16** were isolated at 110 °C reaction temperature, which is a rather drastic decrease for this purely intramolecular experiment. For Ir(I) complex **3** no reaction except for the detection of a small trace of **16** after work-up of the crude reaction mixture can be stated. Unreacted **15** was reisolated in largely quantitative amount, therefore significant side reactions can be excluded.

The cycloaddition experiments clearly provided evidence for the severely different reactivities of complexes **1**–**3** in [2+2+2] cycloaddition reactions, as exemplified by the temperature differences of the reactions. While Co(I) complex **1** gave very good and far superior results compared to **2** or **3** in cyclotrimerizations leading to pyridine derivatives like **10** or **16**, the Rh(I) complex **2** gave better results in cyclotrimerizations leading to pure carbocyclic products, as demonstrated in Table 2. These differences illustrate the preference of the complexes for either pyridine ring formation (for **1**) or formation of carbocyclic arenes (for **2**). The later assumption was corroborated by the fact, that in the reaction of **9** with PhCN catalyzed by **2**, the homocyclization product of **9** was observed as the major product. The Ir(I) complex **3** was shown to be highly unreactive in these cyclotrimerizations, not giving any substantial amounts of the expected products.

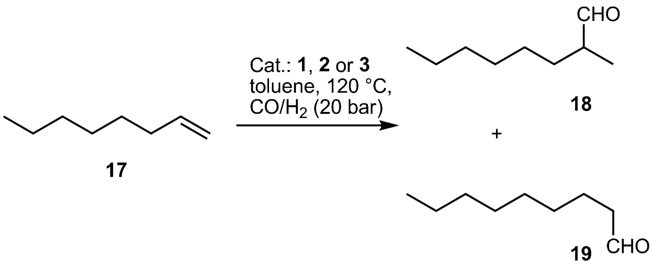
Catalytic Properties in Other Reactions

Hydroformylation

The reactivity of group 9 metal complexes (in the oxidation state +1) in hydroformylation reactions has been known for a long time and is now broadly applied.[20] Prominent examples of catalyst precursor complexes are the Wilkinson catalyst, $RhCl(PPh_3)_3$, or the cobalt hydride $HCo(CO)_4$, which can be generated *in situ* from $Co_2(CO)_8$ in the presence of hydrogen gas and heat. In both examples, an electronically unsaturated hydrido complex is assumed to be the active species.[21] Recently, also iridium(I) precursor compounds together with phosphines were found to be suitable and general catalysts for the hydroformylation of olefins under rather mild conditions.[22] However, for complexes **2** and **3** it is documented that CpM–H species can be formed by insertion into the C–H bond of one of the coordinated olefins, at least under photochemical conditions.[12,16] We decided to investigate the question if this enables complex **1**, **2** and **3** to promote hydroformylation reactions under thermal conditions at higher temperatures (Table 4).

For this investigation, 1-octene (**17**) was chosen as model substrate.[23] The experimental results revealed that only Rh(I) complex **2** gave quite acceptable

Table 4. Hydroformylation of 1-octene with group 9 metal-olefin complexes **1**-**3**.



Entry	Catalyst[a]	**18/19** [%][b]	*n*/*iso*	**20** [%][b]	**21** [%][b,c]
1	**1** (Co)	7	50:50	–	29
2	$Co_2(CO)_8$	94	70:30	5	–
3	**2** (Rh)	65	37:63	15	14
4	$[Rh(acac)(CO)_2]$	92	40:60	5	3
5	**3** (Ir)	6	67:33	68	19
6	[Ir(acac)(COD)]	12	50:50	88	–

[a] In each experiment 0.1 mol% catalyst was used.[b] The products where identified by GC analysis and calibrated against pure samples of **17**, **18**, **19**, **20** (octane) and **21** (2-octene) as reference.

[c] **21** is composed of *cis*- and *trans*-2-octene.

yields of **18** and **19** as expected hydroformylation products (entry 3). It turned out that the complex **1** and **3** provided only low yields of the aldehydes **18** and **19** (entries 1 and 5). Although **1** is highly reactive in cycloaddition reactions, the formation of the aldehydes **18** and **19** is inhibited. The unreacted 1-octene (63%) is probably the result of the decay of **1** or the formation of a comparable unreactive carbonyl complex under the hydroformylation conditions, although isomerization of the double bond was observed to a larger extent. Ir(I) complex **3** on the other hand consumed 94% of the 1-octene, but yielded **18** and **19** with just 6%, the major products being *n*-octane and 2-octene (entry 5). Hydrogenation and isomerization but to a significantly lesser extent were also observed for **2** (Entry 3). To probe the influence of the Cp anion, the reactions were done in comparison to cyclopentadienyls with ligand-free ("naked") catalyst precursor complexes (entries 2, 4 and 6). If the Cp anion has an effect on the reaction a change in reactivity and *n*/*iso* ratio of the obtained aldehydes or the product composition should be observed. The differences in the *n*/*iso* ratio of the hydroformylation products in the reactions promoted by **1** and **3** are significant. For the Rh(I) congener **2** practically no influence of Cp was observed except for a lower yield compared to $[Rh(acac)(CO)_2]$. It is noteworthy, that for **1**–**3** isomerization was significantly higher than for the reference complexes.

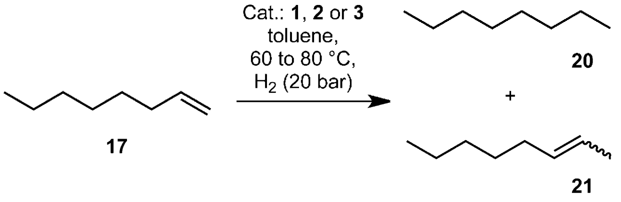
Hydrogenation

Hydrogenation reactions are a classical area of utilization for the higher group 9 metals, while cobalt plays practical no role in this regard.[24] In the hydroformylation reaction of **17** with **1**–**3**, the formation of *n*-octane in varying amounts was observed. These interesting results lead us to the question if hydrogenation of **17** under mediation of the metal-olefin complexes can become a general pathway in the presence of pure hydrogen. The results of these experiments performed in an autoclave with 20 bar of hydrogen pressure are shown in Table 5.

To our surprise we found that all tested complexes **1**–**3** catalyzed the hydrogenation reaction, albeit to largely different extents. In the case of **1** and **2** the conversions of 1-octene were nearly quantitative, while complex **3** left 24% of the 1-octene (**17**) unreacted. The exact determination of the product mixture compositions proved a significant difference. The hydrogenation reaction catalyzed by Co(I) complex **1** afforded the products *n*-octane (**20**) and 2-octene (**21**) in similar quantities. In addition, 3-octene (17%) was also identified in the product mixture. While the Rh(I) precursor complex **2** formed *n*-octane (**20**) as the sole product in quantitative yield, the Ir(I)-catalyzed reaction gave significantly less yield with 66% of **20**, together with a small amount of 2-octene (**21**, 10%), but without any 3-octene being formed.

In conclusion, we found that all three group 9 metal-trimethylvinylsilane complexes **1**–**3** are active catalysts in the hydrogenation reaction of 1-octene (**17**). Rh complex **2** proved to be the most efficient and selective catalyst, which also complies with the wide use of rhodium complexes as catalysts for many

Table 5. Hydrogenation of 1-octene with group 9 metal-olefin complexes **1**–**3**.



Entry	Catalyst[a]	Conversion of **17** [%][b]	Yield of **20** [%][b]	Yield of **21** [%][b,c]
1	**1** (Co)	98	39	42[d]
2	**2** (Rh)	100	100	–
3	**3** (Ir)	76	66	10

[a] In each experiment 2 mol% catalyst were used.

[b] The products were identified by GC analysis and referenced against calibrated pure **17**, **20** and **21** and *cis*/*trans*-3-octene.

[c] **21** is composed of *cis*- and *trans*-2-octene.

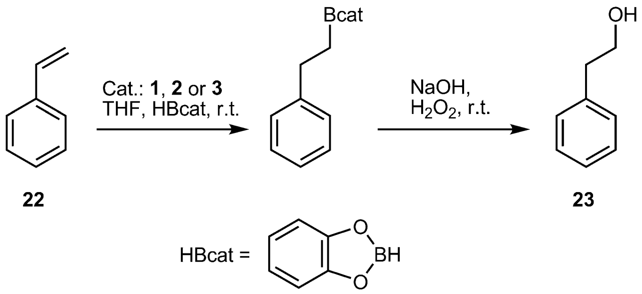
[d] 3-Octene in 17% was detected as a by-product.

hydrogenation reactions. Co(I) complex **1** on the other hand gave a mixture of hydrogenation and isomerization products, and despite the interesting fact that hydrogenation reactivity was observed with this very reactive cyclopentadienyl cobalt complex, the degree of the isomerization side reactions made **1** an unattractive hydrogenation catalyst. Finally, the Ir(I) congener **3** expectedly showed significant hydrogenation activity under the chosen reaction conditions, which was smaller compared to that of rhodium, but larger than that of cobalt.

Hydroboration

A large number of catalytic heterofunctionalization reactions like, for example, hydroboration or hydrosilylation have utilized rhodium or iridium complexes as catalysts.[25] Especially the hydroboration reaction has found widespread use due to the versatile nature of the resulting boronates and boronic acids, which can be further functionalized or act as nucleophilic coupling partners in Suzuki–Miyaura couplings.[26] While Co-catalyzed hydroborations are rather rare,[27] Rh- or Ir-phosphine complexes have been found to catalyze hydroboration processes and are frequently used.[28]

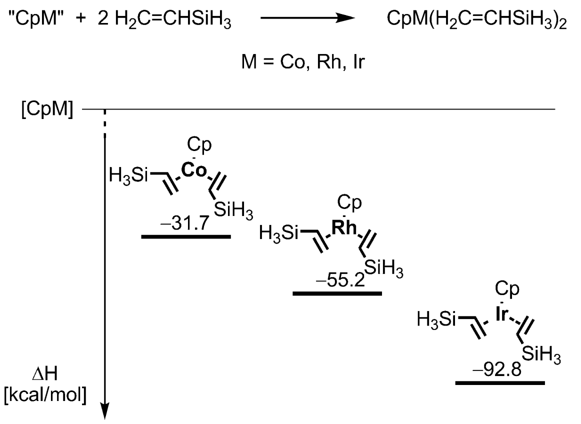
We investigated the hydroboration/hydrolytic oxidation sequence of styrene (**22**) with catecholborane as a standard system to study the catalytic activity (Scheme 5). Unfortunately, the yields of the alcohol **23** were found to be rather small in all cases, even though **23** can be found in traces *via* NMR and GC analytics.



Scheme 5. Attempted hydroboration reaction with styrene and catecholborane.

Computational Studies

To gain some deeper insight into the reactivity behaviour of complexes **1**–**3** in the cycloaddition process, we exemplarily performed calculations on the relative bonding energies of the individual metal-olefin bonds and the exchange processes with acetylenes. The computational method and model are given in the Supporting Information. Several computational mechanistic studies on the general mechanisms of cycloaddition reactions have been published,[4] and also investigations comparing CpCo and CpRh fragments specifically in the formation of pyridines have been released by Kirchner et al.[29]



Scheme 6. Model formation reaction of group 9 metal-vinylsilane complexes for computational calculations.

It can be assumed that the remarkable differences in reactivity of complexes **1**–**3** during the [2+2+2] cycloaddition are a consequence of the bonding nature of the metal core and the coordinating olefins. We calculated the energies of some initial steps of the cycloaddition process for evaluating the observed differences in reactivity. Firstly, we calculated the energies of the formation of group 9 metal-olefin complexes, using vinylsilane as the model olefin. (Scheme 6). Both the computed enthalpies and reaction free energies of formation reveal that this reaction is favoured energetically. The energy of formation from the coordination of the vinylsilane to the "CpM" fragment increases from Co ($\Delta H = -31.7$ kcal mol^{-1}, $\Delta G = -5.4$ kcal mol^{-1}) to Rh ($\Delta H = -55.2$ kcal mol^{-1}, $\Delta G = -28.8$ kcal mol^{-1}) and Ir ($\Delta H = -92.8$ kcal mol^{-1}, $\Delta G = -64.9$ kcal mol^{-1}) significantly. These energetic changes indicate the increased complex stability from Co to Rh and Ir on one hand; and the decreased reactivity on the other hand. This agrees very well with the macroscopic appearances of complexes **1**–**3**, i.e., Co(I) complex **1** is stable only at low temperatures and Rh(I) complex **2** and Ir(I) complex **3** are basically air- and temperature-stable. Therefore, the ease of ligand displacement and stability of the complexes certainly play an important role for the reactivity assessment.

Furthermore, we have calculated the energy for the bis-acetylene complexes at the three different CpM fragments as described above for the vinylsilane complexes. The reaction enthalpy as well as the free energy factors reveal that this is again energetically

$$\mathrm{CpM(H_2C{=}CHSiH_3)_2} \xrightarrow{\mathrm{2\ HC{\equiv}CH}} \mathrm{CpM(HC{\equiv}CH)_2} + \mathrm{2\ H_2C{=}CHSiH_3}$$

M = Co, Rh, Ir

Scheme 7. Computational calculations on the exchange reaction for acetylene and vinylsilane.

advantageous and the coordination of the two acetylenes increases ΔH and ΔG in the same order as calculated for the vinylsilane above [Co ($\Delta H = -33.4$ kcal mol^{-1}, $\Delta G = -13.5$ kcal mol^{-1}); Rh ($\Delta H = -51.2$ kcal mol^{-1}, $\Delta G = -31.3$ kcal mol^{-1}); Ir ($\Delta H = -87.2$ kcal mol^{-1}, $\Delta G = -65.1$ kcal mol^{-1})].

Finally, we computed the parameters of the exchange reaction between the CpM-vinylsilane complexes with acetylene (Scheme 7). As a result it is found that the exchange reaction is favoured both in enthalpy and entropy for M = Co ($\Delta H = -1.7$ kcal mol^{-1}, $\Delta G = -8.2$ kcal mol^{-1}), while for M = Rh the reaction is disfavoured by enthalpy, but favoured by entropy ($\Delta H = +4.0$ kcal mol^{-1}, $\Delta G = -2.4$ kcal mol^{-1}). For M = Ir the reaction is again adverse by enthalpy, but slightly favoured by entropy ($\varDelta H = +5.5$ kcal mol^{-1}, $\Delta G = -0.2$ kcal mol^{-1}). These energetic changes reveal that the exchange reaction should take place easily for M = Co at low temperature, and become possible for M = Rh at significantly enhanced temperature, while becoming unlikely for M = Ir even at higher temperature. This difference in reactivity has been observed in Table 2 and Table 3 for the related cycloaddition reactions.

To explain the increased stability of CpM complexes from M = Co to Rh and Ir, we have analyzed the structure and bonding between the metal centre and the acetylene ligands. At first, we have compared the energy difference between the singlet and triplet states of CpM. For CpCo, the triplet state in C_{5v} symmetry is 37.0 kcal mol^{-1} more stable than the singlet state in C_1 symmetry. For CpRh, the triplet state in C_{5v} symmetry is 14.3 kcal mol^{-1} more stable than the singlet state in C_s symmetry. For CpIr, however, the triplet state has C_s symmetry and the C_{5v} symmetrical structure represents a high order saddle point on the potential energy surface; the triplet ground state in C_s symmetry is only 0.3 kcal mol^{-1} more stable than the singlet state in C_s symmetry. This shows that CpCo has a very stable triplet state compared to CpRh and CpIr.

On the basis of the natural bonding orbital analysis it is found that CpIr has the strongest interaction with the acetylene ligand compared to CpRh and CpCo. For example, the computed C≡C bond in $\mathrm{CpIr(HC{\equiv}CH)_2}$ is longer and has weaker Wiberg bond indices (1.260 Å and 2.282) than in $\mathrm{CpRh(HC{\equiv}CH)_2}$ (1.248 Å and 2.392) and in $\mathrm{CpCo(HC{\equiv}CH)_2}$ (1.243 Å and 2.414). Furthermore, the Ir–C≡ bond has a stronger Wiberg bond index (0.559) than the Rh–C≡ (0.497) and Co–C≡ (0.490) bonds. This shows that CpIr has stronger interactions with the acetylene ligand compared to CpRh and CpCo. All these findings are in line with the observed stability and reactivity of the corresponding complexes.

The subsequent steps of the catalytic cycle are different for the three metals with respect to the nature of the initially formed metallacycle: while cobalt forms a metallacyclopentadiene, for rhodium and iridium rather a metallacyclopentatriene might be proposed.[29,30] However, the exergonic order of the oxidative cyclization of the alkynes again favours cobalt over rhodium and iridium.

Conclusions

In the presented investigation we systematically compared the reactivities of the three group 9 metals cobalt, rhodium and iridium in complexes with identical ligand framework of the type $\mathrm{CpM(H_2C{=}CHSiMe_3)_2}$ (M = Co, Rh and Ir) in [2+2+2] cycloaddition and other addition reactions. The Rh(I) and Ir(I) complexes have been prepared *via* new routes and the molecular structure of $\mathrm{CpRh(H_2C{=}CHSiMe_3)_2}$ (**2**) was determined and compared with that of the Co(I) complex **1**.

The [2+2+2] cycloaddition reactions proved $\mathrm{CpCo(H_2C{=}CHSiMe_3)_2}$ (**1**) as most reactive in those reactions where pyridines are formed, however, $\mathrm{CpRh(H_2C{=}CHSiMe_3)_2}$ (**2**) was found to be the best catalyst for the cyclotrimerization of triynes. $\mathrm{CpIr(H_2C{=}CHSiMe_3)_2}$ (**3**) only gave traces in all cycloaddition reactions investigated, therefore this complex proved to be not suitable as a catalyst under the reactions conditions investigated. The reaction temperatures for the complexes were very different. Exemplarily, **1** was active at 0 °C already, while for **2** 100 °C needed to be applied.

In hydroformylation reactions of 1-octene (**17**), **2** clearly was the most successful catalyst, and **1** preferably gave isomerization of the olefin double bond. Comparable results were observed in the hydrogenation of 1-octene (**17**), where **2** gave a quantitative yield of *n*-octane (**20**), **3** produced besides octane a small amount of isomerzation product and **1** catalyzed hydrogenation and isomerization reactions to the same extent. Finally, the examination of hydroboration as a test reaction gave no results useful for making statements on reactivity differences for **1**–**3**.

Calculations on the reaction of the 'CpM' fragment with vinylsilane showed, that the stability of the bis-olefin complexes increases significantly from cobalt to iridium, which is congruent with the observed reactivity trends. In summary, strong effects on the reactivity were observed for the group 9 metals with identical ligand frameworks for [2+2+2]cycloaddition and different addition reactions.

Experimental Section

General Methods

All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk techniques if not stated otherwise. All solvents were obtained from commercial sources and were freshly distilled prior to use. Trimethylvinylsilane was purified by distillation before use. The synthesis of cobalt complex **1** has been described before.[11]

Synthesis of Complexes

Synthesis of 4: The complex **4** has been prepared by bubbling ethylene (1 bar) through a solution of $RhCl_3 \cdot 3H_2O$ (1.0 g, 3.8 mmol) in methanol (20 mL) and water (2 mL) for 20 h at room temperature. Filtration of the resulting slurry and drying of the red solid gave **4**; yield: 0.525 mg (1.3 mmol, 71%).

Synthesis of 5: To a solution of **4** (504 mg, 1.3 mmol) in *n*-hexane (6 mL) an excess of trimethylvinylsilane (3 mL, 20.7 mmol) was added and the mixture stirred for 1 hour at room temperature. The volatiles were removed and the residue was dried under reduced pressure. The pure red-colored **5** was obtained; yield: 861 mg, (1.2 mmol, 98%). ^{1}H NMR (C_6D_6, 300 MHz, 20°C): $\delta = 0.43$ (s, 36H, SiC*H*$_3$), 0.96 (dd, 4H, $^3J = 15$ Hz, 11 Hz, C*H*SiCH$_3$), 3.24 (d, 4H, $^3J = 11$ Hz, *cis*-C*H*$_2$), 3.76 (d, 4H, $^3J = 15$ Hz, *trans*-C*H*$_2$).

Synthesis of 2: To a solution of **5** (920 mg, 1.3 mmol) in Et_2O (10 mL) a solution of NaCp (0.75 mL, 1.5 mmol, 2 M in THF) was added dropwise and the mixture stirred for 3 h at room temperature. After filtration (G4 frit) of the slurry, the solvent was removed from the filtrate and the residue was dried under reduced pressure. The yellow complex **2** was obtained; yield: 901 mg (2.4 mmol, 90%); mp 95–96°C. ^{1}H NMR (C_6D_6, 400 MHz, 20°C): $\delta = -0.34$ (ddd, $^3J = 14$ Hz, 11 Hz, $^2J_{Rh,H} = 0.7$ Hz, 2H, C*H*Si), 0.10 (s, 18H, SiC*H*$_3$), 2.25 (dd, $^3J = 11$ Hz, $^2J_{Rh,H} = 0.7$ Hz, 2H, C*H*$_2$ *cis*), 2.84 (dd, $^3J = 14$ Hz, $^2J_{Rh,H} = 1.0$ Hz, 2H, C*H*$_2$ *trans*), 4.99 (d, $^2J_{Rh,H} = 0.5$ Hz, 5H, C$_5$*H*$_5$); ^{13}C NMR (C_6D_6, 100 MHz, 20°C): $\delta = 0.50$ [s, Si(*C*H$_3$)], 39.0 (d, $^1J_{Rh,C} = 0.7$ Hz, *C*H$_2$), 52.9 (d, $^1J_{Rh,C} = 0.7$ Hz, *C*HSi), 87.4 (d, $^1J_{Rh,C} = 0.7$ Hz, *C*$_5$H$_5$); ^{29}Si NMR (C_6D_6, 79 MHz, 20°C): $\delta = -0.18$ (s, *Si*CH$_3$); MS (EI): *m/z* = 368 [M$^+$] (4), 268 [M$^+$–H$_2$C=CHSiMe$_3$] (100), 168 [M$^+$–2(H$_2$C=CHSiMe$_3$)] (9s). Crystals suitable for X-ray crystal structure analysis were obtained by storing a saturated ethanol/dichloromethane solution of **2** at –4°C.

Synthesis of 6: The addition of cyclooctene (200 mg, 2.0 mmol) to a solution of $(NH_4)_3IrCl_6 \cdot 3H_2O$ (0.45 g, 1.0 mmol) in *iso*-propanol (3 mL) and water (9 mL) for 2 h at 90°C led to precipitation of a red solid. The filtration of the resulting slurry and drying of the red residue **6**; yield: 140 mg (0.15 mmol, 31%).

Synthesis of 8: The complex **8** was prepared by bubbling ethylene (1 bar) through a solution of **6** (200 mg, 0.2 mmol) in *n*-hexane (20 mL) for 16 h at –78°C. The decantation of the resulting slurry and drying of the grey residue furnished **7**. Without isolation, residual **7** was dissolved in Et_2O (10 mL) and mixed with an excess of trimethylvinylsilane (2 mL, 13.8 mmol) and stirred for 4 h at –50°C. The volatiles were removed from the residue which was dried under vacuum to furnish the red-coloured **8**; yield: 53% (106 mg, 0.1 mmol) of. ^{1}H NMR (C_6D_6, 300 MHz, 20°C): $\delta = 0.35$ (s, 36H, SiC*H*$_3$), 1.04–1.14 (m, 4H, C*H*SiCH$_3$), 2.54 (dd, 4H, $^3J = 11$ Hz, $^2J_{Ir,H} = 0.8$ Hz, C*H*$_2$ *cis*), 3.61 (d, 4H, $^3J = 14$ Hz, C*H*$_2$ *trans*).

Synthesis of 3: To a solution of **8** (200 mg, 0.2 mmol) in *n*-hexane (5 mL) a solution of NaCp (0.2 mL, 0.4 mmol, 2 M in THF) was added dropwise and the mixture stirred for 30 min at 0°C. After that time the slurry was allowed to warm to room temperature and was stirred for additional 30 min. After filtration (G4 frit) of the slurry, the solvent was removed from the filtrate and the residue was dried under reduced pressure. The yellow-colored complex **3** was obtained; yield: 100 mg (0.2 mmol, 47%); mp 101–103°C. ^{1}H NMR (C_6D_6, 300 MHz, 25°C): $\delta = -0.683$ (dd, $^3J = 12$ Hz, 10 Hz, 2H, C*H*Si), 0.09 (s, 18H, SiC*H*$_3$), 1.73 (d, $^3J = 10$ Hz, 2H, C*H*$_2$ *cis*), 2.69 (d, $^3J = 12$ Hz, 2H, C*H*$_2$ *trans*), 4.90 (s, 5H, C$_5$*H*$_5$); ^{13}C NMR (C_6D_6, 75 MHz, 25°C): $\delta = 0.5$ [s, Si(*C*H$_3$)], 19.3 (s, *C*H$_2$), 34.1 (s, *C*HSi), 82.4 (s, *C*$_5$H$_5$); ^{29}Si NMR (C_6D_6, 79 MHz, 25°C): $\delta = 1.21$ (s, *Si*CH$_3$); MS (CI, positive, isobutane): *m/z* = 458 [M$^+$] (100).

General Procedures for Reactions with Complexes 1–3

General procedure for the catalytic [2+2+2]cycloaddition of diyne 9 with benzonitrile: 1,6-Heptadiyne (**9**, 1.0 mmol) and benzonitrile (2.0 mmol) were dissolved in THF (4 mL) and stirred at 0°C. The appropriate trimethylvinylsilane complex (**1**, **2**, or **3**, 0.05 mmol) dissolved in Et_2O (0.25 mL) was added dropwise and the solution was stirred for various times (2 min in the case of **1** at 0°C, 24 h with **2** and **3** at 100°C). The product was separated *via* column chromatography with *n*-hexane/EtOAc (4:1) as eluent and **10** or resulting side-products were isolated. The product was identified by its NMR and GC-MS data.[11]

General procedure for the catalytic [2+2+2]cycloadditions with triyne 11 and 12 and cyanodiyne 15: For complex **1**: in a Schlenk flask the triyne **11** or **12** or the cyanodiyne **15** (in each case 1.0 mmol) were dissolved in THF at 0°C. A solution of **1** in ether (0.05 mmol) was added and the reaction mixture stirred for 2 h at 0°C. After that time, the solvent was removed under reduced pressure and the residue was purified by column chromatography with *n*-hexane/EtOAc (6:1 v/v) as the eluent. The corresponding product (**13**, **14** or **16**) was identified by its ^{1}H and ^{13}C NMR data and comparison with the reported data.[31]

For complexes **2** and **3**: in a Schlenk flask the triynes **11** or **12** or the cyanodiyne **15** (in each case 1.0 mmol) and the respective complex were dissolved in toluene and heated to 100°C for 18 h. After cooling the mixture, the solvent was removed under reduced pressure and the residue was purified by column chromatography with *n*-hexane/EtOAc (6:1 v/v) as the eluent. The corresponding product (**13**, **14** or **16**) was identified as mentioned before.

General procedure for the catalytic hydroformylation of 1-octene (17): The olefin (**17**, 10.2 mmol) was added under argon to a solution of the metal precursor **1** (pre-cooled solution in ether), **2** or **3** (0.1 mol%) in toluene (20 mL). The reaction mixture was transferred into an autoclave, which was then heated to 80 °C under introduction of syngas. After 2 h the temperature of the reaction mixture was raised to 120 °C in the case of **1** and **3** and to 100 °C for **2**. Following 22 h reaction time, the autoclave was allowed to cool down to room temperature, and the pressure was released. The reaction mixture was analyzed immediately by gas chromatography.

General procedure for the catalytic hydrogenation of 1-octene (17): The olefin (**17**, 1.0 mmol) was added under argon to a solution of the metal precursor (2.0 mol%) in toluene (20 mL). The reaction mixture was transferred into an autoclave, which was then heated to 60 °C. Hydrogen was then introduced and heating continued for 2 h, then the reaction mixture was heated for 22 h at 80 °C. After the reaction time, the autoclave was allowed to cool down to room temperature, and the pressure was released. The reaction mixture was analyzed immediately by gas chromatography.

General procedure for the catalytic hydroboration of styrene (22) with catecholborane: To a solution of **22** (0.1 g, 1.0 mmol) and HBcat (1.0 mmol, 1 M in THF) in THF (3 mL) a solution of the catalyst (5 mol% in the case of **1** in Et_2O and for **2** and **3** in 0.5 mL THF), was added dropwise and the mixture stirred for 2 h at room temperature. After quenching with EtOH (2 mL) the solution was mixed with NaOH (2 M, 4 mL) and H_2O_2 (4 mL, 30% v/v in water). The slurry was stirred for 3 h, before the reation mixture was extracted with Et_2O several times. The combined organic phases were washed with brine and NaOH (2 M) and dried with $MgSO_4$. Traces of product **23** were identified by GC and ^{1}H NMR.[32]

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