4298 *Organometallics* **2010,** *29,* 4298–4304
DOI: 10.1021/om100692k

ORGANOMETALLICS
Article

Highly Reactive Cyclopentadienylcobalt(I) Olefin Complexes

Marko Hapke,* Nico Weding, and Anke Spannenberg

Leibniz-Institut für Katalyse e.V. (LIKAT) an der Universität Rostock, Albert-Einstein-Strasse 29a, D-18059 Rostock, Germany

Received July 14, 2010

The reduction of cobaltocene with metallic potassium in the presence of trimethylvinylsilane yielded the new CpCo(I) complex [CpCo($H_2C{=}CHSiMe_3$)$_2$] (**6**). Complex **6** turned out to be an ideal starting material for substitution reactions with functionalized mono- and diolefins, giving access to either new [CpCo(olefin)$_2$] complexes such as **7** (trichlorovinylsilane) and **12** (dimethyl fumarate) or CpCo(diolefin) complexes such as **8** (diallyl ether), **9** (1,5-hexadiene), **10** (1,4-pentadiene), and **11** (1,1,3,3-tetramethyldivinyldisiloxane) with essentially quantitative yields. These complexes are rarely accessible by other methods or the direct reduction method using alkali metals. The complexes **6**–**9** were unambiguously characterized by X-ray structure analysis, which is reported for the first time for these types of complexes, giving way for the structural comparison. Computational calculations on the olefin ligand exchange processes with **6** display the different stabilities and reactivity trends of the different CpCo(I)-olefin complexes. The extraordinarily high reactivity and the application of complexes **6** and **9** were demonstrated in [2+2+2] cycloaddition reactions of different diynes with nitriles, yielding the substituted isoquinoline derivatives with good yields within short reaction times and under very mild conditions. The presented complexes show higher activities compared to [CpCo(COD)] (**3**) while possessing advantages in preparation and handling compared to [CpCo($H_2C{=}CH_2$)$_2$] (**4**).

Introduction

The basis of transition metal-catalyzed catalytic reactions is the presence of a catalyst precursor in the form of a metal complex containing one or several so-called spectator ligands, which are susceptible to dissociation, yielding the catalytically active complex fragment under preferably mild conditions.[1] Often these stable catalyst precursor complexes consist of transition metal compounds following the 18-electron rule, which requires the dissociation of ligands to provide the coordinatively unsaturated and therefore reactive metal center. While the reactivity and selectivity of these complexes is in general governed by the metal and the tight covalently or coordinatively bound ligands, the reactivity is strongly influenced by the lability of coordinated spectator ligands. Olefins have often found increasing importance in the preparation as well as reactivity control of late transition metal complexes.[2] The structural versatility of olefins and the fine-tunability of their donor/acceptor properties certainly contribute to the continued interest in this class of ligands for catalytic endeavors. The utilization of olefins as stabilizing ligands can be done either in defined, stable complexes or as additives in the intermediate generation of highly reactive, organometallic species, most often compounds with low-valent metal centers. Exciting examples for the first case can be found especially for the late transition metals such as Ni(0)-olefin complexes[3] or the Pd(0)[4] and Pt(0)[5] congeners, where a diverse number of isolated compounds is known. Compared to Ni(0)-olefin complexes the situation changes for isoelectronic M^+ complexes of the neighboring element of the first transition metal row, namely, η^5-cyclopentadienyl(Cp)Co(I)-olefin complexes. Here the chemistry of olefin complexes started major development only after the groundbreaking work of Jonas,[6] who was able to establish an access to CpCo($H_2C{=}CH_2$)$_2$, which is now commonly called the Jonas reagent (**4**, Scheme 1).[7] Derivatives containing tethered Cp substituents and ethylene ligands have also been reported.[8] Intimately connected to the preparation and synthetic application of low-valent cobalt complexes were a variety of cobalt-mediated cycloaddition reactions,[9] with

---

*To whom correspondence should be addressed. E-mail: marko.hapke@catalysis.de.

[1] Hartwig, J. F. *Organotransition Metal Chemistry*; University Science Books: Sausalito, 2010; Chapter 5.

[2] Johnson, J. B.; Rovis, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 840.

[3] Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185.

[4] (a) Krause, J.; Cestaric, G.; Haack, K.-J.; Seevogel, K.; Storm, W.; Pörschke, K.-R. *J. Am. Chem. Soc.* **1999**, *121*, 9807. (b) Blum, K.; Chernyshova, E. S.; Goddard, R.; Jonas, K.; Pörschke, K.-R. *Organometallics* **2007**, *26*, 5174, and references therein.

[5] Berthon-Gelloz, G.; Schumers, J.-M.; Lucaccioni, F.; Tinant, B.; Wouters, J.; I. E. Markó, *Organometallics* **2007**, *26*, 5731, and cited references.

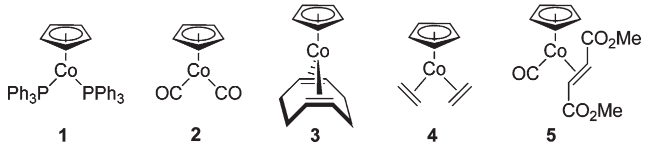
[6] Reviews: (a) Jonas, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 520. (b) Jonas, K. *Pure Appl. Chem.* **1984**, *56*, 63. (c) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295.

[7] Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716; *Angew. Chem. Suppl.* **1983**, 1005.

[8] (a) Butenschön, H. *Chem. Rev.* **2000**, *100*, 1527. (b) Yong, L.; Butenschön, H. *Chem. Commun.* **2002**, 2852.

[9] Hegedus, L. S.; Söderberg, B. C. G. *Transition Metals in the Synthesis of Complex Organic Molecules*, 3rd ed.; University Science Books: Sausalito, 2010.

Scheme 1. Cobalt(I) Complexes Frequently Used for [2+2+2] Cycloaddition Reactions



special emphasis on cyclotrimerization reactions.[10] The early developments in this area with respect to complex organic synthesis have been highlighted *inter alia* with the synthesis of (±)-estrone by Vollhardt et al.[11]

Today, complexes of the entire periodic table triad consisting of cobalt, rhodium, and iridium have found broad use in different cyclotrimerization reactions, favorably yielding substituted arenes, heteroarenes, and biaryls,[12] including the asymmetric synthesis of biaryl compounds.[13] In the case of cobalt-based catalysts still a rather small number of isolable CpCo(I) compounds is frequently applied (Scheme 1).

From the CpCo(I) complexes shown in Scheme 1, **1**−**4** have been well known for a rather long time now, compared to complex **5**, which has been reported only recently by Gandon et al.[14] They exemplify the difficulties in balancing sufficient stabilization of the catalytically active species on one side, while on the other these spectator ligands must be labile enough to liberate the active catalyst complex under preferably mild conditions. If the stabilizing ligands are too tightly bound, these catalyst complexes require external energy supply by either heating to elevated temperatures or light or both together, to efficiently generate the catalytically active species, such as **1**−**3** and **5**. Complex **4** proved to be reactive at much lower temperatures, but requires careful handling under inert conditions and storage under an atmosphere of ethylene because even storage under nitrogen or argon can lead to decomposition. Compound **3** can be handled for short periods of time in air, but heat or irradiation is required to activate this catalyst precursor.

Results and Discussion

Synthesis and Structure of the CpCo(I) Olefin Complexes. The reductive abstraction of Cp ligands from transition metal complexes is a known but rather little used methodology. The usefulness was first demonstrated by the preparation of **4** from cobaltocene using alkali metals in the presence of ethylene.[7] This methodology also gave way for the preparation of other CpCo(I) complexes with unfunctionalized cyclic diolefins such as 1,5-cyclooctadiene (COD), yielding compound **3**. Since then, the use of **4** was reported in several cases, partially including low reaction temperatures (up to −20 °C).[15] However, during our studies of cobalt-catalyzed cycloaddition reactions,[16] we came across the question of whether the reactivity of **4** and the relative stability of complexes like **3** or **5** can be combined to comparably stable but more reactive Co(I) complexes. In addition we were interested in the question of whether Co(I) complexes containing functionalized olefins can be synthesized, because the direct preparation was hampered by the use of reactive alkali metals and no other general synthetic access is known so far.[17]

In order to avoid the use of gaseous ethylene, we focused on olefins that are liquids and easily removable from the reaction mixture but yet stable against the strongly reductive conditions of the complex preparation and also capable of providing at least some significant bonding to the metal center. These efforts led us to the application of trimethylvinylsilane as the ligand of choice (Scheme 2). The convenient reaction of cobaltocene and potassium in the presence of trimethylvinylsilane at −78 °C resulted in the formation of **6** as a red compound in high yield (80%).[18]

The single-crystal X-ray structure analysis confirmed the formation of the [CpCo($H_2C{=}CHSiMe_3)_2$] (**6**) (Figure 1).[19]

---

(10) (a) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 505. (b) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248.

(11) Review: Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

(12) Recent reviews: (a) Chopade, P. R.; J. Louie, J. *Adv. Synth. Catal.* **2006**, *348*, 2307. (b) Heller, B.; Hapke, M. *Chem. Soc. Rev.* **2007**, *36*, 1085. (c) Agenet, N.; Busine, O.; Slowinski, F.; Gandon, V.; Aubert, C.; Malacria, M. *Org. React.* **2007**, *68*, 1. (d) Tanaka, K. *Synlett* **2007**, 1977. (e) Scheuermann neé Taylor, C. J.; Ward, B. D. *New J. Chem.* **2008**, *32*, 1850. (f) Hess, W.; Treutwein, J.; Hilt, G. *Synthesis* **2008**, 3537. (g) Varela, J. A.; Saá, C. *Synlett* **2008**, 2571. (h) Galan, B. R.; Rovis, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 2830, and cited references.

(13) (a) Bringmann, G.; Price Mortimer, A. J.; Keller, P. A.; Gresser, M. J.; Garner, J.; Breuning, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 5384. (b) Tanaka, K. *Chem. Asian J.* **2009**, *4*, 508. (c) Shibata, T.; K. Tsuchikama, K. *Org. Biomol. Chem.* **2008**, *6*, 1317.

(14) Geny, A.; Agenet, N.; Iannazzo, L.; Malacria, M.; Aubert, C.; Gandon, V. *Angew. Chem., Int. Ed.* **2009**, *48*, 1810.

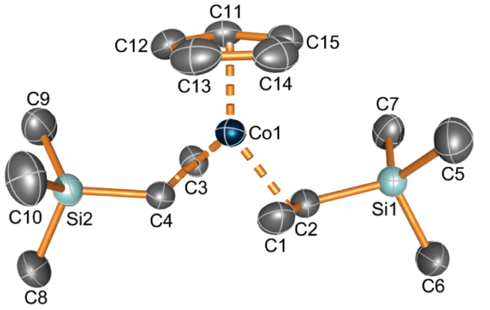
(15) Recent examples for the use of **4**: (a) Sehnal, P.; Stará, I. G.; Šaman, D.; Tichý, M.; Míšek, J.; Cvačka, J.; Rulíšek, L.; Chocholoušová, J.; Vacek, J.; Goryl, G.; Szymonski, M.; Císařová, I.; Starý, I. *Proc. Natl. Acad. Sci.* **2009**, *106*, 13169. (b) Leboeuf, D.; Gandon, V.; Aubert, C.; Malacria, M. *Chem.—Eur. J.* **2009**, *15*, 2129. (c) Amslinger, S.; Aubert, C.; Gandon, V.; Malacria, M.; Paredes, E.; Vollhardt, K. P. C. *Synlett* **2008**, 2056. (d) Aubert, C.; Betschmann, P.; Eichberg, M. J.; Gandon, V.; Heckrodt, T. J.; Lehmann, J.; Malacria, M.; Masjost, B.; Paredes, E.; Vollhardt, K. P. C.; Whitener, G. D. *Chem.—Eur. J.* **2007**, *13*, 7443. (e) Ampt, K. A. M.; Duckett, S. B.; Perutz, R. N. *Dalton Trans.* **2007**, 2993. (f) Hrdina, R.; Stará, I. G.; Dufková, L.; Mitchel, S.; Císařová, I.; Kotora, M. *Tetrahedron* **2006**, *62*, 968. (g) Goswami, A.; Maier, C.-J.; Pritzkow, H.; Siebert, W. *J. Organomet. Chem.* **2005**, *690*, 3251.

(16) (a) Hapke, M.; Kral, K.; Fischer, C.; Spannenberg, A.; Gutnov, A.; Redkin, D.; Heller, B. *J. Org. Chem.* **2010**, *75*, 3993–4003. (b) Heller, B.; Redkin, D.; Gutnov, A.; Fischer, C.; Bonrath, W.; Karge, R.; Hapke, M. *Synthesis* **2008**, 69. (c) Heller, B.; Gutnov, A.; Fischer, C.; Drexler, H.-J.; Spannenberg, A.; Redkin, D.; Sundermann, C.; Sundermann, B. *Chem.—Eur. J.* **2007**, *13*, 1117. (d) Gutnov, A.; Heller, B.; Fischer, C.; Drexler, H.-J.; Spannenberg, A.; Sundermann, C.; Sundermann, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 3795.

(17) Habermann, D. Ph.D. Thesis, Universität Bochum, 1980.

(18) Complex **6** has been reported to be synthesized by adaption of the Jonas protocol, without description of experimental details, and the NMR data have been provided: Lenges, C. P.; Brookhart, M.; Grant, B. E. *J. Organomet. Chem.* **1997**, *528*, 199.

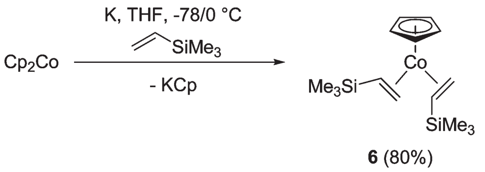
(19) (a) Crystal data for **6**: $C_{15}H_{29}CoSi_2$, $M_r = 324.49$, triclinic, space group P_1, $a = 6.8151(5)$ Å, $b = 11.5177(9)$ Å, $c = 11.9438(9)$ Å, $\alpha = 77.994(6)°$, $\beta = 75.525(6)°$, $\gamma = 87.846(6)°$, $V = 887.80(12)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.214$ g·cm^{-3}, $\mu = 1.086$ mm^{-1}, $T = 200$ K, 10 000 reflections measured, 3758 independent reflections ($R_{int} = 0.0307$), 3187 reflections observed [$I > 2\sigma(I)$], final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0265$, $wR_2 = 0.0676$, R indices (all data): $R_1 = 0.0334$, $wR_2 = 0.0696$, 193 refined parameters. (b) Crystal data for **7**: $C_9H_{11}Cl_6CoSi_2$, $M_r = 446.99$, monoclinic, space group $C2/c$, $a = 15.9701(11)$ Å, $b = 6.8829(3)$ Å, $c = 15.3137(9)$ Å, $\beta = 96.381(5)°$, $V = 1672.9(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.775$ g·cm^{-3}, $\mu = 2.106$ mm^{-1}, $T = 200$ K, 8882 reflections measured, 1573 independent reflections ($R_{int} = 0.0294$), of which 1210 were observed [$I > 2\sigma(I)$], final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0342$, $wR_2 = 0.0845$, R indices (all data): $R_1 = 0.0482$, $wR_2 = 0.0886$, 102 refined parameters. (c) Crystal data for **8**: $C_{11}H_{15}CoO$, $M_r = 222.16$, monoclinic, space group $P2_1/n$, $a = 11.3734(4)$, $b = 7.4820(3)$, $c = 11.7728(5)$ Å, $\beta = 106.919(3)°$, $V = 958.45(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.540$ g·cm^{-3}, $\mu = 1.744$ mm^{-1}, $T = 200$ K, 11 675 reflections measured, 2032 independent reflections ($R_{int} = 0.0234$), of which 1623 were observed [$I > 2\sigma(I)$], final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0210$, $wR_2 = 0.0461$, R indices (all data): $R_1 = 0.0314$, $wR_2 = 0.0478$, 142 refined parameters. (d) Crystal data for **9**: $C_{11}H_{15}Co$, $M_r = 206.16$, monoclinic, space group Pn, $a = 5.6233(6)$ Å, $b = 12.5738(13)$ Å, $c = 6.7557(7)$ Å, $\beta = 100.803(8)°$, $V = 469.20(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.459$ g·cm^{-3}, $\mu = 1.767$ mm^{-1}, $T = 200$ K, 5314 reflections measured, 1911 independent reflections ($R_{int} = 0.0695$), of which 1734 were observed [$I > 2\sigma(I)$], final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0412$, $wR_2 = 0.0917$, R indices (all data): $R_1 = 0.0454$, $wR_2 = 0.0930$, 108 refined parameters.



6

Figure 1. ORTEP drawing of the molecular structure of **6** in the crystal (hydrogens have been omitted).

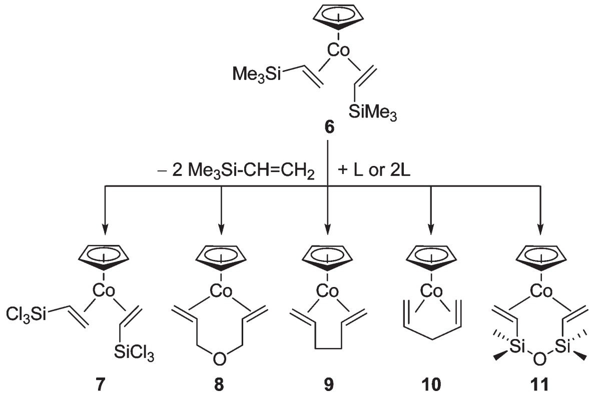
Scheme 2. Preparation of the Bis(monoolefin) Complex 6 from Cobaltocene



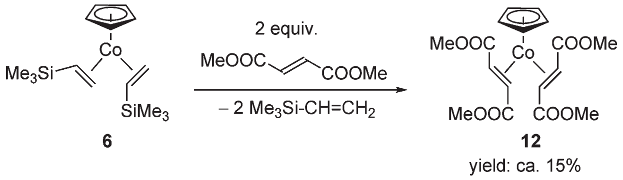
To the best of our knowledge, **6** is the first structurally characterized CpCo(I)-bis(monoolefin) complex with an unsubstituted Cp ring.[20] Besides one Cp ligand the structure possesses two trimethylvinylsilane ligands coordinating to the cobalt(I) center in a distorted trigonal-planar mode with the Me_3Si groups of the olefins pointing in opposite directions.[21] While the electron-rich olefin is coordinating to the Co(I) center, the double-bond character of the olefins vanishes [$d_{\mathrm{cov}}(\mathrm{C{=}C}) = 1.34$ Å,[22] $d(\mathrm{C1{-}C2}) = 1.409(3)$ Å, and $d(\mathrm{C3{-}C4}) = 1.408(2)$ Å], which points to the existence of significant back-bonding. The olefins coordinate to the Co center in a twist orientation similar to that observed by Brookhart et al. for $[\mathrm{Cp^*Co(H_2C{=}CHSiMe_3)_2}]$,[23] probably due to the steric demand of the Me_3Si substituent at the olefin (see C1−Co−C3 and C2−Co−C4). In comparison to $[\mathrm{Cp^*Co(H_2C{=}CHSiMe_3)_2}]$, **6** is significantly more labile. Low-temperature NMR studies revealed that **6** decomposes slowly at temperatures higher than −30 °C and therefore needs to be stored under inert conditions at low temperatures.[24]

The high reactivity of **6** led to determining if and to what extent the CpCo fragment can be stabilized by other functionalized mono- and diolefins. Hence we investigated the use of **6** in ligand substitution reactions with other olefins. The results proved that **6** is a very suitable precursor for the preparation of a number of new CpCo(I) complexes with mono- as well as diolefins most of which are not directly accessible via reduction or any other known route (Scheme 3). The reaction times are very short, and the substitution reactions gave after facile workup quantitative yields of complexes **7**−**11**, which were all characterized by NMR and mass spectrometry. They in general turned out to be more sensitive compounds compared to complex **3**, containing a cyclic diene and which can be handled for short periods of time in air. Whereas the silane-based complexes **6** and **7** are favorably stored at low temperatures, **8**−**11** are stable at ambient temperatures.[25] However, they can all be handled safely by applying normal Schlenk techniques. The direct synthesis from the reduction of cobaltocene by potassium in the presence of the corresponding olefin was attempted for complex **9**. Although the formation of **9** was confirmed by NMR, the isolation of the pure compound turned out to be difficult and yielded the complex as a red oil. The yield was estimated to be about 35%, the isolated product containing small amounts of paramagnetic impurities.

Scheme 3. Preparation of Olefin Complexes 7−11 from the Precursor Complex 6



Scheme 4. Preparation of Olefin Complexes 12 from 6 and Dimethyl Fumarate



We also examined the substitution reaction of the solid electron-deficient olefin dimethyl fumarate with complex **6** (Scheme 4). As it turned out, isolation of the expected substitution product **12** after the reaction was much more difficult compared to the liquid olefins used up to this point. The reason was mainly that isolation of **12** by recrystallization after removal of the solvent was hampered by the cocrystallization of product together with free dimethyl fumarate and unknown reaction byproducts. Obviously here not only clean substitution takes place but presumably also a side-reaction. However, analytical verification of the formation of complex **12** was found possible.[26]

---

(20) An X-ray structure determination of **4** was mentioned, but has never been published: Benn, R.; Cibura, K.; Hofmann, P.; Jonas, K.; Rufińska, A. *Organometallics* **1985**, *4*, 2214.

(21) The following angles (deg) were found in the trigonal-planar coordination: DB1−Co1−DB2 = 96.1°; DB1−Co1−Cp = 132.5°; DB2−Co1−Cp = 131.5° [here, DB1 (C1, C2) and DB2 (C3, C4) are the center of the double bonds and Cp is the centroid of the cyclopentadienyl ring].

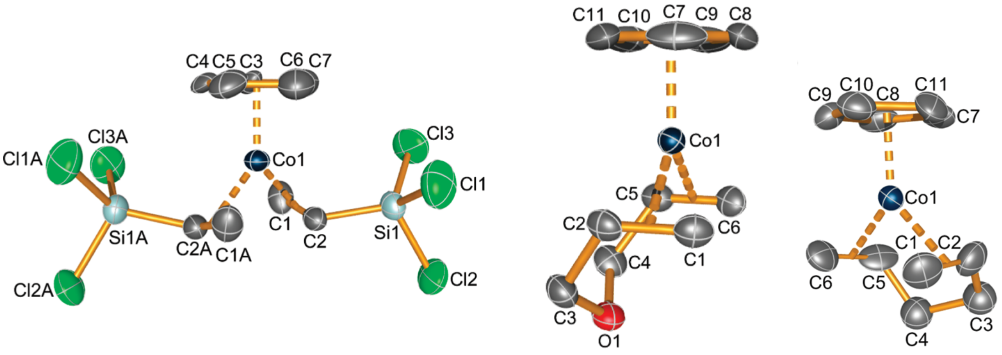
(22) Pyykkö, P.; Atsumi, M. *Chem.—Eur. J.* **2009**, *15*, 12770.

(23) Lenges, C. P.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 6965.

(24) Characterization of the product by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy was possible (see Supporting Information). Solutions of **6**, however, can be stored for months at −30 °C in the freezer and used for subsequent reactions without problems.

(25) The syntheses of **9** and **10** from **4** have been decribed, including isomerization reactions of the coordinated olefins over long periods of time: Cibura, K. Ph.D. Thesis, Ruhr-Universität Bochum, 1985. However, besides the ^{1}H and ^{13}C NMR data no molecular structures were described and the synthesis described in our paper starting from **6** afforded the pure complexes fast and quantitatively.

(26) NMR and MS analysis proved the formation of **12**; the spectra can be found in the Supporting Information.



7 **8** **9**

Figure 2. Molecular structures of CpCo(I)-olefin complexes **7**, **8**, and **9**.

We were able to obtain crystals suitable for X-ray crystallographic studies of complexes **7**, **8**, and **9**, which are rare examples of CpCo(I) complexes with monoolefin and nonconjugated diene ligands exhibiting interesting features (Figure 2).[19] The observed NMR spectra reveal the high symmetry of the complexes; however, in the solid state this can only be found exactly in complex **7**, which exhibits C_2 symmetry. The silyl-group-containing compounds **6** and **7** are more distorted than those with a carbon atom neighboring the double bond [deviation from planarity: **6** (C1−C2−C3−C4) = −22.26(15)°, **7** (C1−C2−C1A−C2A) = 26.2(4)°, **8** (C1−C2−C5−C6) = −1.17(15)°, and **9** (C1−C2−C5−C6) = 10.1(5)°].[27] Only complex **8** exhibits a nearly perfect coplanar arrangement of the coordinated olefins. As found for complex **6** the double-bond widening of the coordinated olefins in all new Co(I) complexes is observed [**7**: *d*(C1−C2) = 1.379(5); **8**: *d*(C1−C2) = 1.396(3), *d*(C5−C6) = 1.397(3); **9**: *d*(C1−C2) = 1.387(8), *d*(C5−C6) = 1.409(4) Å]. Comparable distances were observed in complex **3**.[28] The substitution of the double bonds with either electron-donating or -accepting silyl groups in **6** and **7** is also displayed in the slightly different olefin bond lengths.

The investigation by NMR spectroscopy corroborated the successful olefin exchange reactions for complexes **7**−**12**. The signals for the coordinated olefins were shifted to higher field as compared to the free olefins. It is worth mentioning that the shifts of the complexed monoolefins in complex **6** and **7** partially show rather drastic shifts for the uncomplexed/complexed olefins.[29] The NMR data clearly point out the formation of only one isomer, as did the determined molecular structure. The shift difference for the geminal proton of the olefin carbon bearing the silyl group is nearly 8 ppm (for **6**: δ = −1.63 ppm, $\Delta\delta$ = 7.71 ppm; for **7**: δ = −1.50 ppm, $\Delta\delta$ = 7.75 ppm), presenting a very large shift for these protons. The shift in complex **6** is even about 1.2 ppm larger than found for the corresponding proton in the Rh congener [CpRh($H_2C{=}CHSiMe_3$)$_2$].[30] These shift differences are comparably much higher than the differences observed for the uncomplexed/complexed protons at the other olefin carbon atom in **6** and **7**, which are in the range between 3 to 4 ppm. These extraordinarily large differences were not observed in complexes **8**−**12**, where shifts in the range of 2.0 and 4.7 ppm were observed. The geminal olefin proton at the carbon atom connected to the siloxane group in complex **11** containing the disiloxane ligand is shifted about 5.1 ppm high field compared to the free diolefin ligand. This is significantly less than observed in **6** or **7** and might be caused by the slightly different steric arrangement of the diolefin around the cobalt metal center.

Comparison of Computed Energies of the Complexes. In order to obtain more detailed insight into the exchange process, we calculated the relative energetic parameters of the process and found that **6** is the most reactive component (therefore set as the zero point) in the series of complexes **3**, **4**, and **6**−**12** (Scheme 5).[31] Even **4** is about 7.5 kcal/mol more stable than **6**, which is comparable to the also slighthly more stable trichlorosilyl-substituted analogue **7** (8.5 kcal/mol). Substitution reactions with diolefins such as COD (for **3**), 1,5-hexadiene (for **9**), or divinyldisiloxane (for **11**) are expectably entropically benefited by the appearance of a chelating effect compared to the application of monoolefins such as ethylene or trichlorovinylsilane and therefore more stable. The entropic contribution to the free energy of the complex formation with these dienes (like for **3**, **8**−**11**) significantly adds to the ease of the substitution.

Evaluation of Reactivity. Besides the development of this systematic procedure for the preparation of CpCo(I) complexes with functionalized olefins and their structural evaluation, reactivity of these complexes is a central aspect for catalytic applications. From that perspective we chose complexes **6** and **9** to be tested in cycloaddition reactions. Due to the lability of the monoolefin ligands, as exemplified in **4**, these complexes show enormous catalytic activity especially in [2+2+2] cycloaddition reactions at rather low temperatures compared to complexes such as **1**−**3** or **5**. We chose the reactions between different diynes and nitriles yielding substituted isoquinolines as the testing ground (Table 1). The reactions applying complex **6** as the catalyst gave acceptable to very good isolated yields (up to 92%) over the course of several minutes' reaction time for the reaction of 1,6-heptadiyne (**13**) with different nitriles (**16**−**19**). The use of the internal alkyne **14**, possessing bulky terminal *tert*-butyl groups, still gave 53% yield of pyridine **20** for this more

---

(27) Also compare the following angles: **7**: C2−Co1−C2a 90.48(12)°, C1−Co1−C1a 112.8(3)°; **8**: C1−Co1−C6 89.52(9)°, C2−Co1−C5 94.10(7)°, C1−Co1−C5 105.06(8)°, C2−Co1−C6 106.16(8)°; **9**: C1−Co1−C6 93.2(2)°, C2−Co1−C5 83.3(2)°, C1−Co1−C5 97.4(2)°, C2−Co1−C6 106.6(2)°.

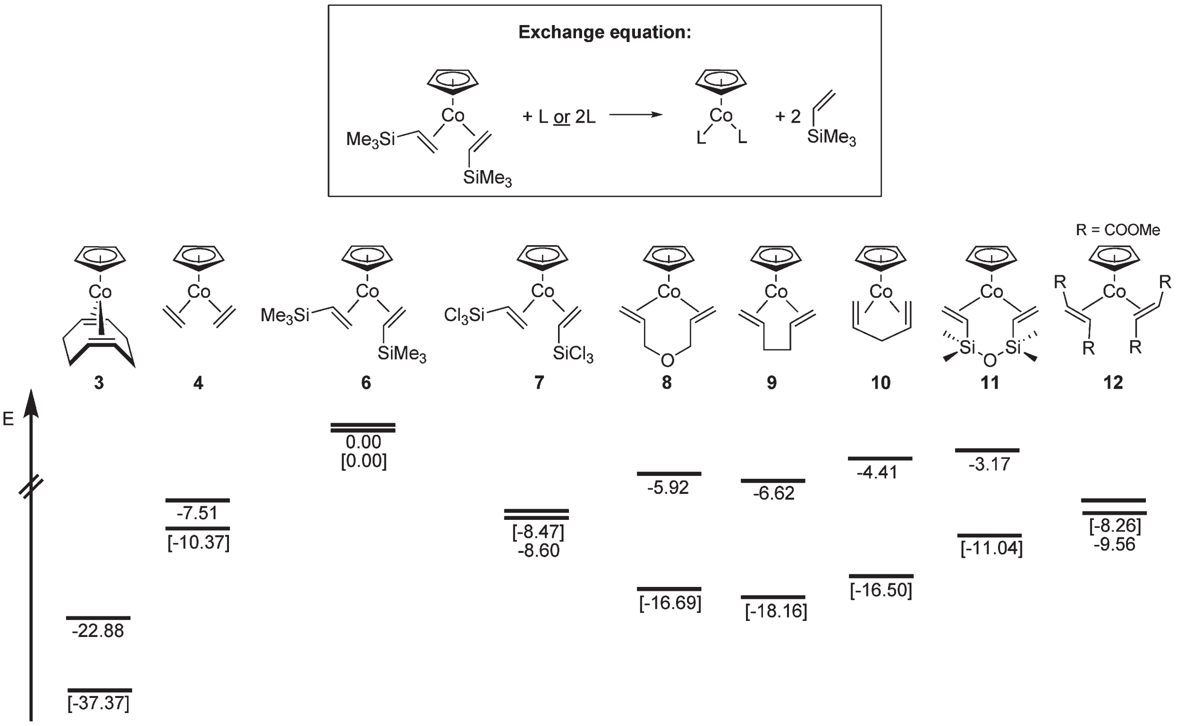
(28) Ondracek, J.; Schehlmann, V.; Maixner, J.; Kratochvil, B. *Collect. Czech. Chem. Commun.* **1990**, *55*, 2447.

(29) For an overview of the different observed shifts see the table in the Supporting Information.

(30) Belt, S. T.; Duckett, S. B.; Haddleton, D. M.; Perutz, R. N. *Organometallics* **1989**, *8*, 748.

(31) Details for the calculations on the relative energetics of the substitution reaction can be found in the Supporting Information.

Scheme 5. Energetic Parameters (enthalpies and free energies [in brackets] in kcal/mol) of the Substitution Reaction for CpCo(I) Complexes 3, 4, and 6−12



challenging diyne substrate. Finally the reaction of 1,7-octadiyne (**15**) with PhCN gave the isoquinoline derivative **20** with somewhat lower yield (46%). For further corroboration we also investigated the reactivity of complex **9**, which was found to be rather stable compared to the above-mentioned monoolefin complexes as well as **8**, **10**, and **11**.[32] It should present a good compromise between complex stability and sufficient reactivity, on the basis of efficient release of the catalytically active fragment under mild conditions. As it turned out, the cycloaddition reaction between **13** and benzonitrile was efficiently catalyzed at 40 °C reaction temperature, yielding the pyridine **19** within a few hours with excellent, 98%, yield. The cycloadditions of diynes **14** and **15** with PhCN gave the products **20** and **21** with somewhat lower or even higher yield. Additionally, the reaction of **13** and PhCN catalyzed by **9** can be performed successfully by using nondried, commercially available THF solvent under standard conditions, yielding **19** with still 92% yield. Obviously for reactions using complex **9** no rather explicitly anhydrous reaction conditions are needed, making this complex a viable alternative catalyst precursor for cycloaddition reactions. The use of CpCo(COD) (**3**) in these reactions for comparison at 40 °C did not yield any product, proving that comparably much more activation energy was necessary.

The extraordinarily high reactivity of the CpCo(I) complexes can be exemplified by another observation. For a number of cobalt-catalyzed cycloaddition reactions utilizing *in situ* generated catalyst systems based on a cobalt(II) salt, heteroatomic ligands such as diphosphines, diimines, or disulfide ligands, and zinc as the reductant, chlorinated solvents are used regularly.[33] We added chlorinated solvents such as dichloromethane, chloroform, or tetrachloromethane to solutions of complex **6** or **9** in THF at room temperature. A rapid color change from red to green was observed. The analysis of the reaction products after removal of the volatile components showed that a cobaltocenium salt was obtained, possessing a tetrachlorocobaltate counterion, forming a compound of the structure $[(Cp_2Co)_2(CoCl_4)]$ (Scheme 6). The source of the chloride is undoubtedly the solvent, which can be explained only by the occurrence of C−Cl activation by a reactive cobalt species. These observations are in agreement with a recent report by Braunstein et al., where they found C−Cl activation in dichloromethane by low-valent cobalt(I) complexes.[34] A comparable reaction by $Cp^*Co(CO)_2$ required irradiation energy for the C−Cl activation process, and the reaction stopped after the oxidative addition step.[35] The observation of the disproportionation of CpCo halides into cobaltocene salts has been reported by Maitlis et al. before.[36]

Conclusion

In summary, we report on the synthesis of the new CpCo(I) complex **6**, containing two trimethylvinylsilane ligands, using the reduction of cobaltocene by potassium metal in the presence of the olefin. Complex **6** was established as an excellent starting material for the preparation of a number of different CpCo(I) complexes by fast and quantitative substitution reactions with functionalized olefins, yielding the complexes **7**−**12**, which cannot be prepared by the direct reduction or any other route. The investigations highlighted for the first time the unambiguous determination of the

---

[32] Complex **9** was found to be unchanged in the composition of its crystal form after about two weeks in air. However, the evaporation of a NMR sample of **9** and leaving the solid residue open to air resulted in decomposition of the complex after 24 h, as proven by NMR.

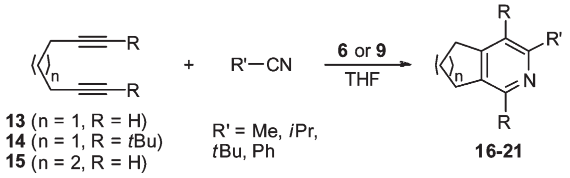
[33] Examples: (a) Hilt, G.; Hengst, C.; Hess, W. *Eur. J. Org. Chem.* **2008**, 2293. (b) Hilt, G.; Hess, W.; Vogler, T.; Hengst, C. *J. Organomet. Chem.* **2005**, *690*, 5170.

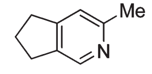
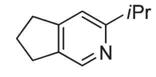
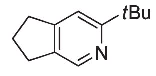
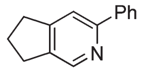
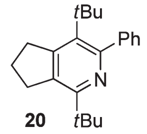
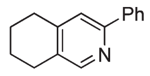
[34] Pattacini, R.; Jie, S.; Braunstein, P. *Chem. Commun.* **2009**, 890.

[35] Olson, W. L.; Nagaki, D. A.; Dahl, L. F. *Organometallics* **1986**, *5*, 630.

[36] Roe, D. M.; Maitlis, P. M. *J. Chem. Soc. A* **1971**, 3173.

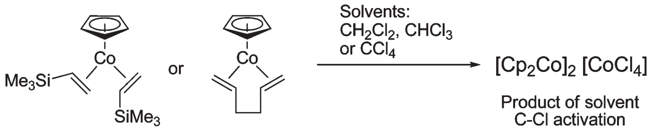
Table 1. Investigation of 6 and 9 in Cycloaddition Reactions



Nitrile	Diyne	Catalyst	Product	Yield [%][a]
MeCN	13	6[b]	 16	57
iPrCN	13	6[b]	 17	86
tBuCN	13	6[b]	 18	71
PhCN	13	6[b]	 19	92
		9[c]		98
PhCN	14	6[b]	 20	53
		9[c]		31
PhCN	15	6[b]	 21	46
		9[c]		63

[a] Isolated yields. [b] Reaction conditions: 5 mol % **6**, RT. [c] Reaction conditions: 6 mol % **9**, 40 °C.

Scheme 6. Reaction of Complexes 6 and 9 with Chlorinated Hydrocarbons



6 9

molecular structure of a series of these new CpCo(I)-olefin complexes. Evaluation of the reactivity of complexes **6** and **9** in cocyclotrimerization reactions between diynes and nitriles yielding isoquinolines spotlighted the extraordinary catalytic activity of these catalyst precursor complexes. The presented new CpCo(I)-olefin complexes are highly promising candidates for further investigations of their catalytic properties, and the methodology presents a general mild access to the interesting CpCo(I) fragment. Further investigations to exploit the full synthetic potential also with respect to the synthesis of highly active chiral Co(I) complexes are underway.

Experimental Section

General Methods. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk techniques. All solvents were received from commercial sources and were freshly distilled prior to use. Trimethylvinylsilane, trichlorovinylsilane, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, bis(prop-2-enyl) ether, penta-1,4-diene, and hexa-1,5-diene were purified by distillation before use. Cobaltocene was used without purification.

Synthesis of 6. Cobaltocene (0.5 g, 2.6 mmol) and potassium (0.109 g, 2.8 mmol) were dissolved in Et_2O (10 mL) and stirred at −78 °C. The trimethylvinylsilane (1.8 g, 18.2 mmol) was added dropwise via syringe, and the brown slurry was stirred for 5 days at −78 °C. After this time the solvent was removed under reduced pressure and the residue was dissolved in 10 mL of *n*-pentane and filtered over a Schlenk frit. The resulting red solution was evaporated under reduced pressure to give 0.678 g (80%) of **6**. ^{1}H NMR (CD_2Cl_2, 400 MHz, −50 °C): δ −1.63 (t, ^3J(H,H) = 12.7 Hz, 2H, C*H*Si), 0.07 (s, 18H, SiCH_3), 2.26 (d, ^3J(H,H) = 10.6 Hz, 2H, CH_2 *cis*), 2.49 (d, ^3J(H,H) = 14.6 Hz, 2H, CH_2 *trans*), 4.69 (s, 5H, C_5H_5) ppm. ^{13}C NMR (CD_2Cl_2, 100 MHz, −50 °C): δ −0.57 (s, Si(CH$_3$)), 40.1 (s, CH$_2$), 49.3 (s, *C*HSi), 83.0 (s, C_5H$_5$) ppm. ^{29}Si NMR (CD_2Cl_2, 79 MHz, −50 °C): δ 0.94 (*Si*CH$_3$) ppm. Crystals suitable for X-ray structure analysis were obtained by storing a saturated diethyl ether solution of **6** at −40 °C.

General Procedure for the Olefin Substitution Reaction, Exemplified for the Preparation of 7. To a stirred solution of [CpCo($H_2C{=}CHSiMe_3$)$_2$] (**6**) in Et_2O (5 mL, 1.0 mmol, 0.2 M) was added dropwise an excess of trichlorovinylsilane (0.8 g, 5.0 mmol) at −30 °C over a period of 2 min. The resulting solution was stirred for 5 min, and the solvent was removed under reduced pressure at −20 °C. Drying under vacuum achieved 0.443 g (quant.) yield of **7**. ^{1}H NMR (C_6D_6, 300 MHz, 25 °C): δ −1.50 (dd, 2H, ^3J(H,H) = 10.7 Hz, C*H*Si), 2.17 (d, 2H, ^3J(H,H) = 10.6 Hz, CH_2 *cis*), 2.61 (d, 2H, ^3J(H,H) = 14.1 Hz, CH_2 *trans*), 4.53 (s, 5H, C_5H_5) ppm. ^{13}C NMR (C_6D_6, 75 MHz, 25 °C): δ 41.40 (s, *C*H$_2$), 46.15 (*C*HSi), 87.00 (s, C_5H$_5$) ppm. ^{29}Si NMR (CD_2Cl_2, 79 MHz, −50 °C): δ 5.31 (*Si*Cl$_3$) ppm. Crystals suitable for X-ray structure analysis were obtained by cooling a saturated diethyl ether solution of **7** to −40 °C.

General Procedure for the [2+2+2] Cycloaddition Reactions Catalyzed by Complex 6. The appropriate diyne (**13**−**15**, 1.0 mmol) and nitrile (2.0 mmol) were dissolved in THF (4 mL) and stirred at room temperature. Complex **6** (0.016 g, 0.05 mmol) dissolved in Et_2O (0.25 mL) was added dropwise, and the red solution was stirred for a few (2−10 min) minutes, after which the diyne starting material had disappeared. The product was separated via column chromatography with *n*-hexane/EtOAc (6:1 v/v) as eluent, yielding the appropriate isolated pyridines **16**−**21** as products.

General Procedure for the [2+2+2] Cycloaddition Reactions Catalyzed by Complex 9. The appropriate diyne (**13**−**15**, 1.0 mmol) and nitrile (2.0 mmol) were dissolved in THF (4 mL) and stirred at room temperature. Complex **9** (0.012 g, 0.06 mmol) was dissolved in Et_2O (0.25 mL) and added dropwise, and the brown solution was stirred for a few hours at 40 °C. The product was separated via column chromatography with *n*-hexane/EtOAc (6:1 v/v) as eluent, yielding the appropriate isolated pyridines **19**−**21** as products.

Acknowledgment. This work was supported by the Leibniz-Institut für Katalyse e.V. (LIKAT). M.H. thanks Prof. Uwe Rosenthal for his support and helpful discussions and comments.

Supporting Information Available: Copies of ^{1}H NMR and ^{13}C NMR spectra for the cobalt compounds, tables of selected X-ray data for complexes **6**−**9**, details on the reaction of **6** and **9** with chlorinated solvents, details on the calculations and characterization data for the organic compounds **16**−**21**. CIF files giving crystallographic data for complexes **6**−**9** are also available. This material is available free of charge via the Internet at http://pubs.acs.org.