The first metal complexes of bicyclopropylidene, a unique tetrasubstituted alkene ligand

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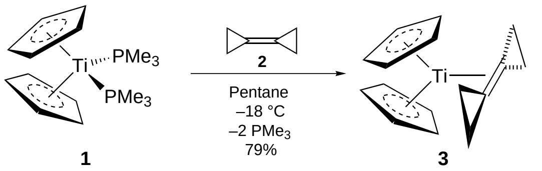
The reactions of bicyclopropylidene 2 with bis(cyclopentadienyl)bis(trimethylphosphane)titanium(II) 1 and with the cobalt chelate 4 give the first known metal complexes of bicyclopropylidene 3 and 7, respectively, in good yields; the bicyclopropylidene cobalt complex 7 is characterized by an X-ray crystal structure analysis which shows a severe out-of-plane bending of the alkenic ligand, indicating considerable back-bonding which goes along with a release of strain in the ligand.

The organometallic chemistry of cyclopropane derivatives is dominated by ring opening reactions.[1,2] However, metal-mediated substitutions on vinylcyclopropane derivatives[3] and cycloadditions with methylenecyclopropane **5** and its derivatives[4–7] can also be achieved with retention of the ring. In view of their high-lying HOMOs,[8,9] methylenecyclopropane **5** and especially bicyclopropylidene **2** should be strong π-bases capable of efficiently donating electron density into the vacant orbitals of transition metals. In particular, strained alkenes have an increased ability to accept back-bonding and therefore are preferentially coordinated to transition metals,[10–13] and it is this feature which is frequently used to stabilize otherwise unstable alkenes and alkynes by complexation.[14,15] Indeed, some transition metal, including cobalt, complexes of methylenecyclopropane have been reported.[4,16]

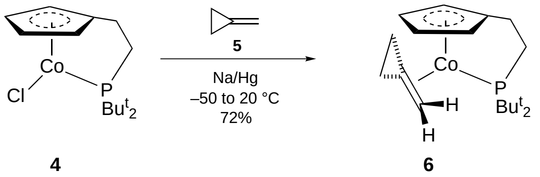
Here, we report on the synthesis and the structural characterization of the first transition metal complexes of **2**,[17] which contains a more highly strained double bond[18] than methylenecyclopropane **5**.

A first attempt to bind an intact bicyclopropylidene unit to a metal was made by use of the titanocene fragment. (Alkene)bis(cyclopentadienyl)titanium(II) complexes are known, and they are 16e complexes.[19] If there were a tendency towards ring opening of a bicyclopropylidene ligand by oxidative addition, it should happen with this complex fragment attached. One way to prepare titanium complexes with sensitive ligands starts from titanocene dichloride, which can easily be converted to $Cp_2Ti(PMe_3)$ **1**.[20,21] Treatment of **1** with 1.16 equiv. of **2** in pentane gave (η^2-bicyclopropylidene)(bis-η^5-cyclopentadienyl)titanium(II) **3** in 79% yield as a green solid (Scheme 1), which was characterized by its ^{1}H and ^{13}C NMR spectra‡ as well as by a correct elemental analysis. While signals for the CH_2 and cyclopentadienyl carbon atoms are clearly observed at δ 15.3 and 116.7 as a triplet and a doublet, respectively, the signal assigned to the coordinated quaternary carbon atoms of the bicyclopropylidene ligand appears as a singlet of only low intensity at δ 93, a value which is in accord with those observed for related compounds.[22] A structural investigation of **3** has so far been precluded because suitable crystals for an X-ray structure analysis could not be obtained. Anyhow, **3** is the first example of an (alkene)bis(cyclopentadienyl)titanium(II) complex without a supporting PR_3 ligand or stabilizing methyl groups on the cyclopentadienyl ligands.[22]



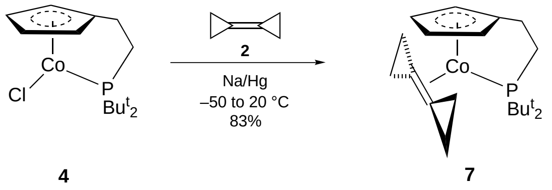
Scheme 1

Complexation of sensitive ligands without subsequent reactions is also possible with the {[2-(di-*tert*-butylphosphanyl)-*P*-ethyl]-η^5-cyclopentadienyl}cobalt(I) fragment (CoCp#), with which the cyclopentadienyl ligand and the pending phosphane side arm coordinate at the metal to form a rather stable chelate.[23–25] For oligomerization reactions, frequently observed at normal cyclopentadienyl cobalt, to occur with this complex fragment, an advance decomplexation of the phosphane side arm would be necessary. In this case the phosphane side arm normally wins the competition with an external ligand for entropic reasons. A reliable method for the preparation of such complexes is the reductive complexation starting with the paramagnetic chloro complex **4** in the presence of sodium amalgam and the new ligand.[26] As a first test, **2** was treated with **4** at low temperature in this manner and gave a 72% yield of complex **6** (Scheme 2), which was identified by its spectral data. The NMR spectra show two signals for alkenic protons and two signals for non-alkenic cyclopropyl carbon atoms indicating an orientation of the methylenecyclopropane ligand as in formula **6**. In the mass spectrum the molecular ion peak is observed (*m*/*z* 350, 19%), the base peak resulting from decomplexation of **1**.



Scheme 2

Next, **2** was treated with **4** in the presence of sodium amalgam, and the corresponding cobalt complex **7** (Scheme 3) was obtained in even higher yield (83%) as large brown crystals of up to 7 mm edge length after crystallization from diethyl



Scheme 3

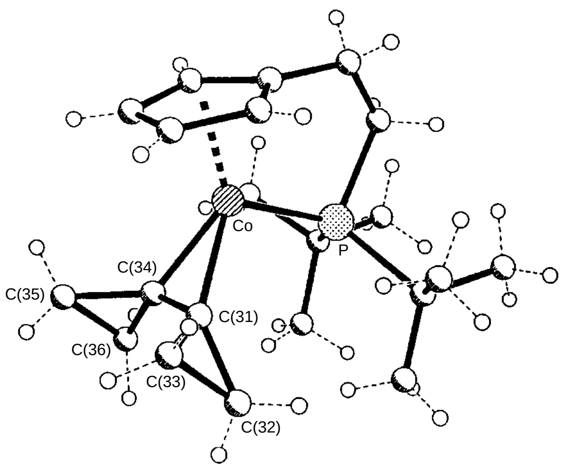


Fig. 1 Structure of the bicyclopropylidene cobalt complex **7** in the crystal.‡ Selected bond lengths (Å) and angles (°): Co–C(31) 1.956(4), Co–C(34) 1.965(3), C(31)–C(34) 1.401(5), C(31)–C(32) 1.482(5), C(32)–C(33) 1.499(12), C(33)–C(31)–C(32) 61.2(5), C(33)–C(31)–C(34) 129.5(5), C(32)–C(31)–C(34) 131.5(5), C(31)–C(34)–C(36) 133.8(3), C(31)–C(34)–C(35) 129.8(3).

ether. The NMR spectra indicate a plane of symmetry through the cobalt atom and the center of the double bond as in formula **7**. As for **6**, in the mass spectrum of **7** the molecular ion peak is observed (*m*/*z* 376, 27%), and the base peak also results from bicyclopropylidene decomplexation.

A suitable crystal of compound **7** was subjected to an X-ray structural analysis (Fig. 1). According to this the bicyclopropylidene ligand has undergone a remarkable out of plane bending by 40° at both termini of the double bond. This indicates a large back-bonding effect accepted by bicyclopropylidene, which is also documented by the long bond length of the coordinated double bond (1.401 Å) as compared to that in uncoordinated **2** (1.314 Å[27]). As a result of the complexation the double bond of bicyclopropylidene is expanded by *ca.* 6.6%. It is instructive to compare these numbers with those of ethene and the ethene complex corresponding to **7**. The bond length of ethene is 1.330 Å, in the ethene complex corresponding to **7** this value is 1.396 Å,[24] an increase of only 5.0%. The bonds in **2** and **7** adjacent to the double bond are of similar length, whereas the single bond opposite the double bond is significantly shortened from 1.544 Å in **2** to 1.499 Å in complex **7**. This is a consequence of the change in hybridization of the coordinated carbon atoms from sp^2 towards sp^3, causing a smaller endocyclic interorbital angle and thus shorter distal bonds in the ring.

A DTA–TG analysis revealed the remarkable thermal stability of **7**, as it can be heated up to 160 °C without decomposition. At 168 °C a strongly exothermic reaction takes place [$\Delta H = -52.1$ kcal mol^{-1} (1 cal = 4.184 J)]. A relative loss of mass of 11.5% is measured which, with a molecular mass of **7** of 376 g mol^{-1} corresponds to a loss of 40 g mol^{-1}, the molecular mass of cyclopropene. This suggests that the bicyclopropylidene ligand decomposes at elevated temperature. After the DTA–TG analysis the material was analyzed by FAB–MS indicating an M$^+$ peak at *m*/*z* 1304. This hints towards the formation of a (CoCp#)$_4$ cluster with three cyclopropane rings.

In conclusion, bicyclopropylidene can be used as a ligand in transition metal complexes of early and late transition metals. The ligand displays a strong back-bonding effect as evidenced by the X-ray crystal structure analysis of the cobalt complex. We are currently investigating the chemistry of bicyclopropylidene complexes and related compounds with special emphasis of their thermochemical behaviour.

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Footnotes and References

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‡ Crystal structure analysis of **7**: $C_{21}H_{34}CoP$: crystal size 0.70 × 0.60 × 0.60 mm, crystal system triclinic, space group $P\bar{1}$ with three molecules in the asymmetric unit, $a = 9.658(1)$, $b = 14.731(2)$, $c = 21.282(4)$ Å, $\alpha = 84.21(2)$, $\beta = 80.64(1)$, $\gamma = 88.46(1)°$, $U = 2972.1(8)$ Å^3, $Z = 6$, $D_c = 1.262$ g cm^{-3}, $3.51 < \theta > 25.06°$, Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $T = 153(2)$ K, 17 372 measured reflections, 10 506 independent reflections, no absorption correction, structure solution with direct methods with SHELXS-86, refinement with SHELXL-93, 401 free parameters, hydrogen atoms in geometrically calculated positions, $R_1 = 0.0544$ [$I > 2\sigma(I)$], $wR_2 = 0.1208$ (all data), refinement to F^2, min., max. residual electron density −1.304, 1.304 e Å^{-3}. CCDC 182/686.

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