Olefin-Metal π-Interactions of Mercury and Zinc Ions in Complexes of Neutral Quinolylcyclopentadiene Derivatives

Markus Enders,*[a] Gunter Ludwig,[a] and Hans Pritzkow[a]

Dedicated to Professor Walter Siebert on the occasion of his 65th birthday

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The donor-functionalised cyclopentadiene derivative **1** acts as a neutral chelate ligand and forms the zinc and mercury complexes **2** and **3** upon treatment with $HgCl_2$ or $ZnCl_2$. Due to the predefined geometry of **1**, the MCl_2 moieties are found in close proximity to the π-system of the cyclopentadiene. In the mercury compound **3** there is some evidence for a bond between the d^{10}-ion and the ring carbon atoms, although this is not conclusive. The zinc compound **2**, however, clearly shows an interaction between the metal atom and the cyclopentadiene fragment. At the same time the bond between the Cp ring and the Me_3Si group is weakened.

Introduction

Coordination compounds of d^{10}-metals with olefins are very common for Ni, Pd and Pt. The metal-olefin interaction is strengthened by back bonding of d-electrons into the anti-bonding olefin-π-orbitals. In d^{10}-metal ions with one or two positive charges, the d-orbitals are contracted and therefore the electrons in these orbitals are much less accessible for back bonding to π-acceptor ligands such as carbon monoxide or olefins. Therefore metal carbonyl or olefin complexes of group 11 cations or group 12 dications are much less common and are less stable than similar neutral group 10 compounds.[1] However, Hg^{2+} is known to interact with arenes and a few examples have been studied by X-ray diffraction.[2]

A metal ion can be fixed in proximity to an olefinic system by the judicious choice of rigid chelating ligands. With such ligands it is possible to study weak interactions between metal atoms and π-electrons. We report here the use of quinoline-functionalised cyclopentadiene derivatives for such investigations, as these ligands possess an adequate rigid geometry.

Results and Discussion

Previously we have found that quinoline-functionalised cyclopentadiene derivatives can bind transition metal atoms through the nitrogen donor and two carbon atoms of the cyclopentadiene ring.[3] Attempts to isolate similar compounds with d^{10}-metal cations have been unsuccessful. In order to increase the donor ability of the pentadiene system, the trimethylsilyl derivative **1** was used as a ligand. Compound **1** was described by us some time ago and it reacts with $TiCl_4$ or $ZrCl_4$ with elimination of Me_3SiCl and formation of η^5-cyclopentadienyl complexes.[4] The solid state structure of **1** has now been investigated and is shown in Figure 1. The Me_3Si group lies in the 3-position relative to the quinoline substituent. The bond C12−Si1 is relatively long [1.924(2) Å] compared to the same distance in other cyclopentadiene derivatives with a Me_3Si substituent [average value 1.88 Å].[5]

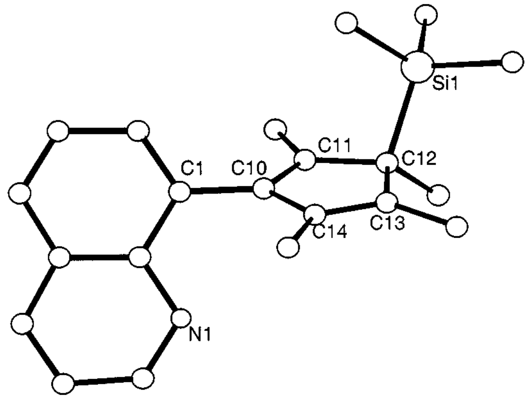

Figure 1. Solid-state structure of **1**; hydrogen atoms are omitted for clarity; selected bond lengths [Å]: C1−C10 1.482(2), C10−C11 1.357(2), C11−C12 1.504(2), C12−C13 1.508(2), C13−C14 1.352(2), C14−C10 1.464(2), C12−Si1 1.924(2), Si1−C_{Me} 1.863−1.869(2)

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[a] Anorganisch-Chemisches Institut der Universität,
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: (internat.) + 49-(0)6221/545-609
E-mail: markus.enders@urz.uni-hd.de

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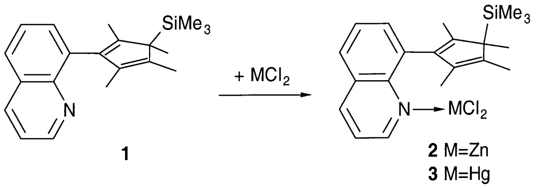
Compound **1** was treated with zinc dichloride and with mercury dichloride (Scheme 1). In analogy to the synthesis of titanium or zirconium complexes, the elimination of trimethylsilyl chloride was expected with formation of cyclopentadienyl half-sandwich complexes. In fact anhydrous $ZnCl_2$, which is insoluble in toluene, slowly dissolves in the presence of a solution of **1** in toluene. After stirring for 16 h a yellow precipitate was obtained in 75% yield. Addition of hexane to a dichloromethane solution of this new compound led to the formation of yellow crystals suitable for X-ray diffraction. However, the structure analysis showed that an addition product of $ZnCl_2$ and **1** had been formed rather than the expected half-sandwich compound (Figure 2).



Scheme 1. Formation of **2** and **3**

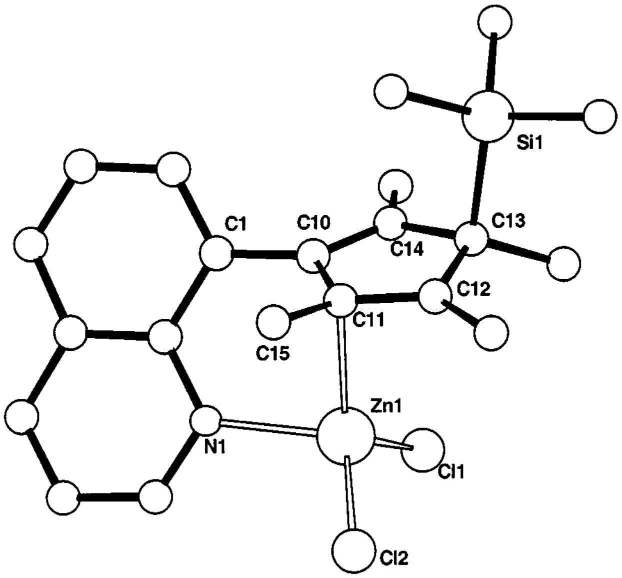


Figure 2. Solid-state structure of **2**; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: C1−C10 1.475(3), C10−C11 1.467(3), C11−C12 1.376(3), C12−C13 1.486(3), C13−C14 1.486(3), C14−C10 1.358(3), C13−Si1 1.985(3), Si1−C_{Me} 1.856−1.867(3) Zn1−N1 2.080(2), Zn1−C11 2.316(2), Zn1−C12 2.735(2), Zn1−C10 2.639(2), Zn1−Cl1 2.216(1), Zn1−Cl2 2.219(1); C11−Zn1−Cl1 123.6(1), C11−Zn1−Cl2, 106.7(1), C11−Zn1−N1 89.4(1), Cl1−Zn1−Cl2 117.9(1), C10−C11−C15 123.8(2), C10−C11−C12 108.2(2), C12−C11−C15 126.3(2).

The zinc atom is coordinated in a distorted tetrahedral manner by two chlorine atoms, the nitrogen donor and one sp^2-carbon atom of the cyclopentadiene ring. The coordination of the neutral carbocyclic ring to the zinc atom is confirmed not only by a carbon-zinc distance of 2.316(2) Å but also by the strong pyramidalisation of the $ZnLCl_2$ fragment (L = nitrogen donor). The ligand framework in **2** shows some differences from the solid state structure of the free ligand **1**. Due to the interaction of the carbon atom C11 with the zinc atom, the bonding vector C11−C15 does not lie in the plane defined by the cyclopentadiene system but forms an angle of 15°. The Si1−C13 bonding vector approaches an orthogonal orientation (76°) to the best plane of the cyclopentadiene ring. In addition, the Si1−C13 bond length [1.985(3) Å] is considerably longer than the respective silicon-carbon bonds in **1**. To the best of our knowledge, the interaction of a zinc atom with a neutral olefinic π-system has not been observed previously in the solid state.[5] Many compounds are known where anionic $C_5R_5^-$ ligands bind to Zn^{2+} ions. In $[Zn(\eta^2\text{-}C_5H_5)_2]_n$ one zinc atom is coordinated by three cyclopentadienyl ligands in an η^2 binding mode with one short (2.04−2.19 Å) and one long (2.42−2.48 Å) metal-carbon bond.[6]

The NMR spectra of **2** show a higher symmetry than in the solid state. The four methyl substituents of the five-membered ring give only two signals in the ^1H and ^{13}C NMR spectrum. This can only be explained by a dynamic process where the zinc atom and the Me_3Si group are changing their positions at the five-membered ring. We were not able to freeze out this process by cooling to lower temperatures (down to 170 K in the ^1H NMR spectrum at 200 MHz). The ^1H NMR spectrum of the ligand **1** exhibits four broad resonances at room temperature for the four methyl groups of the ring. A fast exchange occurs at higher temperatures.[4] The higher fluxionality of **2** compared to that of **1** shows the influence of the zinc-carbon interaction, which weakens the bond between the $SiMe_3$ group and the five-remembered ring.

The reaction between **1** and $HgCl_2$ leads to an orange yellow solution, from which yellow needles of the new compound **3** were obtained by addition of hexane. The NMR spectra of redissolved crystals showed signals indicating the presence of several different species in solution. The elemental analysis proves that **3** is an adduct of **1** with one equivalent of $HgCl_2$. The X-ray analysis reveals that two isomers — a monomer and a dimer — are present in the solid state. The molecular structure of the monomeric complex is shown in Figure 3.

The mercury atom is surrounded by one nitrogen, two chlorine and two carbon atoms of the cyclopentadiene ring. The coordinated sp^2-carbon atoms are interconnected by a single bond [C31−C35: 1.479(6) Å]. The interaction between the metal and the two carbon atoms, with distances of 2.957(4) and 3.000(5) Å, seems to be weak. The N2−Hg2−Cl3−Cl4 unit remains nearly trigonal planar, in contrast to the geometry in the zinc compound **2**. In the dimeric isomer shown in Figure 4, the coordination number at mercury is higher. Three chlorine ligands, the nitrogen donor and two carbon atoms of the cyclopentadiene are connected to the metal atom. The two sp^2-carbon atoms are part of an olefinic C−C double bond [C10−C11: 1.359(5) Å]. This double bond is not lengthened by the interaction with the Hg^{2+} ions and is practically equal to the corresponding C−C double bond in **1** [1.357(2)]. The dis-

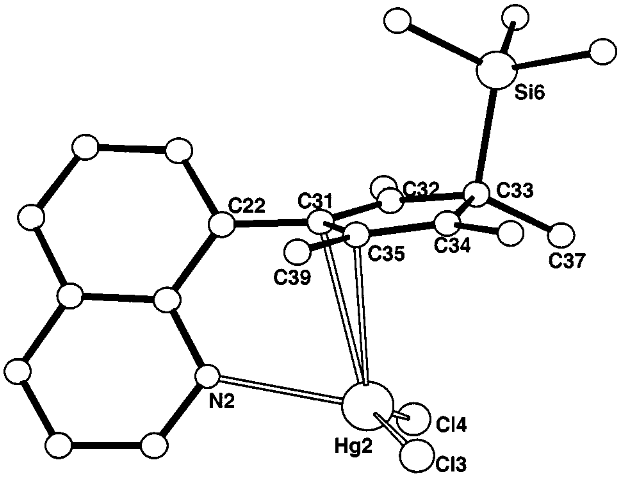


Figure 3. Part of the solid-state structure of **3** (monomeric Hg complex); hydrogen atoms are omitted for clarity; selected bond lengths[Å] and angles [°]: C22−C31 1.480(6), C31−C32 1.359(6), C32−C33 1.503(6), C33−C34 1.501(7), C34−C35 1.345(7), C35−C31 1.479(6), C33−Si6 1.956(5), Hg2−N2 2.391(4), Hg2−Cl3 2.356(1), Hg2−Cl4 2.358(1), Hg2−C31 2.957(4), Hg2−C35 3.000(5); N2−Hg2−Cl3 108.5(1), N2−Hg2−Cl4 110.5(1), Cl3−Hg2−Cl4 137.3(1)

tances between the mercury atoms and the linked carbon atoms are shorter in the dimeric compound (2.81 and 2.88 Å) than in the monomeric one (2.96 and 3.00 Å). In known Hg^{II}-arene complexes, the mercury-carbon distances vary considerably, from 2.56 Å[2a][2b] to 3.11 Å[2c][2d] and 3.33 Å.[2e]

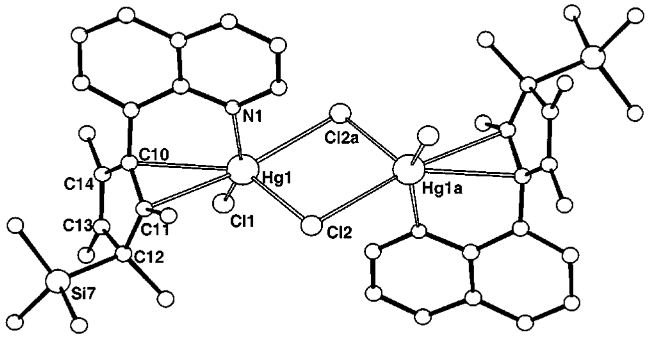


Figure 4. Part of the solid-state structure of **3** (dimeric Hg complex); hydrogen atoms are omitted for clarity; selected bond lengths[Å] and angles [°]: C10−C11 1.359(5), C11−C12 1.498(5), C12−C13 1.498(6), C13−C14 1.356(6), C14−C10 1.464(6), C12−Si7 1.949(4), Hg1−Cl1 2.365(1), Hg1−Cl2 2.549(1), Hg1−Cl2a 2.946(1), Hg1−Hg1a 3.985(1), Hg1−C10 2.813(4), Hg1−C11 2.879(4); Cl1−Hg1−Cl2 113.1(1), Cl1−Hg1−Cl2a 88.9(1), Hg1−Cl2−Hg1a 92.70, N1−Hg1−Cl1 151.1(1)

A comparison of the positions of the $SiMe_3$ groups in the solid-state structures of **1**, **2** and **3** shows significant differences. The C_{Cp}−Si bond lengths become longer when going from **1** to **3** and to **2** [1.924(2), 1.949(4), 1.985(3), respectively]. The value for the zinc compound **2** is much larger than for a normal Si−C bond. In addition, the angles between the Si−C_{Cp} bonding vectors and the corresponding planes of the five-membered rings become larger in the same order (**1**: 62°, **3**: 71°, **2**: 76°). As other Lewis acids such as $TiCl_4$ react with **1** with substitution of the $SiMe_3$ group, the compounds **3** and **2** may be described as snapshots of this electrophilic substitution reaction where the metal fragment attacks from one face of the five-membered ring and the $SiMe_3$ group is released at the other face.

Experimental Section

All reactions were carried out under a nitrogen or argon atmosphere. Compound **1** was prepared by the reported procedure.[4]

2: A total of 300 mg (0.93 mmol) of the trimethylsilyl derivative **1** was added to a suspension of zinc(II)chloride (130 mg, 0.95 mmol) in 30 mL of toluene. The solution was stirred for 16 hours. The resulting yellow precipitate was separated by filtration and dried in vacuum. The solid was dissolved in dichloromethane and layered with 10 mL of hexane. Compound **2** crystallised from the hexane phase at −30 °C as yellow cubes, which were suitable for X-ray analysis. Dichloromethane, which is present in the single crystals, was removed by pulverising the solid and evaporation under vacuum. Yield 310 mg (0.68 mmol, 72%). ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 0.12$ [s, 18 H, $Si(CH_3)_3$], 1.83 (s, 6 H, Cp-CH_3), 1.99 (s, 6 H, Cp-CH_3), 7.66−7.75 (m, 3 H), 7.80−8.02 (m, 1 H), 8.57 (d, $J_{H,H} = 6.0$ Hz, 1 H), 8.96 (d, $J_{H,H} = 3.2$ Hz, 1 H). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): $\delta = -2.53$ [$Si(CH_3)_3$], 13.6 (Cp-CH_3), 14.0 (Cp-CH_3), 122.6, 128.5, 128.6, 133.0, 141.5, 151.3 ($CH_{quinoline}$). MS (EI): *m/z* (%) =322 (2) [$Cp^QSiMe_3^+$], 306 (5) [$Cp^QSiMe_2^+$], 249 (41) [Cp^QH^+], 108 (51) [$ClSiMe_3^+$], 93 (100) [$ClSiMe_2^+$], 74 (84) [$SiMe_3^+$], 65 (64) [Zn^+].

3: A total of 360 mg (1.12 mmol) of the trimethylsily-derivative **1** was added to a suspension of mercury(II)chloride (320 mg, 1.19 mmol) in 20 mL of toluene. The solution was stirred for 48 hours and the resulting orange solid was separated by filtration. The yellow solution was concentrated and layered with 10 mL of hexane. Compound **3** crystallised as bright yellow needles from the hexane phase, which were suitable for X-ray analysis; yield 320 mg (0.54 mmol, 48%). MS (FAB): *m/z* (%) = 558 (6) [$M^+ - Cl$], 322 (100) [$Cp^QSiMe_3H^+$], 248 (80) [Cp^{Q+}], 147 (55). $C_{21}H_{27}Cl_2HgNSi$ (593.03): calcd. C 42.53, H 4.59, N 2.36; found C 42.76, H 4.60, N 2.37.

Crystal Structure Determinations:

1: $C_{21}H_{27}NSi$, monoclinic, $P2_1/c$, $a = 13.5835(9)$, b 16.3449(11), $c = 8.6546(6)$ Å, $\beta = 101.0150(10)°$, $V = 1886.1(2)$ Å^3, $Z = 4$, $d_{calcd.} = 1.132$ g cm^{-3}, 4491 reflections, 316 parameters, $R1 = 0.0445$, $wR2 = 0.129$.

2·1/2CH$_2$Cl$_2$: $C_{21.5}H_{28}Cl_3NSiZn$, monoclinic, $C2/c$, $a = 34.954(17)$, $b = 8.414(4)$, $c = 17.501(9)$ Å, $\beta = 113.07(2)°$, $V = 4735(4)$ Å^3, $Z = 8$, $d_{calcd.} = 1.403$ g cm^{-3}, 4163 reflections, 361 parameters, $R1 = 0.0285$, $wR2 = 0.0656$.

3: $C_{21}H_{27}Cl_2HgNSi$, triclinic, $P\bar{1}$, $a = 10.5069(2)$, $b = 13.9186(2)$, $c = 15.7285(3)$ Å, $\alpha = 85.213(1)°$, $\beta = 78.735(1)$, $\gamma = 88.288(1)°$, $V = 2247.76(7)$ Å^3, $d_{calcd.} = 1.752$ g cm^{-3}, 10594 reflections, 486 parameters, $R1 = 0.0305$, $wR2 = 0.0791$.

Data were collected on a Siemens Stoe AED2 (−70 °C, **2**) or on a Bruker AXS SMART1000 (−85 °C **1**, −100 °C **3**) diffractometer equipped with Mo-K_α radiation and in the ω-scan mode. An empirical absorption correction was applied. The structures were solved by direct methods (SHELXS-86 [7]) and refined by full-matrix least-squares techniques (SHELXL-93 [7]) based on F^2 using all measured reflections and with anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were located and refined isotropically for **1** and **2**, for **3** they were inserted in their calculated positions.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-168388 (**1**), -16389 (**2·1/2CH$_2$Cl$_2$**) and -168390 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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