In conclusion, we have shown that rigid spacers with C_n ($n = 3$, 4) sp carbon chains are suitable novel types of molecular building blocks in the construction of molecular rods. Compounds containing these types of spacers exhibit interesting photophysical properties and tunable electronic communication between the terminal sites upon change of the carbon chain length. Currently we are investigating the application of such spacers, including the ones with longer chain lengths, in the construction of functional supramolecular systems capable of performing, for example, directional intramolecular electron/energy transfer.

Experimental Section

All reactions were carried out in a nitrogen atmosphere unless otherwise noted.

General procedure for the monomeric complexes MC_2P_2e and MC_nP_4 ($n =$ 3, 4): A solution of $[M(bpy)_2Cl_2]$ ($M = Ru$ or Os) (1.0 equiv) in ethylene glycol (20 mL) was added dropwise to a refluxing solution of C_3P_4, C_4P_4, or C_2P_2e (typically, 2.2–3.0 equiv) in THF. The resulting mixture was heated under reflux for 15 h. An excess of NH_4PF_6 was then added and the mixture was heated under reflux for up to 60 h to ensure the completion of reaction. The solution was cooled to room temperature, and the THF portion of the reaction mixture was removed by rotary evaporation. The resulting ethylene glycol solution was added dropwise to a saturated solution of KPF_6 in H_2O. The precipitate was collected by vacuum filtration, washed with H_2O (3×20 mL) and diethyl ether (3×20 mL), then dried in vacuo. The product was then purified by column chromatography (basic alumina, acetonitrile/toluene (60/40) eluent).

General procedure for the synthesis of the homobimetallic complexes MC_nP_4M ($M = Ru$ or Os, $n = 3$ or 4): A hot solution of C_nP_4 (1.0 equiv, $n = 3$ or 4) in THF was added dropwise to a hot solution of $[M(bpy)_2Cl_2]$ ($M = Ru$ or Os) (2.2 equiv) in ethylene glycol (20 mL) at approximately 120 °C. The resulting mixture was refluxed for 15 h, then allowed to cool to room temperature. An excess of NH_4PF_6 was added and the mixture was then refluxed for up to 60 h to ensure the completion of reaction. The mixture was again cooled to room temperature, and the THF portion of the solvent mixture was removed by rotary evaporation. The resulting ethylene glycol solution was added slowly to a saturated solution of KPF_6 in H_2O. The precipitate was collected by vacuum filtration, washed with H_2O (3×20 mL) and diethyl ether (3×20 mL), and dried in vacuo. The homobimetallic product was isolated by column chromatography as the second fraction, using basic alumina and acetonitrile as eluent, from the corresponding monometallic complex.

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The First Homoleptic Metallabenzene Sandwich Complex[**]

Ulli Englert, Frank Podewils, Ingo Schiffers, and Albrecht Salzer[*]

In connection with our previous studies on the reactivity of "half-open" metallocenes, we have found examples for the insertion of organometallic fragments into the "open" side of pentadienyl ligands, leading to the formation of metallacyclic six-membered ring ligands (Scheme 1).[1, 2] Using Wade's rules, this can be regarded as the expansion of an *arachno* to a *nido* structure. The metallabenzenes thus formed (exchange of CH for an isolobal metal fragment) are one of the rarest, but nevertheless most interesting representatives of metallacycles of the transition elements.[3] They are considered to be

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[*] Prof. Dr. A. Salzer, Priv.-Doz. Dr. U. Englert,
Dipl.-Chem. F. Podewils, I Schiffers
Institut für Anorganische Chemie der Technischen Hochschule
D-52056 Aachen (Germany)
Fax: (+49) 241-8888-288
E-mail: albrecht.salzer@ac.rwth-aachen.de

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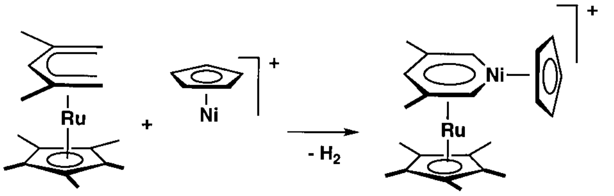
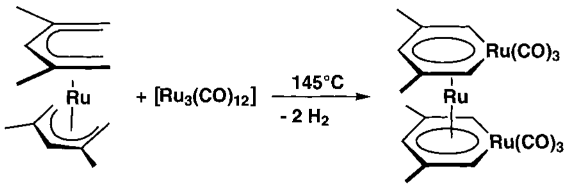


Scheme 1.

intermediates in the alkyne oligomerization,[4] but are also of fundamental interest with respect to their possible aromatic character.[4–6]

In contrast, heterocycles of the main group elements such as $[C_5H_5BR]^-$ or C_5H_5P, which are formed by isolobal exchange of CH by BR^- or P, have been well known and investigated over the last 30 years. They are eminently suitable as ligands for metal–sandwich complexes.

After having developed a new, very efficient route to the "open" ruthenocene $(C_7H_{11})_2Ru$ (**1**),[7] we have also investigated the possible insertion of unsaturated metal fragments into **1**. Surprisingly, the thermolysis of **1** in the presence of $Ru_3(CO)_{12}$ does not lead to simple, but to double insertion of two $Ru(CO)_3$ units into all four terminal C–H bonds in *endo* position (Scheme 2). To our knowledge, **2** is the first sandwich complex comprising two metallacyclic ligands. A formal dissection of **2** shows that $(CO)_3Ru^-$ is isolobal to CH and BH^-; the organometallic ligand $[C_5H_5Ru(CO)_3]^-$ can therefore also possibly be considered as an equivalent of boratabenzene $[C_5H_5BH]^-$.



1 **2**

Scheme 2.

Complex **2** is lemon-yellow and air-stable, decomposes at temperatures above 170°C, and can be sublimed at 90°C under high vacuum without decomposition. The carbon atoms directly coordinated to ruthenium show a typical low-field shift ($\delta = 128.3$), which is however less pronounced than in previous examples.[2] The mass spectrum shows characteristic peaks corresponding to the consecutive loss of all six CO groups as well as the formation of tetramethylruthenocene.

Large prismatic crystals of **2** can be grown from benzene within hours. The single-crystal X-ray diffraction study[8] confirms the structure of a bis(metallabenzene) sandwich complex (Figure 1). The two rings show an exact *syn*-ecliptical conformation, but are not completely coplanar, but tilted by 18° towards each other; the two $Ru(CO)_3$ units are both bent away from the plane formed by the five carbon atoms by approximately 15°. Similar values have been found for other ruthenabenzenes. Various explanations have been put forward for this phenomenon, among them the optimization of Ru–C and Ru–Ru bond lengths[1] as well as steric repulsion[4] but the latter is clearly not the case for **2**.

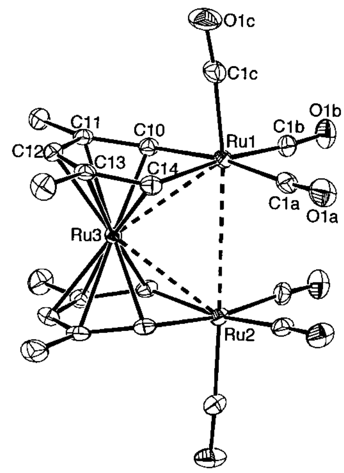


Figure 1. Structure of **2** in the solid state (PLATON[9]). Selected bond lengths [°]: Ru1–Ru3 2.831(2), Ru2–Ru3 2.812(2), Ru1–Ru3 3.382(2), Ru1–C10 2.076(3), Ru1–C14 2.062(3), Ru1–C1a 1.965(3), Ru1–C1b 1.939(3), Ru1–C1c 1.863(3).

The *syn*-ecliptical arrangement of the ring ligands appears surprising at first, considering that "open" metallocenes show a preference for the *gauche*-ecliptic conformation[10] and other heterosubstituted bis(arene) complexes preferentially show *anti*-ecliptic conformations or are disordered in the solid state with a low barrier of rotation.[11] Comparable exceptions are distiba- and dibismaferrocene, for which a bonding interaction of the two heteroatoms has been postulated.[12] Preliminary results of an extended-Hückel MO calculation make it likely that all three ruthenium atoms in **2** are linked through a multicenter bond.[13] The distance between the two ring ruthenium atoms is 3.38 Å and therefore only 20% longer than the bond to the central ruthenium atom (ca. 2.82 Å). It is considerably shorter than the sum of the van der Waals radii and the distance between the two heteroatoms in the distiba- and dibismaferrocenes (3.58–3.69 Å). The C–C bond lengths within the metallacycle are very similar (1.39–1.43 Å), while the Ru–C bond lengths are somewhat longer than in previous examples.[1, 4] The Ru–C bond to the equatorial carbonyl groups is significantly longer than that to the axial ligand. This is plausible, as the *trans* configuration of carbonyl- and pentadienylylidene ligand should result in a mutual bond weakening. The *syn*-ecliptical conformation appears to persist in solution, as **2** shows five CO absorptions in the IR spectrum in agreement with symmetry class C_{2v}.

Complex **2** can be protonated to a hydride species that can be isolated as a solid ($\delta(^1H) = -16.1$) and is reversibly oxidized to a monocation (+0.8 V against SCE). All properties of **2** therefore point to a pronounced similarity to classical metallocenes. Current investigations will show, whether this also applies to its reactions (metalation, ring transfer etc.).

The possible aromaticity of metallabenzenes has been extensively discussed by R. Hoffmann[5] and J. Bleeke.[6] Compound **2** shows structural properties typical for this class of compounds, such as approximate ring planarity and delocalized bonding within the ring.

We had postulated in a previous publication that "bis(metallabenzene) complexes or even tripledecker compounds with a central metallabenzene ring should be stable".[2] The first part of this statement has now been verified, possibly a consequence of the previously observed property of metallabenzenes to form more stable metal–π bonds than classical arenes.[3] An additional intra-ring interaction of the two ring metals, as observed for the first time in **2**, could make a further contribution to the stabilization of multidecker structures.

Experimental Section

2: A solution of bis(dimethylpentadienyl)ruthenium (**1**) (0.29 g, 1.0 mmol) in nonane (35 mL) was refluxed with $Ru_3(CO)_{12}$ (1.28 g, 2.0 mmol) overnight. The solvent was evaporated under reduced pressure and the residue was taken up in hexane and purified by chromatography on silica gel. The yellow fraction was collected and recrystallized from benzene or toluene, yield 0.11 g (17%). ^{13}C NMR (125.7 MHz, CD_2Cl_2): $\delta = 198.9$ (CO), 193.9 (CO), 128.3 (C1), 111.3 (C2), 94.4 (C3), 25.5 (CH_3); ^1H NMR (500 MHz, CD_2Cl_2): $\delta = 6.23$ (t, $^4J = 1.5$ Hz, 2H), 5.62 (d, $^4J = 1.5$ Hz, 4H), 1.72 (s, 12H, CH_3); IR (cm^{-1}, hexane): $\tilde{\nu} = 2074$m, 2049m, 2010s, 1995w, 1980m.

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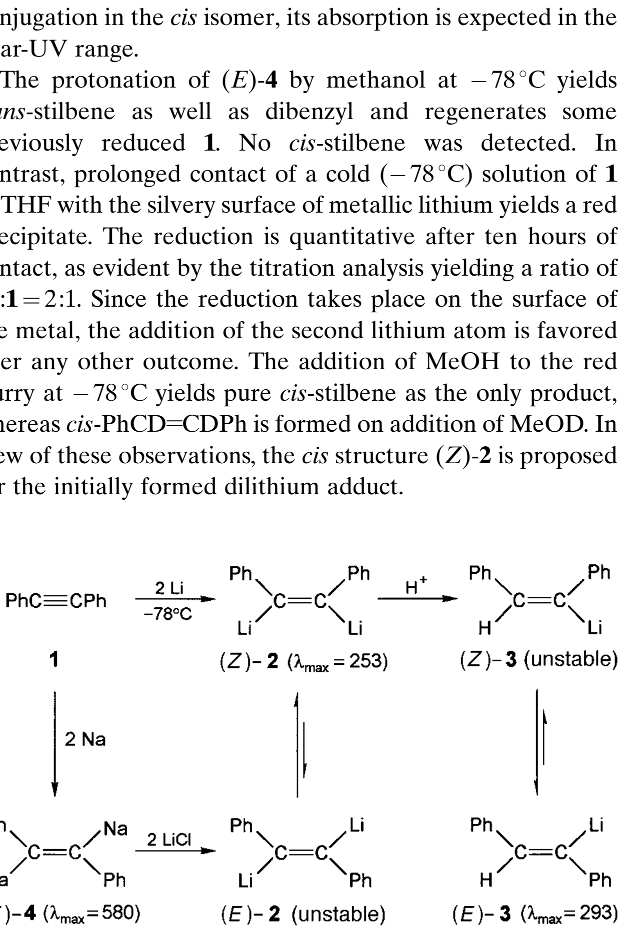
Mechanism of Reduction of Diphenylacetylene by Metallic Lithium

Adalbert Maercker, Michael Kemmer, Hsien C. Wang, Da-Hai Dong, and Michael Szwarc*

The reduction of a cold (−78 °C) solution of diphenylacetylene (tolane, **1**) in THF by metallic sodium or lithium was reported previously.[1] When the solution is kept for five hours in contact with a sodium mirror, **1** is reduced quantitatively to the disodium adduct (*E*)-**4**. Its absorption at long wavelength ($\lambda_{max} = 580$ nm, $\varepsilon = 6.4 \times 10^4$) implies a conjugated *trans* structure of the adduct. Since steric hindrance prevents the conjugation in the *cis* isomer, its absorption is expected in the near-UV range.

The protonation of (*E*)-**4** by methanol at −78 °C yields *trans*-stilbene as well as dibenzyl and regenerates some previously reduced **1**. No *cis*-stilbene was detected. In contrast, prolonged contact of a cold (−78 °C) solution of **1** in THF with the silvery surface of metallic lithium yields a red precipitate. The reduction is quantitative after ten hours of contact, as evident by the titration analysis yielding a ratio of Li:**1** = 2:1. Since the reduction takes place on the surface of the metal, the addition of the second lithium atom is favored over any other outcome. The addition of MeOH to the red slurry at −78 °C yields pure *cis*-stilbene as the only product, whereas *cis*-PhCD=CDPh is formed on addition of MeOD. In view of these observations, the *cis* structure (*Z*)-**2** is proposed for the initially formed dilithium adduct.



The addition of a cold solution of LiCl in THF to the cold solution of (*E*)-**4** yields again the red precipitate that forms *cis*-stilbene on protonation by MeOH. Apparently, the *trans*-disodium adduct (*E*)-**4** is converted into the *cis*-dilithium adduct upon substitution of sodium by lithium. Although the mechanism of this conversion is unknown, we might conclude that the *cis*-dilithium adduct (*Z*)-**2** is more stable than its *trans* isomer (*E*)-**2**.

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[*] Prof. M. Szwarc, Dr. H. C. Wang, D.-H. Dong
Loker Hydrocarbon Research Institute
University of Southern California
University Park, Los Angeles, CA 90089-1661 (USA)
Fax: (+1)619-259-6022

Prof. A. Maercker, Dr. M. Kemmer
Institut für Organische Chemie der Universität Siegen (Germany)