Angewandte Chemie

Metallocenes

Electrophilic Double-Sandwiches Formed by Interaction of [Cp_2Fe] and [Cp_2Ni] with the Tridentate Lewis Acid [(o-C_6F_4Hg)$_3$]**

*Mason R. Haneline and François P. Gabbaï**

Dedicated to Professor Hubert Schmidbaur
on the occasion of his 70th birthday

As part of our contribution to the supramolecular chemistry of mercury polyfunctional Lewis acids,[1] we have been involved in the study of trimeric perfluoro-*ortho*-phenylene mercury, [(o-C_6F_4Hg)$_3$] (**1**),[2] a simple tridentate Lewis acid. This derivative, which complexes a number of electron-rich species,[1c,3] also interacts with arenes including naphthalene, pyrene, and triphenylene to afford binary stacks where the arene is π coordinated to the mercury centers of **1**.[4] This supramolecular complexation mode leads to a perturbation of the photophysical properties of the arene which displays intense room-temperature phosphorescence as a result of a mercury heavy-atom effect.[5] Our continuing interest in the supramolecular chemistry of **1** led us to extend the scope of our studies to metal complexes featuring accessible aromatic ligands. Herein, we describe the synthesis, structures, and properties of electrophilic double-sandwich complexes formed by the interaction of **1** with ferrocene and nickelocene.[6]

Dark orange crystals of the ferrocene adduct [**1**-CpFeCp-**1**] (**2**) and dark red crystals of the nickelocene adduct [**1**-CpNiCp-**1**] (**3**) were obtained upon evaporation of CH_2Cl_2 solutions containing **1** and the corresponding metallocene (Scheme 1). The 2:1 stoichiometry of these adducts was confirmed by elemental analysis. Both compounds showed no sign of decomposition upon exposure to air for several months thus indicating that **1** stabilizes the usually air-sensitive 20-electron nickelocene complex against aerobic oxidation.[7] Compounds **2** and **3** crystallize in the monoclinic space group $C2/m$ and are isomorphous (Figure 1).[8] With Hg–$C_{metallocene}$ separations ranging from 3.20–3.24 Å, the carbon atoms of the Cp rings of the metallocene are in close

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[*] M. R. Haneline, Prof. Dr. F. P. Gabbaï
Chemistry Department
Texas A&M University 3255 TAMU
College Station, Texas 77843-3255 (USA)
Fax: (1) 979-845-4719
E-mail: gabbai@mail.chem.tamu.edu

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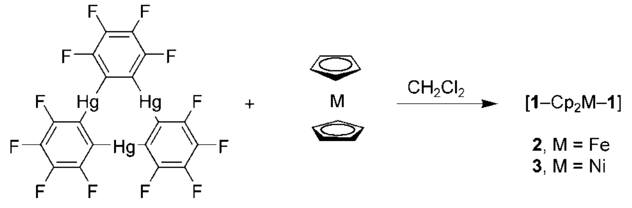

Scheme 1.

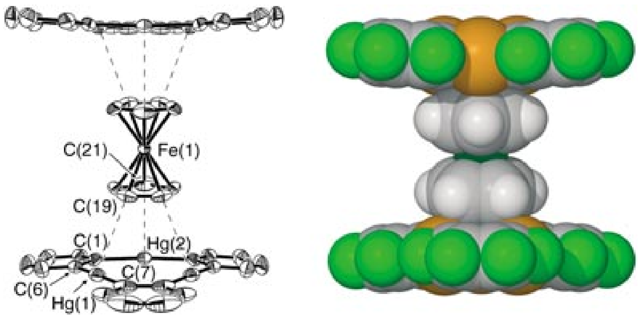

Figure 1. Left: ORTEP view of **2** (thermal ellipsoids set at 30% probability, for clarity all hydrogen and fluorine atoms are omitted). Right: Space-filling model of **3**. (C gray, F light green, Hg orange, Ni dark green, H white). Selected bond lengths [Å] and angles [°]: **2**: Hg(1)-C(19) 3.217(11), Hg(2)-C(21) 3.222(18), Hg(1)-C(6) 2.055(14), Hg(1)-C(7) 2.086(13), Hg(2)-C(1) 2.039(12), C(6)-Hg(1)-C(7) 174.8(5), C(1)-Hg(2)-C(1A) 176.2(7); **3** Selected bond lengths [Å] and angles [°] (numbering scheme as for **2**): Hg(1)-C(19) 3.204(12), Hg(2)-C(21) 3.237(17), Hg(1)-C(6) 2.089(9), Hg(1)-C(7) 2.102(14), Hg(2)-C(1) 2.048(9), C(6)-Hg(1)-C(7) 175.4(5), C(1)-Hg(2)-C(1A) 176.4(6).

contact with the mercury centers of **1**. As observed in arene adducts of **1**,[4,5] these distances are within the sum of the van der Waals radii of mercury (1.7–2.0 Å)[9,10] and carbon (1.7 Å).[11] This structural feature indicates the presence of secondary Hg–π interactions which complement attractive electrostatic and dispersion forces present between **1** and the metallocene.[4] The two molecules of **1** are staggered with respect to one another. The bond lengths in the metallocene are unchanged compared to those of the pure metallocene.[12] The perfluorophenylene ring containing the C(1) carbon atom and its symmetry equivalent are bent away from the metallocene and form a dihedral angle of 5° for **2** and 4° for **3** with respect to the plane containing the three mercury atoms. Apparently, this deformation allows for a closer approach of the trinuclear mercury core of **1** to the Cp rings of the metallocene. The remaining phenylene ring which contains the C(7) carbon atom is essentially coplanar with the plane formed by the trinuclear mercury core. While the formation of such electrophilic double sandwiches is unprecedented, we note the existence of a structural parallel with binary compounds such as $[FeCp^*_2]^+[TCNE]^-$ ($Cp^* = C_5Me_5$, TCNE = tetracyanoethylene)[13] and $[Cr(C_6H_6)_2][C_6F_6]$ which feature transition-metal complexes sandwiched between π-acidic molecules.[14]

In **2** and **3**, neighboring molecules of [**1**-CpMCp-**1**] engage in mercuriophilic interactions (Figure 2) with a Hg···Hg separation of 3.4157(16) Å for **2** and 3.3996(17) Å for **3**.

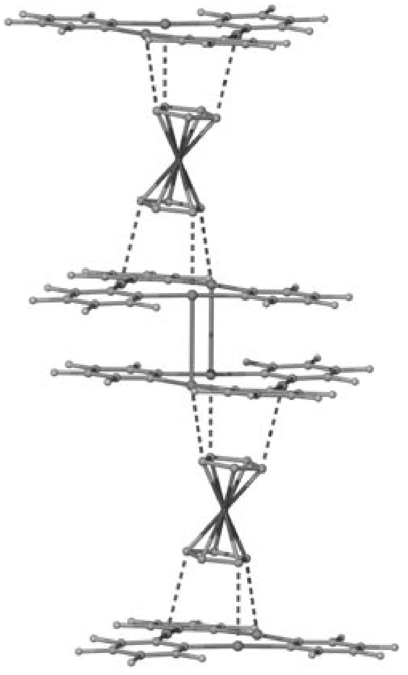

Figure 2. Extended structure of compound **3** showing the Hg···Hg interactions. The structure of compound **2** is identical. For clarity all hydrogen atoms are omitted.

These Hg···Hg separations are within the sum of the van der Waals radius of mercury and are very close to the Hg···Hg separation calculated by Pyykkö for the dimer of dimethyl mercury (3.41 Å).[9,15] This aggregation mode is similar to that observed in the structure of [**1**-μ_3-acetone] which forms dimers held by mercuriophilic interactions of 3.512 Å.[15b] Similar metallophilic interactions are sometimes observed in the structural chemistry of trinuclear coinage-metal complexes.[16–18]

In an effort to provide a rationale for the dark red color of **3** which does not correspond to that of dark green nickelocene, we have recorded and analyzed the visible diffuse reflectance absorption spectra of **3** and nickelocene. The solution absorption spectrum of nickelocene has been reported[19,20] and is dominated by three intense spin-allowed transitions at 426 ($^3A_{2g}\rightarrow{}^3E_{1g}$), 589 ($^3A_{2g}\rightarrow{}^3E_{2g}$), and 695 nm ($^3A_{2g}\rightarrow{}^3E_{1g}$) as well as one weak spin-forbidden transition at 526 nm ($^3A_{2g}\rightarrow{}^1E_{1g}$). The diffuse reflectance spectrum of pristine nickelocene could be satisfactorily modeled on the basis of these four bands, with the spin-forbidden $^3A_{2g}\rightarrow{}^1E_{1g}$ band being the weakest (Figure 3).[21] In the case of **3**, deconvolution of the diffuse reflectance spectrum indicates that the intensity of the spin-forbidden band at 526 nm is greatly increased. The $^3A_{2g}\rightarrow{}^3E_{1g}$ band also appears to be slightly red-shifted to 715 nm. We have already shown that aromatic substrates complexed to **1** experience an external mercury heavy-atom effect which leads to triplet emission.[4,5] It can therefore be proposed that the nickelocene molecule in **3** also experiences a heavy-atom effect which, because of added spin-orbit coupling, increases the intensity of the formally spin-forbidden $^3A_{2g}\rightarrow{}^1E_{1g}$ transition at 516 nm.[22] The diffuse reflectance spectrum of **2** does not display

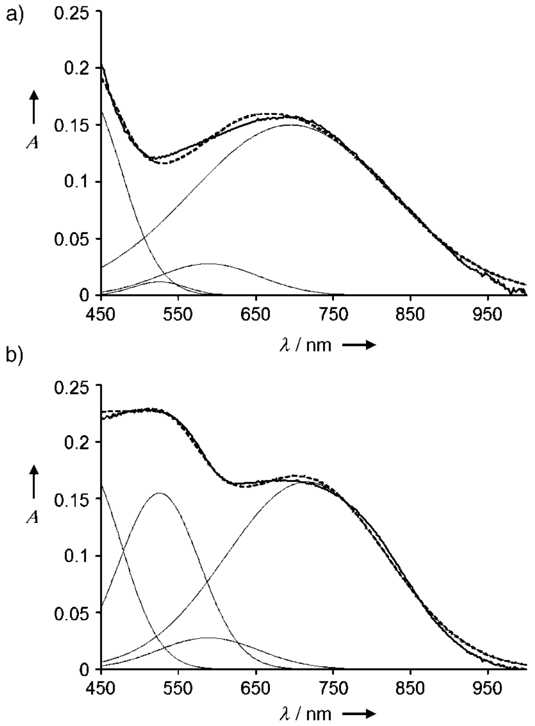

Figure 3. Deconvoluted diffuse reflectance absorption spectra of nickelocene (a) and **3** (b) Bold line = experimental data, broken line = model, thin lines = deconvolution curves.

unusual features and is essentially identical to that of pristine ferrocene.

As indicated by ^{199}Hg NMR spectroscopy, **1** and ferrocene do not form any detectable adducts in CH_2Cl_2. The solid-state ^{13}C MAS NMR spectrum of **2** shows a single resonance signal for the carbon atoms of the Cp ligand at $\delta = 72$ ppm. Therefore, the Hg–π interactions detected in the structure of **2** appear to be weak and do not affect the magnetic environment of the Cp carbon atoms which remain equivalent. Variable-temperature (2–300 K) magnetic susceptibility data were collected on crushed single crystals of compound **3**. The room temperature $\chi_m T$ value of 1.1 emu K mol^{-1} is in good agreement with the spin-only value for free nickelocene ($S = 1$). Below 45 K, however, the value of $\chi_m T$ decreases sharply. This decrease can be attributed to a zero-field splitting effect which arises from spin-orbit coupling.[23] Analysis of the magnetic data on the basis of the equations outlined by Baltzer for an isolated nickelocene[24] affords a zero-field parameter D of 37.65 ± 0.29 cm^{-1} and a g parameter of 2.089 ± 0.003. The zero-field parameter is slightly greater than that estimated for isolated nickelocene ($D = 33.76 \pm 0.70$ cm^{-1}) which might reflect added spin-orbit coupling provided by the six surrounding mercury atoms.[25] Note that weak antiferromagnetic interactions may also be a plausible cause for this greater than expected value of the D parameter.[24,26]

In conclusion, we report the synthesis of the 1:2 ferrocene and nickelocene adducts of **1**. In the solid state, these adducts assume an unusual electrophilic double-sandwich structure in which a molecule of **1** caps each of the Cp ligands. Adduct **3** is air-stable indicating that the 20-electron nickelocene complex is stabilized against oxidation. Although electronic effects cannot be ruled out, this stabilization most likely results from the formation of a tight lattice which physically prevents reaction with oxygen. Finally, in the case of **3**, formation of these sandwiches apparently leads to increased spin-orbit coupling which alters the photophysical and magnetic properties of the nickelocene molecule. Unlike in other donor–acceptor systems involving metallocenes,[13,14] we have found no evidence of charge transfer in **2** and **3**.

Experimental Section

Owing to the toxicity of the mercury compounds discussed in these studies extra care was taken at all times to avoid contact with solid, solution, and air-borne particulate mercury compounds.

2 and **3**: A solution of compound **1** (100 mg, 0.096 mmol) in CH_2Cl_2 (15 mL), was mixed with a solution of the metallocene (100 mg, 0.538 mmol for [Cp_2Fe] and 0.529 mmol for [Cp_2Ni]) in CH_2Cl_2 (5 mL). Crystals, which formed upon slow evaporation of the solvent, were washed with hexanes to remove excess metallocene. This procedure yielded a quantitative amount of dark orange **2** and dark red **3**, respectively. **2**: elemental analysis (%) calcd for $C_{46}H_{10}F_{24}Hg_6Fe$: C 24.29, H 0.44; found: C 24.32, H 0.41. M.p. 300 °C (decomp). **3** elemental analysis (%) calcd for $C_{46}H_{10}F_{24}Hg_6Ni$: C 24.26, H 0.44; found: C 24.50, H 0.49. Decomposes explosively at 275 °C.

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Crystal size $0.24 \times 0.15 \times 0.15$ mm^3, ω-scan mode, measurement range 1.77–23.33°, 1761 unique reflections, 1538 reflections with $I > 2(I)$, $\mu = 19.947$ mm^{-1}. $R1 = 0.0295$, $wR2 = 0.0866$ (all data); **3**: $C_{46}H_{10}F_{24}Hg_6Ni$, $M_r = 2280.79$, monoclinic, space group $C2/m$, $a = 10.554(2)$, $b = 19.509(4)$, $c = 12.299(3)$ Å, $\beta = 109.21(3)°$, $V = 2391.2(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 3.168$ g cm^{-3}. Crystal size $0.51 \times 0.25 \times 0.24$ mm^3, ω-scan mode, measurement range 1.75–23.27°, 1781 unique reflections, 1221 reflections with $I > 2(I)$, $\mu = 19.700$ mm^{-1}. $R1 = 0.0403$, $wR2 = 0.0756$ (all data). CCDC-242588 (**2**) and CCDC-242589 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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