

“Schizoid Reactivity” of 1,1'-Diisocyanoferrocene

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1. Preparative Work

General Considerations: Synthetic work involving air-sensitive compounds was performed under an atmosphere of dry nitrogen by using standard Schlenk techniques or a conventional glovebox. Solvents and reagents were appropriately dried and purified. 1,1'-Diisocyanoferrocene (**1**) was prepared according to the published procedure.^{S1} $[\text{Au}(\text{C}\equiv\text{C}-\text{Fc})]_n$ was prepared from ethynylferrocene and $[\text{AuCl}(\text{SMe}_2)]$ in analogy to closely related compounds.^{S2} NMR spectra were recorded with a Varian Unity INOVA 500 spectrometer operating at 500.13 MHz for ^1H . IR spectra were recorded with a BIO-RAD FTS-40a spectrometer. Elemental analyses were performed by Mikroanalytisches Laboratorium H. Kolbe (Mülheim an der Ruhr, Germany).

Synthesis of (3)₃

A solution of 1,1'-diisocyanoferrocene (**1**) (67 mg, 0.28 mmol) in dichloromethane (15 ml) was added dropwise with stirring to a suspension of $[\text{Au}(\text{C}\equiv\text{C}-\text{Fc})]_n$ (232 mg, 0.57/*n* mmol) in dichloromethane (15 ml). After 14 h the mixture was filtered to remove a small amount of insoluble material. The filtrate was reduced to dryness *in vacuo*. Yield 216 mg (72 %). The crude product was purified by recrystallisation from dichloromethane.

Anal. Calcd for $\text{C}_{108}\text{H}_{78}\text{N}_6\text{Au}_6\text{Fe}_9$: C, 41.26; H, 2.50; N, 2.67. Found C, 40.96; H, 2.57; N, 2.80%.

^1H NMR (CD_2Cl_2): δ 4.04 (“t”, apparent $J = 1.8$ Hz, 6 H), 4.12 (s, 15 H), 4.26 (s, 15 H), 4.27 (“t”, apparent $J = 1.8$ Hz, 6 H), 4.40 (“t”, apparent $J = 2.0$ Hz, 6 H), 4.42 (“t”, apparent $J = 1.7$ Hz, 6 H), 4.52 (“t”, apparent $J = 1.7$ Hz, 6 H), 4.56 (“t”, apparent $J = 1.8$ Hz, 6 H), 5.18 (“t”, apparent $J = 1.9$ Hz, 6 H), 5.41 ppm (“t”, apparent $J = 1.9$ Hz, 6 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 67.9, 68.3, 69.0, 69.5, 70.0, 70.1 (Cp), 70.6 (Cp), 70.8, 71.8, 72.3; the signals of the quaternary C atoms could not be detected with certainty.

IR: $\nu(\text{N}\equiv\text{C})$ 2201, $\nu(\text{C}\equiv\text{C})$ 2155, $\nu(\text{N}=\text{C})$ 1491 cm^{-1} . This assignment is based on data reported for related compounds: The isocyanide band of **1** and of its gold complex $[(\mu\text{-1})(\text{AuCl})_2]_\infty$ is located at 2118 and 2226 cm^{-1} , respectively.^{S3} Two $\nu(\text{C}\equiv\text{C})$ bands are observed for $[\text{Au}(\text{C}\equiv\text{C}\text{-Fc})]_n$ at 1976 and 2011 cm^{-1} . One such band at 1973 cm^{-1} has been reported for the analogous $[\text{Au}(\text{C}\equiv\text{C}\text{-Ph})]_n$, which is shifted to 2130 cm^{-1} in the case of the isocyanide complex $[\text{Au}(\text{C}\equiv\text{C}\text{-Ph})(\text{CN}t\text{Bu})]$.^{S4} The $\nu(\text{C}=\text{N})$ band of $\text{Ph}\text{-C}\equiv\text{C}\text{-C}(=\text{NPh})\text{Ph}$ is located at 1560 cm^{-1} ,^{S5} while it occurs at 1530 cm^{-1} in the case of the mononuclear iminoacyl complex $[\text{Pd}\{\text{C}(\text{C}\equiv\text{C}\text{-Ph})(=\text{NPh})\}\text{-Cl}(\text{PEt}_3)_2]$.^{S6} It is well documented for binuclear complexes that a σ, μ_2 -iminoacyl coordination leads to a notable energy decrease of this band of ca. 60 cm^{-1} with respect to the parent imine.^{S7}

2. Crystallographic Work

Single crystals of $(\mathbf{3})_3$ were obtained by slow cooling of a dichloromethane solution to -40 °C. The crystals were small and of poor quality. Diffraction experiments were carried out within a θ range of 25.5° ; in the refinement process the θ range was limited to 22.5° , which led to a poor data/parameter ratio. To increase this ratio the cyclopentadienyl rings were constrained to regular pentagons. 11 C atoms (attached to the electron-rich metal centres) were included to the model

with isotropic displacement parameters. X-ray structural data are available as a separate file in CIF format. CCDC 641517.

We note that the structurally characterised σ,μ_2 -iminoacyl complexes exhibit C–N bond lengths of ca. 1.30 Å, similar to what we observed for (**3**)₃ (see Figure 1b).^{S8}

References to Supporting Information

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