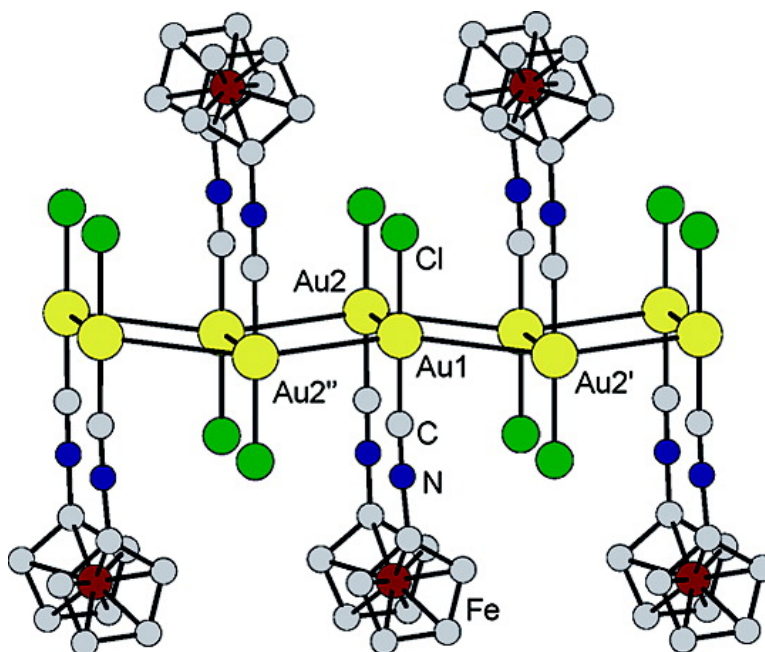


The Interaction of 1,1'-Diisocyanoferrocene with Gold: Formation of Monolayers and Supramolecular Polymerization of an Auophilic Ferrocenophane

Ulrich Siemeling, Dag Rother, Clemens Bruhn, Heinrich Fink, Tobias Weidner, Frank Trger, Alexander Rothenberger, Dieter Fenske, Andreas Priebe, Jrg Maurer, and Rainer Winter

J. Am. Chem. Soc., **2005**, 127 (4), 1102-1103 • DOI: 10.1021/ja0436244 • Publication Date (Web): 06 January 2005

Downloaded from <http://pubs.acs.org> on March 24, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 13 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article



[View the Full Text HTML](#)



The Interaction of 1,1'-Diisocyanoferrocene with Gold: Formation of Monolayers and Supramolecular Polymerization of an Auophilic Ferrocenophane

Ulrich Siemeling,^{*,†} Dag Rother,[†] Clemens Bruhn,[†] Heinrich Fink,[†] Tobias Weidner,[†] Frank Träger,[†] Alexander Rothenberger,[‡] Dieter Fenske,[‡] Andreas Priebe,[§] Jörg Maurer,^{||} and Rainer Winter^{||}

Department of Science and Center for Interdisciplinary Nanostructure Science and Technology (CINSA-T), University of Kassel, D-34109 Kassel, Germany, Institute of Inorganic Chemistry, University of Karlsruhe, D-76128 Karlsruhe, Germany, Kirchhoff Institute for Physics, University of Heidelberg, D-69120 Heidelberg, Germany, and Institute of Inorganic Chemistry, University of Stuttgart, D-70569 Stuttgart, Germany

Received October 20, 2004; E-mail: siemeling@uni-kassel.de

Isocyanides are important ligands in coordination chemistry.¹ They are of great current interest in surface chemistry, where their binding on gold and other metals has been addressed using bi- and tridentate isocyanides.² However, despite their attractive properties, the number of *oligodentate* isocyanides has remained small in comparison to other prominent ligand families.³ Because of our interest in redox-functionalized ligands,⁴ 1,1'-diisocyanoferrocene⁵ (**1**) has caught our attention. **1** is a potentially bidentate ligand, whose chemistry, much to our surprise, has remained unexplored thus far. Its monodentate analogue isocyanoferrocene (**2**), however, has already been investigated in detail. **2** behaves like an aryl isocyanide in complexes such as $(\mathbf{2})\text{Cr}(\text{CO})_5$.⁶ IR data indicate that **1** behaves analogously. It readily forms $(\mathbf{1})[\text{Cr}(\text{CO})_5]_2$ with 2 equiv of $\text{Cr}(\text{CO})_5(\text{THF})$, whereupon the $\nu(\text{NC})$ band shifts from 2118 to 2142 cm^{-1} . This effect is similar to that observed in the case of $(\mathbf{2})\text{Cr}(\text{CO})_5$.^{6d} $(\mathbf{1})[\text{Cr}(\text{CO})_5]_2$ was structurally characterized by X-ray diffraction. It exhibits an eclipsed orientation of the cyclopentadienyl rings with a synclinal arrangement of the two substituents. Spectroelectrochemical investigations have revealed that oxidation of the ferrocene unit of $(\mathbf{1})[\text{Cr}(\text{CO})_5]_2$ ($E^\circ = 0.55$ V vs ferrocenium/ferrocene) leads to a shift of the isocyanide band to 2017 cm^{-1} , a fact that can be explained by a decreased net electron donor ability of $\mathbf{1}^+$.

The distance between the two Cp decks of ferrocene is 3.32 Å, and the molecule shows ball-bearing-like features, since the barrier for ring rotation is very small.⁷ In view of these properties, an investigation of the coordination behavior of **1** toward gold(I) seemed interesting, since in the solid-state auophilic interactions between neighboring molecules in isocyanide gold(I) complexes can lead to *intermolecular* Au–Au contacts below the sum of the estimated van der Waals radii (3.6 Å).^{8,9} We envisaged that here *intramolecular* Au–Au interactions lead to an unprecedented diaura-[6]ferrocenophane. In general, two-coordinate gold(I) compounds experience attractive auophilic interactions if the Au–Au separations are below 3.6 Å; their strength can be up to 10 kcal mol⁻¹ for a dimeric unit, similar to standard hydrogen bonds.^{8,10} The energetic contribution of longer Au–Au contacts is negligible.^{8a} Auophilic association can also lead to oligomers and one- and two-dimensional polymers.

In comparison to ligands such as R₃P, R₂S, etc., isocyanides appear to weaken auophilic bonding in gold(I) compounds,^{11a} as witnessed by Au–Au separations close to the threshold value of 3.6 Å.^{9,11} Very short distances between (RNC)AuX molecules have

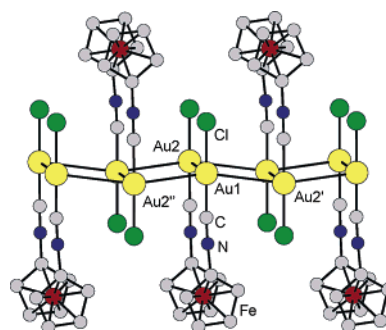


Figure 1. View of the association of **1** in the crystal. Selected bond lengths: Au1–Au2 3.336(1), Au1–Au2' 3.484(1), Au1–Au2'' 3.354(1) Å (Au2': 2 – x, 1 – y, 1 – z; Au2'': 1 – x, 1 – y, 1 – z).

been observed for species that form dimeric aggregates in the solid state. Typical examples are $[\text{MeOC}(\text{O})\text{CH}_2\text{NC}]\text{AuI}$ (3.19 Å) and $(\text{MesNC})\text{AuCl}$ (3.34 Å).^{9d} Gold(I) complexes of oligodentate isocyanides are rare. The only compound of this type that shows some evidence for *intramolecular* Au–Au interactions is $(\text{dmb})\text{AuCN}_2$ (dmb = 1,8-diisocyno-*p*-menthane).¹² The isocyanide groups are located on the same side of the dmb ligand, binding two AuCN units with an Au–Au separation of 3.54 Å. The molecules are aggregated into antiparallel dimers with intermolecular Au–Au distances of 3.49 Å.

The reaction of 1,1'-diisocyanoferrocene (**1**) with AuCl(SMe₂) in dichloromethane afforded $[(\mathbf{1})(\text{AuCl})_2]_\infty$, irrespective of the stoichiometry of the reaction. The compound precipitated immediately upon addition of the first drop of reagent solution, irrespective of whether **1** was added to AuCl(SMe₂) or vice versa. $[(\mathbf{1})(\text{AuCl})_2]_\infty$ proved to be insoluble in all common solvents, including hot acetonitrile, pyridine, 1,2-dichloroethane, dimethyl sulfide, as well as DMSO and DMF. The polymer undergoes ligand substitution with *t*BuNC and Ph₃P in dichloromethane, liberating uncoordinated **1**. Small single crystals of $[(\mathbf{1})(\text{AuCl})_2]_\infty$ were obtained by a diffusion method. The result of the single-crystal X-ray diffraction study is shown in Figure 1.

The molecules adopt the anticipated 3,4-diaura-[6]ferrocenophane structure. The intramolecular Au–Au distance is 3.34 Å, which is essentially identical to the distance between the Cp rings in ferrocene and to the Au–Au separation observed for (MesNC)-AuCl (vide supra). Whereas (MesNC)AuCl is aggregated into dimers, the $(\mathbf{1})(\text{AuCl})_2$ units form one-dimensional chains. The zipperlike arrangement of the molecules leads to a corrugated ribbon of gold atoms composed of two parallel chains, each exhibiting alternating Au–Au distances of 3.35 and 3.48 Å.

[†] University of Kassel.

[‡] University of Karlsruhe.

[§] University of Heidelberg.

^{||} University of Stuttgart.

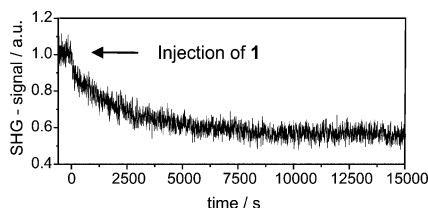


Figure 2. SHG signal recorded during adsorption of **1** on a gold substrate from 30 μM acetonitrile solution. The arrow indicates the time at which the pure solvent was exchanged by the solution of **1**.

The structural and functional similarities of aurophilic and hydrogen bonding have been emphasized in recent studies.¹³ In particular, a striking structural similarity between isocyanide complexes $\text{Me}(\text{CH}_2)_{n-1}\text{NCAuCl}$ and primary alcohols $\text{Me}(\text{CH}_2)_n\text{OH}$ has been pointed out.^{11b} In this context, we note that the conformation and aggregation of the $(\mathbf{1})(\text{AuCl})_2$ units closely resemble that of $\text{Fe}[\text{C}_5\text{H}_4(\text{CHMeOH})]_2$, where intramolecular hydrogen bonding occurs between the two alcoholic substituents; the molecules are aggregated into one-dimensional chains through intermolecular hydrogen bonds, with an antiparallel zipperlike arrangement of neighboring molecules.¹⁴

The insoluble nature of $[(\mathbf{1})(\text{AuCl})_2]_\infty$ is unique for compounds of this kind and, in conjunction with the structural data, indicative of an effective balance between intra- and intermolecular aurophilicity. In view of the great current interest in metal-containing polymers,¹⁵ we note that $[(\mathbf{1})(\text{AuCl})_2]_\infty$ is a new type of polymer with precious metal atoms in the backbone.¹⁶

The chemisorption of **1** on polycrystalline gold from acetonitrile solution was investigated in situ and in real time by using optical second-harmonic generation (SHG).¹⁷ Adsorption of **1** leads to a decrease of the SHG signal due to localization of electrons from the spill out (Figure 2). The data are in perfect agreement with first-order Langmuir kinetics, which indicates direct adsorption of **1** from solution without intermediate states.

Ellipsometric measurements afford an average film thickness value of 14.1 Å. This is in good agreement with the expected value of 8.8 Å estimated from X-ray data of $[(\mathbf{1})(\text{AuCl})_2]_\infty$, since the dimensions of monomolecular, and especially ferrocenyl-containing, films are generally overestimated by ellipsometry.¹⁸ Monolayer formation is further supported by Fourier transform infrared reflection absorption spectroscopy. Comparison of spectra obtained with the modified gold substrate and those obtained from neat **1** reveals characteristic differences. The out-of-plane $\delta(\text{CH})$ bands at 1040, 1028, and 817 cm^{-1} are decreased almost below noise level. This confirms parallel orientation of the cyclopentadienyl ring plane with respect to the surface normal,¹⁹ as expected for the binding of both isocyano groups. On the other hand, in-plane modes such as $\nu(\text{NC})$, $\nu(\text{CC})$, and $\delta(\text{CH})$ and ring distortion found in the IR spectrum of neat **1** at 2118, 1543, 1095, and 855 cm^{-1} , respectively, are clearly identified in the spectrum of **1** on gold. Interaction with the substrate leads to a strong polarization of lone pair electron density into the metal and causes a shift of the $\nu(\text{NC})$ band from 2118 to 2181 cm^{-1} . This compares well with results obtained with other isocyanides² and also with the value of 2226 cm^{-1} found for $[(\mathbf{1})(\text{AuCl})_2]_\infty$. There is no indication for any surface-unbound isocyanide groups in the film. The section from the crystal structure of $[(\mathbf{1})(\text{AuCl})_2]_\infty$ shown in Figure 1 may be taken as a model, cum grano salis, for the arrangement of **1** in self-assembled monolayers on gold.

Acknowledgment. We dedicate this paper to Prof. Hubert Schmidbaur on the occasion of his 70th birthday.

Supporting Information Available: Preparative details and analytical and spectroscopic data. X-ray structural data for $(\mathbf{1})[\text{Cr}(\text{CO})_5]_2$ and $[(\mathbf{1})(\text{AuCl})_2]_\infty$ in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- See, for example: (a) Elschenbroich, C. *Organometallics*, 4th ed.; Teubner: Stuttgart, Germany, 2003; Chapter 14.6. (b) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209–310. (c) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21–86. (d) Malatesta, L.; Bonati, F. *Isocyanide Complexes of Metals*; Academic Press: New York, 1969.
- Recent references: (a) Murphy, K. L.; Tysoe, W. T.; Bennett, D. W. *Langmuir* **2004**, *20*, 1732–1738. (b) Henderson, J. I.; Feng, S.; Bein, T.; Kubiak, C. P. *Langmuir* **2000**, *16*, 6183–6187. (c) Lin, S.; McCarrley, R. L. *Langmuir* **1999**, *15*, 151–159. (d) Ontko, A. C.; Angelici, R. J. *Langmuir* **1998**, *14*, 3071–3078.
- Reviews: (a) Harvey, P. D. *Coord. Chem. Rev.* **2001**, *219–221*, 17–52. (b) Hahn, F. E. *Angew. Chem.* **1993**, *105*, 681–696; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 650–665.
- Reviews: (a) Hirao, T. *Coord. Chem. Rev.* **2002**, *226*, 81–91. (b) Allgeier, A. M.; Mirkin, C. A. *Angew. Chem.* **1998**, *110*, 936–952; *Angew. Chem., Int. Ed.* **1998**, *37*, 894–908.
- van Leusen, D.; Hessen, B. *Organometallics* **2001**, *20*, 224–226.
- (a) Holovics, T. C.; Deplazes, S. F.; Toriyama, M.; Powell, D. R.; Lushington, G. H.; Barybin, M. V. *Organometallics* **2004**, *23*, 2927–2938. (b) Barybin, M. V.; Holovics, T. C.; Deplazes, S. F.; Lushington, G. H.; Powell, D. R.; Toriyama, M. *J. Am. Chem. Soc.* **2002**, *124*, 13668–13669. (c) Knox, G. R.; Pauson, P. L.; Wilson, D.; Solcániová, E.; Toma, S. *Organometallics* **1990**, *9*, 301–306. (d) El-Shihi, T.; Siglmüller, F.; Herrmann, R.; Carvalho, M. F. N. N.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1987**, *335*, 239–247.
- See, for example: Elschenbroich, C. *Organometallics*, 4th ed.; Teubner: Stuttgart, Germany, 2003; Chapter 15.4.3.1.
- (a) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1996**, 561–566. (b) Pathaneni, S. S.; Desiraju, G. R. *J. Chem. Soc., Dalton Trans.* **1993**, 319–322.
- See, for example: (a) White-Morris, R. L.; Stender, M.; Tinti, D. S.; Balch, A. L.; Rios, D.; Attar, S. *Inorg. Chem.* **2003**, *42*, 3237–3244. (b) Wilton-Ely, J. D. E. T.; Ehrlich, H.; Schier, A.; Schmidbaur, H. *Helv. Chim. Acta* **2001**, *84*, 3216–3232. (c) Irwin, M. J.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Yufit, D. S. *J. Chem. Soc., Chem. Commun.* **1997**, 219–220. (d) Schneider, W.; Angermaier, K.; Sladek, A.; Schmidbaur, H. *Z. Naturforsch. B* **1995**, *51*, 790–800.
- Reviews: (a) Pykkö, P. *Angew. Chem.* **2004**, *116*, 4512–4577; *Angew. Chem., Int. Ed.* **2004**, *43*, 4412–4456. (b) Gimeno, M. C.; Laguna, A. *Gold Bull.* **2003**, *36*, 83–92. (c) Fackler, J. P., Jr. *Inorg. Chem.* **2002**, *41*, 6959–6972. (d) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3–10. (e) Pykkö, P. *Chem. Rev.* **1997**, *97*, 597–636. (f) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, *23*, 391–400.
- See, for example: (a) Liao, R.-Y.; Mathieson, T.; Schier, A.; Berger, R. J. F.; Runeberg, N.; Schmidbaur, H. *Z. Naturforsch. B* **2002**, *57*, 881–889. (b) Bachman, R. E.; Fioritto, M. S.; Fetics, S. K.; Cocker, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 5376–5377. (c) Mathieson, T.; Schier, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **2001**, 1196–2000. (d) Bachman, R. E.; Bodolosky-Bettis, S. A.; Glennon, S. C.; Sirchio, S. A. *J. Am. Chem. Soc.* **2000**, *122*, 7146–7147. (e) Jia, G.; Payne, N. C.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1993**, *12*, 4771–4778. (f) Jia, G.; Puddephatt, R. J.; Vittal, J. J.; Payne, N. C. *Organometallics* **1993**, *12*, 263–265. (g) Eggleston, D. S.; Chodos, D. F.; Webb, R. L.; Davis, L. L. *Acta Crystallogr., Sect. C* **1986**, *42*, 36–38. (h) Esperas, S. *Acta Chem. Scand., Ser. A* **1976**, *30*, 527–530.
- (a) Che, C.-M.; Yip, H.-K.; Wong, W.-T.; Lai, T.-F. *Inorg. Chim. Acta* **1992**, *197*, 177–182. (b) Che, C.-M.; Wong, W.-T.; Lai, T.-F.; Kwong, H.-L. *J. Chem. Soc., Chem. Commun.* **1989**, 243–244.
- See, for example: (a) Mendizabal, F.; Pykkö, P.; Runeberg, N. *Chem. Phys. Lett.* **2003**, *370*, 733–740. (b) Codina, A.; Fernández, E. J.; Jones, P. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Pérez, J.; Rodríguez, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 6781–6786. (c) Hunks, W. J.; Jennings, M. C.; Puddephatt, R. J. *Inorg. Chem.* **2002**, *41*, 4590–4598.
- Braga, D.; Maini, L.; Paganelli, F.; Tagliavini, E.; Casolari, S.; Grepioni, F. *J. Organomet. Chem.* **2001**, *637–639*, 609–615.
- (a) Manners, I. *Synthetic Metal-Containing Polymers*; Wiley-VCH: Weinheim, Germany, 2004. (b) Wöhrlé, D.; Pomogailo, A. D. *Metal Complexes and Metals in Macromolecules*; Wiley-VCH: Weinheim, Germany, 2003. (c) Archer, R. D. *Inorganic and Organometallic Polymers*; Wiley-VCH: New York, 2001. (d) Kingsborough, R. P.; Swager, T. M. *Prog. Inorg. Chem.* **1999**, *48*, 123–231.
- Reviews: (a) Puddephatt, R. J. *Macromol. Symp.* **2003**, *196*, 137–144. (b) Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *216–217*, 313–332.
- (a) Boyd, R. W. *Nonlinear Optics*; Academic Press: London, 1992. (b) Shen, Y. R. *Ann. Phys. Chem.* **1980**, *40*, 327–351.
- Ohtsuka, T.; Sato, Y.; Uosaki, K. *Langmuir* **1994**, *10*, 3658–3662.
- (a) Young, J. T.; Boerio, F. J.; Zhang, Z.; Beck, T. L. *Langmuir* **1996**, *12*, 1219–1226. (b) Debe, M. K. *J. Appl. Phys.* **1984**, *55*, 3354–3366.

JA0436244