"Schizoid" reactivity of 1,1′-diisocyanoferrocene†

Ulrich Siemeling,* Dag Rother and Clemens Bruhn

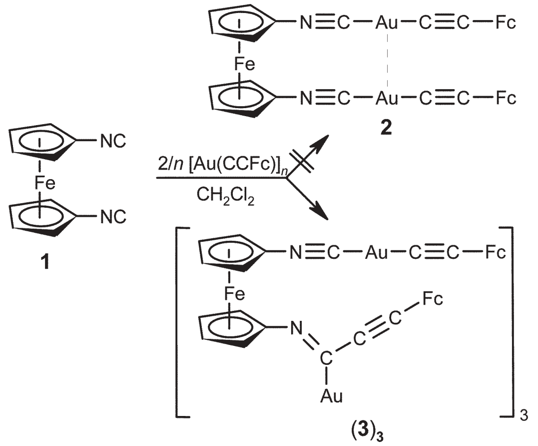
Received (in Cambridge, UK) 15th June 2007, Accepted 17th July 2007
First published as an Advance Article on the web 6th August 2007
DOI: 10.1039/b709063c

The two chemically equivalent functional groups of 1,1′-diisocyanoferrocene each undergo a different specific reaction with the gold(I) acetylide [Au(C≡C–Fc)]$_n$, *viz.* ordinary coordination and extraordinary 1,1-insertion.

Isocyanides are important ligands in coordination chemistry[1] and in surface science.[2] Furthermore, they are of great value for organic synthesis.[3] They undergo α-addition or 1,1-insertion reactions with polar reagents A–B.[3a,4] For example, metalated aldimines are formed in their reaction with organolithium compounds and Grignard reagents, respectively.[4a] Analogous reactions with transition metal M–C bonds afford iminoacyl complexes.[4b,c] In this context, the reaction of isocyanides with transition metal acetylide complexes has been attracting particular attention. This is primarily due to two reasons. First, multiple and successive insertions have been observed with heterodinuclear complexes of the type [{Cl(PR$_3$)$_2$Pd–C≡C–Pt(PR$_3$)$_2$Cl], and even the living polymerisation of aryl isocyanides has been described with this system.[5] Secondly, examples have been reported for the catalytic coupling of isocyanides with terminal alkynes.[6] These reactions afford 1-aza-1,3-enines, which are useful synthons in organic chemistry.[7]

We are interested in the bidentate organometallic isocyanide 1,1′-diisocyanoferrocene (**1**),[8] whose chemistry was completely unde-veloped prior to our work. We[9] and others[10] recently presented first results from the coordination chemistry of **1**. We now report on the intriguing reaction of **1** with the gold(I) acetylide [Au(C≡C–Fc)]$_n$ (Scheme 1).

Gold(I) acetylides are oligo- or polymeric compounds, whose reaction with suitable ligands L affords monomeric complexes of the type [Au(C≡C–R)L], especially with L = PR$_3$, P(OR)$_3$ and RNC.[11] We therefore anticipated the formation of [Fe{C$_5$H$_4$(NC–Au–C≡C–Fc)}$_2$] (**2**) in the reaction of **1** with [Au(C≡C–Fc)]$_n$ (2/*n* equivalents). Furthermore, we expected that, in analogy to the closely related [Fe{C$_5$H$_4$(NC–Au–Cl)}$_2$],[9] **2** would exhibit the intramolecular aurophilic interaction indicated in Scheme 1. Microanalytical data of the product which we obtained in good yield from this reaction agreed well with the composition of **2**. However, its ^{1}H NMR spectrum was incompatible with **2**, since it exhibited too many signals for a species of such symmetry. Characterisation of the product was hampered by its poor solubility in common organic solvents. We eventually succeeded in obtaining single crystals suitable for an X-ray structure analysis,‡ which proved that the product is not **2**, but rather the hexanuclear gold cluster [(Fc–C≡C–Au–C≡N–C$_5$H$_4$)Fe{C$_5$H$_4$–N=C(Au)–C≡C–Fc}]$_3$, which is composed of three subunits **3** (Fig. 1). We note that IR and NMR spectroscopic data are fully in accord with this result. Due to the poor quality of the crystal, the data/parameter ratio of the X-ray structure analysis is rather low. Consequently, a detailed discussion of bond parameters is meaningful only for the heavy atoms.



Scheme 1 Reaction of **1** with [Au(C≡C–Fc)]$_n$ (Fc = ferrocenyl).

The gold cluster exhibits Au–Au distances which are typical for aurophilic interactions,[12] ranging from 3.165(2) to 3.391(2) Å. The cluster core is a triangle of gold atoms whose three sides are each bridged by the N=C unit of a single iminoacyl ligand. Such σ,μ$_2$-bridging iminoacyl ligands RN=CR′ are quite common. In fact, even several clusters are known with a side of an M$_3$ triangle bridged by a σ,μ$_2$-iminoacyl ligand, especially in the chemistry of osmium.[13] In contrast, clusters with two bridged triangular sides of this type are rare.[14] (**3**)$_3$ is unique since bridging of all three sides of an M$_3$ triangle with σ,μ$_2$-RN=CR′ ligands has not been described to date. We note, however, that the general structural motif is not completely unfamiliar in the chemistry of gold. Several triply bridged triangular clusters of the type [Au$_3${σ,μ$_2$-RN=C(OR′)}$_3$] have been reported which contain carbeniate ligands RN=C(OR′), which are akin to iminoacyl ligands RN=CR′. These gold clusters were obtained from the reaction of [AuCl(L)] (L = SMe$_2$, PPh$_3$) with isocyanides RNC in a suitable alcohol R′OH in the presence of KOH.[15] They usually aggregate in the solid state due to aurophilic interactions.[16] For example, [Au$_3${σ,μ$_2$-*p*-Tol-N=C(OEt)}$_3$] forms dimeric units in the crystal through two intermolecular Au–Au contacts.[17] A similar motif is observed for (**3**)$_3$, where two atoms of the Au$_3$ triangle are each connected with a further gold atom – in this case, however, *intra*molecularly. This is caused by the Au–Au contacts present within two of the three subunits of (**3**)$_3$. These Au–Au interactions altogether result in an

---

Institute of Chemistry, University of Kassel, D-34109, Kassel, Germany. E-mail: siemeling@uni-kassel.de; Fax: +49 561 804 4777; Tel: +49 561 804 4576

† Electronic supplementary information (ESI) available: Preparative details and analytical and spectroscopic data. See DOI: 10.1039/b709063c

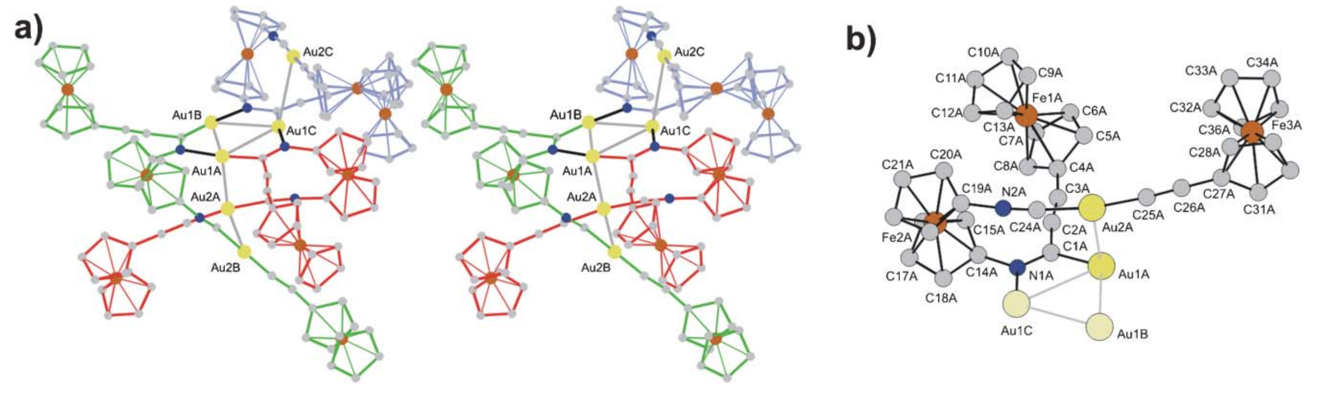


Fig. 1 (a) Molecular structure of $(\mathbf{3})_3$ in the crystal (stereographic representation with subunits marked in different colours). Interatomic distances <4.0 Å in the Au_6 cluster: Au1A–Au1B 3.356(2), Au1A–Au1C 3.278(2), Au1A–Au2A 3.352(2), Au2A–Au2B 3.165(2), Au1B–Au1C 3.284(2), Au1C–Au2C 3.391(2) Å. (b) Molecular structure of the subunit coloured red in (a). Selected bond lengths (Å): C1A–N1A 1.31(3), C1A–C2A 1.40(4), C1A–Au1A 1.98(3), C2A–C3A 1.22(4), C24A–N2A 1.15(3), C24A–Au2A 1.90(3), C25A–C26A 1.25(5), C25A–Au2A 1.95(3), N1A–Au1C 1.99(2).

unprecedented chain of five gold atoms with two neighbouring atoms being bridged by a sixth one.

Finally, we focus our attention on the component of **3** which is based on 1,1′-diisocyanoferrocene (**1**). This unit was formed in a peculiar way. One of the two isocyano groups shows the usual, and expected, coordination of the gold acetylide unit [Au(C≡C–Fc)]. In contrast, the other one has undergone a 1,1-insertion reaction with the Au–C bond of the gold acetylide, thus forming an iminoacyl group. Despite the rapid development of the chemistry of gold during the past two decades,[18] an insertion of an isocyanide into an Au–C bond has been described only twice to date,[19] and just a single example involves a gold(I) species.[19b]

The 1,1-insertion of an isocyanide into an Au–C bond is very unusual as such. It is even more unusual that in the present case this reaction occurs in conjunction with a second, different, reaction. Never before has it been observed that two chemically equivalent groups in a molecule each undergo a different specific reaction with the same reagent. This unprecedented and intriguing behaviour observed for **1** appears to be schizoid. Systematic investigations are currently underway to identify the method in this madness.

We thank UMICORE AG & Co. KG for a generous gift of precious metal compounds. D. R. is grateful to the Otto-Braun-Fonds for a doctoral fellowship.

Notes and references

‡ *Crystal data* for **2**: $C_{110}H_{82}Au_6Cl_4Fe_9N_6$, $M = 3314.07$, triclinic, space group $P\bar{1}$, $a = 13.6125(18)$, $b = 19.243(3)$, $c = 23.262(3)$ Å, $\alpha = 110.426(10)$, $\beta = 104.403(10)$, $\gamma = 108.902(10)^\circ$, $V = 4932.0(15)$ Å^3, $Z = 2$, $T = 133(2)$ K, 13142 reflections, 5764 $>2\sigma(I)$, $wR(I > 2\sigma(I)) = 0.1567$. CCDC 641517. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709063c

1 (*a*) C. Elschenbroich, *Organometallics*, Teubner, Stuttgart, 3rd edn, 2005, pp. 381–383; (*b*) F. E. Hahn, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 650; (*c*) E. Singleton and H. E. Oosthuizen, *Adv. Organomet. Chem.*, 1983, **22**, 209; (*d*) P. M. Treichel, *Adv. Organomet. Chem.*, 1973, **11**, 21; (*e*) L. Malatesta and F. Bonati, *Isocyanide Complexes of Metals*, Academic Press, New York, 1969.

2 Seminal paper: (*a*) J. J. Hickman, P. E. Laibinis, D. I. Auerbach, C. Zou, T. J. Gardner, G. M. Whitesides and M. S. Wrighton, *Langmuir*, 1992, **8**, 357; selected recent publications: (*b*) M. Lazar and R. J. Angelici, *J. Am. Chem. Soc.*, 2006, **128**, 10613; (*c*) D. L. DuBose, R. E. Robinson, T. C. Holovics, D. R. Moody, E. C. Weintrob, C. L. Berrie and M. V. Barybin, *Langmuir*, 2006, **22**, 4599.

3 (*a*) A. Dömling, *Chem. Rev.*, 2006, **106**, 17; (*b*) M. Suginome and Y. Ito, in *Science of Synthesis*, ed. S. Murahashi, Thieme, Stuttgart, 2004, vol. 19, pp. 445–530; (*c*) I. Ugi, B. Werner and A. Dömling, *Molecules*, 2003, **8**, 53; (*d*) I. Ugi, S. Lohberger and R. Karl, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, I. Fleming and C. H. Heathcock, Pergamon, Oxford, 1991, vol. 2, pp. 1083–1109; (*e*) *Isonitrile Chemistry*, ed. I. Ugi, Academic Press, New York, 1971.

4 (*a*) M. B. Smith and J. March, *March's Advanced Organic Chemistry*, Wiley, New York, 6th edn, 2007, pp. 1466–1470; (*b*) Y. Kayaki and A. Yamamoto, in *Current Methods in Inorganic Chemistry*, ed. H. Kurosawa and A. Yamamoto, Elsevier, Amsterdam, 2003, vol. 3, pp. 373–409; (*c*) L. D. Durfee and I. P. Rothwell, *Chem. Rev.*, 1988, **88**, 1059; (*d*) T. Saegusa and Y. Ito in ref. 3*e*, pp. 65–92.

5 (*a*) K. Onitsuka, K. Yanai, F. Takei, T. Joh and S. Takahashi, *Organometallics*, 1994, **13**, 3862; (*b*) K. Onitsuka, T. Joh and S. Takahashi, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 851.

6 (*a*) K. Komeyama, D. Sasayama, T. Kawabata, K. Takehira and K. Takaki, *J. Org. Chem.*, 2005, **70**, 10679; (*b*) K. Komeyama, D. Sasayama, T. Kawabata, K. Takehira and K. Takaki, *Chem. Commun.*, 2005, 634; (*c*) E. Barnea, T. Andrea, M. Kapon, J.-C. Berthet, M. Ephritikhine and M. S. Eisen, *J. Am. Chem. Soc.*, 2004, **126**, 10860.

7 Review: M. D. Stadnichuk, A. V. Khramchikhin, Y. L. Piterskaya and I. V. Suvorova, *Russ. J. Gen. Chem.*, 1999, **69**, 593.

8 D. van Leusen and B. Hessen, *Organometallics*, 2001, **20**, 224.

9 U. Siemeling, D. Rother, C. Bruhn, H. Fink, T. Weidner, F. Träger, A. Rothenberger, D. Fenske, A. Priebe, J. Maurer and R. Winter, *J. Am. Chem. Soc.*, 2005, **127**, 1102.

10 P. J. Shapiro, R. Zehnder, D. M. Foo, P. Perrotin, P. H. M. Budzelaar, S. Leitch and B. Twamley, *Organometallics*, 2006, **25**, 719.

11 Seminal paper: (*a*) G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1962, 3220; selected recent publications: (*b*) J. Vicente, M.-T. Chicote, M. M. Alvarez-Falcón and P. G. Jones, *Organometallics*, 2005, **24**, 5956; (*c*) S. S. Y. Chui, M. F. Y. Ng and C.-M. Che, *Chem. Eur. J.*, 2005, **11**, 1739.

12 Selected reviews: (*a*) P. Pyykkö, *Angew. Chem., Int. Ed.*, 2004, **43**, 4412; (*b*) M. C. Gimeno and A. Laguna, *Gold Bull.*, 2003, **36**, 83; (*c*) J. P. Fackler, Jr., *Inorg. Chem.*, 2002, **41**, 6959; (*d*) H. Schmidbaur, *Gold Bull.*, 2000, **33**, 3; (*e*) P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597.

13 Review:A. J. Deeming, *Adv. Organomet. Chem.*, 1986, **26**, 1.

14 (*a*) K. I. Hardcastle, H. Minassian, A. J. Arce, Y. De Sanctis and A. J. Deeming, *J. Organomet. Chem.*, 1989, **368**, 119; (*b*) C. Choo Yin and A. J. Deeming, *J. Organomet. Chem.*, 1977, **133**, 123.

15 (*a*) A. L. Balch, M. M. Olmstead and J. C. Vickery, *Inorg. Chem.*, 1999, **38**, 3494; (*b*) G. Minghetti and F. Bonati, *Inorg. Chem.*, 1974, **13**, 1600; (*c*) J. E. Parks and A. L. Balch, *J. Organomet. Chem.*, 1974, **71**, 453; (*d*) G. Minghetti and F. Bonati, *Gazz. Chim. Ital.*, 1972, **102**, 205; (*e*) G. Minghetti and F. Bonati, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 429.

16 Review: A. Burini, A. A. Mohamed and J. P. Fackler, Jr., *Comments Inorg. Chem.*, 2003, **24**, 253.

17 A. Tiripicchio, M. Tiripicchio Camellini and G. Minghetti, *J. Organomet. Chem.*, 1979, **171**, 399.

18 Selected reviews: (*a*) A. S. K. Hashmi and G. J. Hutchings, *Angew. Chem., Int. Ed.*, 2006, **45**, 7896; (*b*) H. Schmidbaur and A. Schier, in *Science of Synthesis*, ed. I. A. O'Neil, Thieme, Stuttgart, 2003, vol. 3, pp. 691–761; (*c*) *Gold. Progress in Chemistry, Biochemistry and Technology*, ed. H. Schmidbaur, Wiley, Chichester, 1999.

19 (*a*) W. Henderson, B. K. Nicholson and A. L. Wilkins, *J. Organomet. Chem.*, 2005, **690**, 4971; (*b*) M. Murakami, M. Inouye, M. Suginome and Y. Ito, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3649.