Cyclic Diaminocarbene–Rhodium(I) Complex Tethered to Disulfide: Synthesis and Application to Gold Surface Modification

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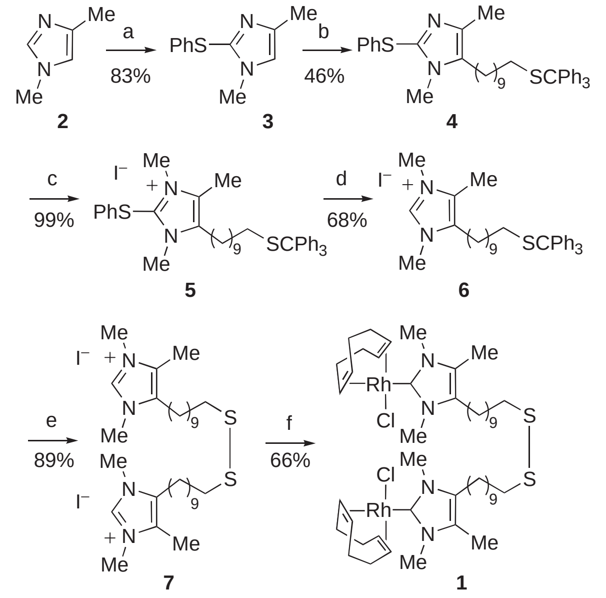
A dimeric *N*-heterocyclic carbene (NHC)–rhodium(I) complex connected with a long chain dialkyl disulfide linker was synthesized, and used for the preparation of a Rh-modified alkane thiolate monolayer on a gold surface.

Formation of self-assembled monolayers (SAM) of alkanethiolate on a gold surface is a versatile and well-established approach for constructing functional surfaces.[1] Immobilization of a metal complex to a gold surface has been attracting growing interest. Foregoing studies have indicated varied utilities of metal-functionalized surfaces.[2] However, the ligands attaching the metal center to the SAM terminal have been limited to those with conventional coordinating moieties such as pyridines, amines, phosphines, etc. Recently *N*-heterocyclic carbenes (NHCs) such as cyclic diaminocarbenes have emerged as strongly σ-donating ligands forming a robust bond with broad spectrum of transition metal species and now expanding their utility in various fields. They are especially useful as a supporting ligand of an organometallic catalyst.[3,4] We report herein the synthesis of a dimeric, disulfide-functionalized *N*-heterocyclic carbene–rhodium(I) complex **1** and preliminary experimental results on its use for the preparation of a monolayer of NHC–Rh(I) complex on a gold surface.

We designed the NHC ligand involved in **1** so that its metal complexes could form a densely packed, highly-ordered monolayer directing the metal centers toward a bulk phase. To this end, we decided to locate the sulfur-terminated alkyl chain onto the ring carbon atom rather than onto one of the nitrogen atoms. In addition, the simplest alkyl (Me) groups were employed as *N*-substituents to reduce the steric demand of the monolayer head groups.



Scheme 1. Reagents and conditions: a) (i) BuLi (1.0 equiv.), THF, −78 °C, 30 min; (ii) PhSSPh (1.0 equiv.), −78 °C, 5.5 h. b) (i) Lithium 2,2,6,6-tetramethylpiperidide (1.2 equiv.), LiCl (2.2 equiv.), THF/DME, −78 °C, 4 h; (ii) $Br(CH_2)_{10}SCPh_3$ (0.88 equiv.), −25 °C, 14 h. c) MeI (5.0 equiv.), $CHCl_3$, reflux, 14 h, 99%. d) 2-Naphthalenethiol (3.0 equiv.), Et_3N (3.0 equiv.), THF, rt, 13 h. e) I_2 (2.1 equiv.), $CHCl_3$, rt, 1.5 h. (f) Ag_2O (2.0 equiv.), CH_2Cl_2, rt, 18 h, in the dark; (ii) $[RhCl(cod)]_2$ (1.0 equiv.), rt, 18 h.

The synthesis of NHC–Rh(I) complex **1** starting with 1,4-dimethylimidazole (**2**)[5] is illustrated in Scheme 1. The C-2 position of **2**, which has the most acidic hydrogen atom, was first protected with phenylthio group through the lithiation with BuLi followed by trapping with PhSSPh to give 2-phenylthioimidazole **3**.[6] Then, the protected imidazole **3** was deprotonated at the second acidic C-5 position with LiTMP/LiCl and was subjected to the alkylation with Ph_3CS-terminated alkyl bromide[7] to afford the S-functionalized, C-alkylated imidazole **4**. This compound was then methylated at the nitrogen atom with MeI to give the imidazolium salt **5**. The selective removal of the 2-PhS group[8] from **5** in the presence of the ω-Ph_3CS group was successful by the treatment with 2-naphthalenethiol/Et_3N in THF,[9] giving C-2 free imidazolium salt **6**. The treatment of **6** with I_2 caused oxidative cleavage of the S–CPh_3 bond and the simultaneous S–S bond formation, resulting in the formation of dimeric imidazolium **7** with a disulfide linkage.[10] Finally, the treatment of *N*-heterocyclic carbene precursor **7** with Ag_2O followed by the reaction with $[RhCl(cod)]_2$[11] gave, after repeated precipitation from CH_2Cl_2/hexane, the corresponding NHC–Rh(I) complex **1** as yellow solid. The ^1H and ^{13}C NMR as well as ESI-MS analysis confirmed the dimeric structure with a disulfide linkage.[12]

To the best of our knowledge, complex **1** is the first example of a Rh(I) complex bearing a disulfide group. It should be noted that a disulfide is potentially a ligand toward late transition metals.[13–15] Indeed, the both stoichiometric[14] and catalytic[15] reactions between Rh species and disulfides have so far been reported. In the event, however, the isolation of complex **1** confirmed that the Rh(I) center bearing the highly σ-donating NHC ligand is compatible with the S–S functionality under the conditions employed in the present study. Comparison of the ^1H and ^{13}C NMR spectra of complex **1** with those of imidazolium salt **7** in the disulfide region indicated no interaction between the Rh atoms and the disulfide moiety.

The modification of a gold surface with NHC–rhodium complex **1** was then carried out by immersing a gold substrate

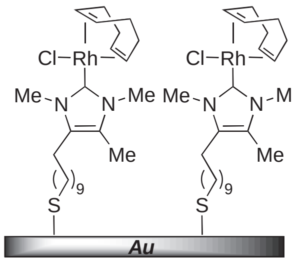


Figure 1. Expected gold surface modified with complex **1**.

(evaporated onto a Ti-coated glass plate) in a 1.0 mM THF solution of **1** at rt for 20 h. The XPS (X-ray photoelectron spectroscopy) analysis of the modified gold surface indicated the existence of Rh (3d at 308.9 eV), N (1s at 400.9 eV), Cl (2p at 198.5 eV), and S (2p at 162.9 eV) atoms, confirming the successful anchoring of the NHC–Rh(I) complex on the surface. The relative peak intensities are well consistent with the monolayer structure as shown in Figure 1.[16] Notably, it seems that the terminal thiolate group forms a stable covalent bond with the surface Au atoms without coordinating to the rhodium center. This is the first incorporation of *N*-heterocyclic carbene metal complexes into the alkane thiolate monolayer on a gold surface.

In summary, a dimeric *N*-heterocyclic carbene (NHC)–rhodium(I) complex connected with a long chain dialkyl disulfide linker was synthesized, and used for the preparation of a Rh-modified alkane thiolate monolayer on a gold surface. Efforts aimed at catalytic applications of the NHC–rhodium monolayer are ongoing in our laboratory.

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7 The Ph_3CS-terminated alkyl bromide $Br(CH_2)_{10}SCPh_3$ was prepared from Ph_3CSH, 1,10-dibromodecane (4.4 equiv.), and NaH (6.9 equiv.) in refluxing THF for 28 h (49% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.40 (m, 6H, phenyl), 7.30–7.17 (m, 9H, phenyl), 3.40 (t, $J = 6.9$ Hz, 2H, $BrCH_2$), 2.13 (t, $J = 7.2$ Hz, 2H, SCH_2), 1.84 (qn, $J = 6.9$ Hz, 2H, $BrCH_2CH_2$), 1.39–1.18 (m, 14H, $SCH_2(CH_2)_7$).

8 Reductive deprotection of the phenylthio group in imidazole **4** with Bu_3SnH in the presence of AIBN (2,2′-azobisisobutyronitrile) as a radical initiator gave 47% yield of the deprotected imidazole, albeit with Bu_3Sn-derived impurities. The tin impurities could not be separated by several column chromatographies nor several reported procedures.

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10 The spectral data for **7**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.08 (s, 2H, NCHN), 3.915 (s, 6H, NCH_3), 3.925 (s, 6H, NCH_3), 2.68 (t, $J = 7.2$ Hz, 4H, CH_2S), 2.61 (t, $J = 7.2$ Hz, 4H, $NCCH_2$), 2.27 (s, 6H, $NCCH_3$), 1.67 (qn, $J = 7.2$ Hz, 4H, CH_2CH_2S), 1.53 (qn, $J = 7.2$ Hz, 4H, $NCCH_2CH_2$), 1.38–1.26 (m, 24H, alkyl CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3 (2C, NCHN), 131.1 (2C, $NCCH_2$), 127.1 (2C, $NCCH_3$), 74.1 (2C, $NCCH_2$), 39.1 (2C, CH_2S), 34.1 (2C, NCH_3), 34.1 (2C, NCH_3), 29.2 (2C), 29.2 (2C), 29.1 (2C), 29.0 (2C), 29.0 (2C), 29.0 (2C), 28.6 (2C), 28.3 (2C), 22.5 (2C, $NCCH_3$); IR (neat) ν/cm^{-1} 3150 (w), 3017 (w), 2926 (s), 2854 (s), 1630 (m), 1576 (s), 1452 (m), 1415 (m), 1201 (m), 1124 (w), 1088 (w), 807 (s).

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12 The spectral data for **1**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.98 (m, 4H, COD CH), 3.98 (s, 6H, NCH_3), 3.96 (s, 6H, NCH_3), 3.27 (m, 4H, COD CH), 2.68 (t, $J = 7.2$ Hz, 4H, CH_2S), 2.50–2.30 (m, 8H, COD CH_2), 2.38 (t, $J = 7.2$ Hz, 4H, $NCCH_2$), 2.03 (s, 6H, $NCCH_3$), 2.02–1.84 (m, 8H, COD CH_2), 1.67 (qn, $J = 7.2$ Hz, 4H, CH_2CH_2S), 1.52–1.16 (m, 28H, alkyl CH_2); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 178.9 (d, $^1J_{\mathrm{Rh-C}} = 52.1$ Hz, 2C, NCRh), 129.1 (2C, $NCCH_2$), 124.9 (2C, CCH_3), 97.2 (d, $^1J_{\mathrm{Rh-C}} = 7.4$ Hz, 2C, COD CH), 97.2 (d, $^1J_{\mathrm{Rh-C}} = 6.9$ Hz, 2C, COD CH), 67.2 (d, $^1J_{\mathrm{Rh-C}} = 14.9$ Hz, 4C, COD CH), 38.7 (2C, CH_2S), 34.4 (2C, COD CH_2), 34.4 (2C, COD CH_2), 32.6 (2C, COD CH_2), 32.5 (2C, COD CH_2), 29.1 (4C), 28.9 (2C), 28.8 (2C), 28.8 (6C), 28.5 (2C), 28.5 (2C), 28.1 (2C), 23.1 (2C, $NCCH_2$), 8.4 (2C, $NCCH_3$); HRMS (ESI, MeOH) Found: 1019.3685. Calcd for $C_{48}H_{82}ClN_4Rh_2S_2$ (M − Cl): 1019.3780.

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16 The XPS characterization is based on the comparison with monolayers consisting of a related structure and with the data for complex **1** deposited on oxidized silicon. Details of surface characterization will be reported elsewhere.

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