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Adduct between (η-Cyclopentadienyl)(1,2-diphenyl-1,2-ethylenedithiolato)rhodium(III) and Quadricyclane

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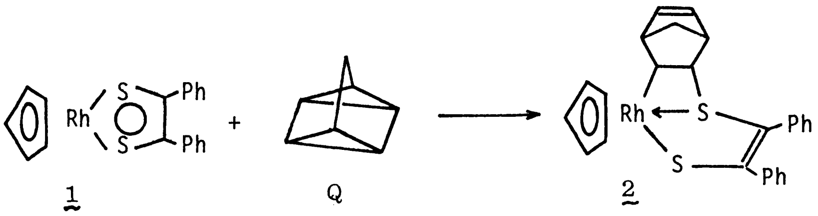
(η-Cyclopentadienyl)(1,2-diphenyl-1,2-ethylenedithiolato)rhodium(III) complex (**1**) reacts with quadricyclane (Q) to give a 1:1 adduct in which Rh and S of the complex are bridged by 5-norbornene-2,3-diyl group. The adduct dissociates to give **1** and norbornadiene upon irradiation with a medium pressure mercury lamp.

Dithiolatometal complexes are among so-called "non-innocent complexes" which have unique electronic structures.[1] The metalladichalcogenolene ring, a five-membered ring containing a transition metal atom and two chalcogen atoms, is considered as an aromatic ring. However, the ring shows very interesting reactions. A remarkable property of the metalladichalcogenolene rings in (η-cyclopentadienyl)(1,2-ethylenedichalcogenato)metal complexes is the unsaturation at metal and chalcogen atoms. The addition reactions occur at these sites. We have reported the bridging by an alkyne (dimethyl acetylenedicarboxylate)[2] and by alkylidene groups[3] between the metal atom and one of the chalcogen atoms.

We report here another type of the addition reaction to the metalladichalcogenolene ring, the addition of quadricyclane, accompanied by the isomerization of quadricyclane to 5-norbornene-2,3-diyl structure. In the reaction between bis(1,2-ethylenedithiolato)metal (metal = Ni, Pd, Pt) and quadicyclane, the addition reaction was observed, but the bridging occurred between two sulfur atoms.[4]

The adduct 2 is formed easily by refluxing solutions of the dithiolato-rhodium complex **1**[5] (0.12 mmol) in 10 cm^3 of Q (100 mmol) at 110 °C for 6 h. The pure product was obtained by chromatography (column, silica gel (Wako gel C-300 supplied by Wako Junyaku Co.); eluent, dichloromethane). The yield of the adduct **2** was 85% (based on the dithiolato complex).



1 Q **2**

Norbornadiene, an isomer of quadricyclane, did not react with **1** .

The structure of the adduct **2** was determined by elemental analysis and by spectroscopies.[6] In spite of any efforts, we could not prepare a single crystal of the adduct.

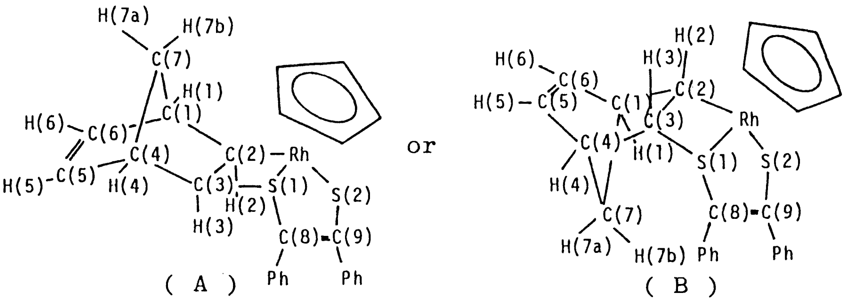
The elemental analysis (Found: C, 62.02; H, 4.86%. Calcd for $C_{18}H_{19}O_4RhS_2$: C, 62.15; H, 4.61%) and the observation of the parent peak at m/z = 502 in MS indicate that the product is a 1:1 adduct between **1** and Q.

The coupling (J = 23.6 Hz) between the rhodium and the carbon (at the 2-position in the formula) of the hydrocarbon indicates the bond formation between Rh and C of the hydrocarbon.

The bridging between metal and sulfur atoms can be concluded from similarity in the ^{13}C NMR of **2** to that of an alkylidene adduct (**3** : adduct between (η -cyclopentadienyl)(1-methoxycarbonyl-1,2-ethylenedithiolato)cobalt(III) and ethoxycarbonylmethylidene), the structure of which has been determined by X-ray diffraction.[3] The key signals are those appearing at δ = 117.9 and 163.8 which are assigned to the carbon atoms in the metalladithiolene ring. In the alkylidene adduct, the signal of C attached to the bridged S appears at δ= 113.6, while that of the other carbon appears at δ = 174.0.

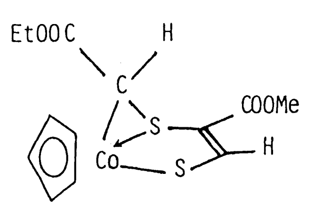
A norbornene structure can be assigned to the hydrocarbon moiety from the following considerations. The adduct has two signals due to olefinic protons at δ = 5.95 and 6.38 in ^1H NMR and two signals due to olefinic carbons (of the C_7H_8 hydrocarbon moiety) at δ = 132.1 and 142.6 in ^{13}C NMR. This indicates that the adduct has a norbornene-type double bond. The other ^1H NMR signals can be well assigned based on the norbornene structure.

The so-called W-type long range coupling[7] between the proton at the bridge (H(7a)) and H(3) shows that H(3) is situated in the endo-position and, therefore, the Rh and S add to the hydrocarbon in the exo-position. The structure of A or B can be given for the adduct. At present, we do not have enough information to determine the configuration of the adduct.



(A) (B)

Proposed structure for adduct **2**



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For some organometallic compounds, the formation of metallacycle compounds has been reported in the reactions with strained hydrocarbons.[8] However, only a few reports have appeared on the insertion of unsaturated hydrocarbons into the metal-sulfur bonds. The so far reported reactions are the insertion of alkynes into Rh-S,[2,9] Mo-S,[10] and Mn-S bonds.[11] The present findings should be interesting in the interactions of sulfur containing metal complexes with strained hydrocarbons.

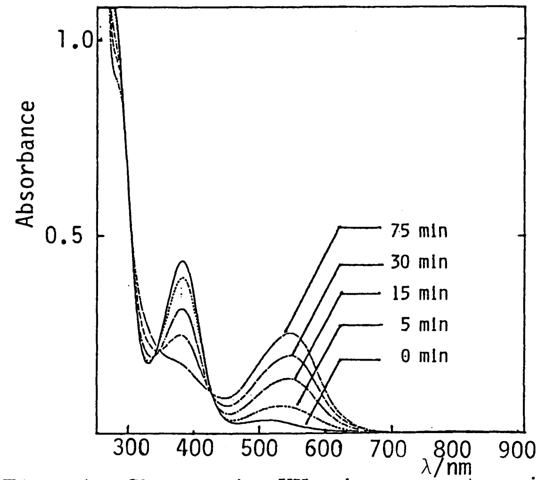


Fig. 1. Change in UV-vis. spectra in the irradiation with 365 nm light

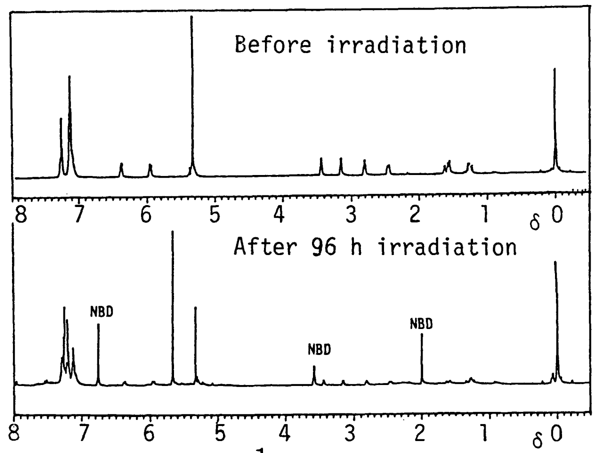
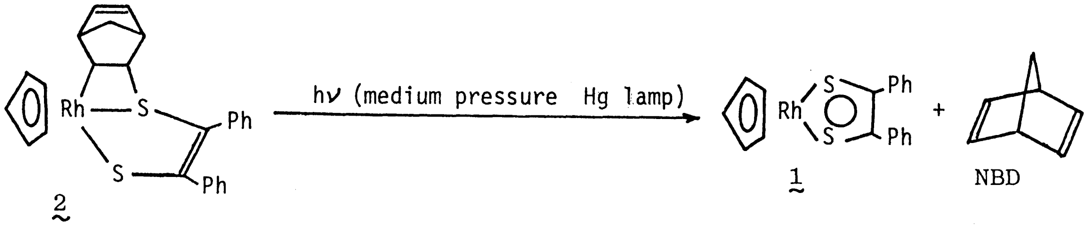


Fig. 2. Change in ^{1}H NMR in the irradiation with a medium pressure Hg lamp

In the reaction of 1 with Q, the C_7H_8 moiety adds between Rh and S of the dithiolato complex; this reaction results in valence isomerization of Q to the 5-norbornene-2,3-diyl structure. The fact that 1 does not react with NBD indicates that the addition does not occur after the isomerization.

Among the properties of the adduct, its photochemical behavior should be noted. The adduct 2 is photoreactive. The spectral changes in UV-vis. and ^{1}H NMR during the irradiation with a medium pressure mercury lamp (in the case of UV-vis. spectral change, with the filtered light of 365 nm) are shown in Figs. 1 and 2. The appearance of the absorption around 560 nm in UV-vis. spectra shows the regeneration of the (free) dithiolatorhodium complex 1. The ^{1}H NMR indicates the formation of NBD and the (free) dithiolato complex 1.



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5) The dithiolato complex has been synthesized by the one-step reaction of [Rh(cp)(cod)] (cod = 1,5-cyclooctadiene), diphenylacetylene, and elemental sulfur.

Complex **1**: Deep violet crystals; mp 236-237 °C; UV-vis. (CH_2Cl_2) 550 (ε 8900), 387 (ε 970), 286 (ε 16000), and 257 nm (ε 50100); IR (KBr disk) 3110, 1467, 1350, 835, 772, 750, and 708 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 5.66 (5H, s, cp) and 7.10-7.56 (10H, m, Ph); MS (70 eV) m/z (rel intensity) 410 (38, M^+), 232 (100, $CpRhS_2$), 178 (83), 168 (24, CpRh), 105 (22), 83 (23), 81 (33), 69 (46), 60 (39), 57 (56), 56 (78), and 55 (45). Found: C, 55.11; H, 3.81%. Calcd for $C_{19}H_{15}RhS_2$: C, 55.61; H, 3.68%.

6) Adduct **2**: Orange crystals; mp 155-156 °C; UV-vis. (CH_2Cl_2) 513 (ε 610), 384 (ε 8700), and 236 nm (ε 29000); IR (KBr disk) 1600, 1540, 1450, 1260, 740, and 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.25 (1H, ddd, $J_{H(7a)-H(7s)}$ = 12.6 Hz, $J_{H(7a)-H(3)}$ = 6.8 Hz, $J_{H(7a)-H(2)}$ = 1.8 Hz, H(7a)), 1.60 (1H, dd, $J_{H(7s)-H(7a)}$=12.6 Hz, $J_{H(7s)-H(4)}$ = 4.2 Hz, H(7s)), 2.45 (1H, dd, $J_{H(3)-H(7a)}$ = 6.8 Hz, $J_{H(3)-H(2)}$ = 1.5 Hz, H(3)), 2.81 (1H, ddd, $J_{H(4)-H(7s)}$ = 4.2 Hz, $J_{H(4)-H(5)}$ = 3.3 Hz, $J_{H(4)-H(6)}$ = 0.7 Hz, H(4)), 3.15 (1H, d, $J_{H(1)-H(6)}$ = 3.1 Hz, H(1)), 3.44 (1H, dd, $J_{H(2)-H(7a)}$ = 1.8 Hz, $J_{H(2)-H(3)}$ =1.5 Hz, H(2)), 5.33 (5H, s, cp), 5.95 (1H, ddd, $J_{H(6)-H(5)}$ = 5.6 Hz, $J_{H(6)-H(1)}$ = 3.1 Hz, $J_{H(6)-H(4)}$ = 0.7 Hz, H(6)), 6.38 (1H, dd, $J_{H(5)-H(6)}$ = 5.6 Hz, $J_{H(5)-H(4)}$ = 3.3 Hz, H(5)), 7.14 (8H, m, Ph) and 7.26 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 35.2 (C(7)), 50.0 (C(3)), 51.7 (C(4)), 54.4 (C(1)), 65.9 (J_{Rh-C} = 25.6 Hz, C(2)), 89.6 (J_{Rh-C} = 3.7 Hz, cp), 117.9 (C(8)), 126.1 (Ph), 127.4 (Ph), 127.8 (Ph), 128.1 (Ph), 128.5 (Ph), 129.8 (Ph), 132.1 (C(6)), 139.1 (Ph), 141.5 (J_{Rh-C} = 2.4 Hz, Ph), 142.6 (C(5)), and 163.8 (C(9)); MS (70 eV) m/z (rel intensity) 502 (37, M^+), 410 (60, M-NBD), 232 (100, $CpRhS_2$), 200 (4, CpRhS), and 168 (24, CpRh).

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