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REACTION OF SULFUR DIOXIDE WITH NEW DINUCLEAR RHODIUM COMPOUNDS

THOMAS E. BITTERWOLF

Department of Chemistry, U.S. Naval Academy, Annapolis, MD 21402 (U.S.A.)

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Summary

The reaction of sulfur dioxide with two new dinuclear rhodium compounds has been examined. The dinuclear compounds are unique in that two cyclopentadienylrhodium moieties are coupled by a methylene linkage between the rings. This linkage appears to result in geometric and kinetic factors which favor reactions in which Rh–Rh bond formation may occur. Reaction of $CH_2[CpRh(CO)]_2$-μ-CO with SO_2 results in the formation of a μ-SO_2 derivative, $CH_2[CpRh(CO)]_2$-μ-SO_2, and a second compound which may be an SO_2 adduct of $CH_2[CpRh(CO)]_2$-μ-CO. Reaction of SO_2 with $CH_2[CpRh(ene)_2]_2$ gives a μ-S_2O_4 derivative which is the first example of a bridging dithionite compound in the rhodium series.

We have recently reported [1,2] the synthesis of $CH_2[CpRh(CO)_2]_2$ (**1**) and described the facile decarbonylation reaction of **1** to give $CH_2[CpRh(CO)]_2$-μ-CO (**2**). The ease with which this reaction proceeds appears to be the result of (a) a highly favorable molecular geometry in which a Rh–Rh bond can be achieved without significant strain, and (b) the rate enhancement which comes about when two potentially reactive species are held in close proximity. We speculated that other reactions which result in the formation of Rh–Rh bonds might be favored for **1** and similar compounds. As a test of this possibility, we have examined the reactions of **2** and a new dinuclear complex, $CH_2[CpRh(ene)_2]_2$ (**3**), with SO_2. These reactions have yielded a new μ-SO_2 dinuclear rhodium complex as well as the first observed μ-S_2O_4 rhodium compound. The syntheses and spectral evidence for these new compounds are presented in this paper.

Results and discussion

Herrmann and his coworkers [3] have reported that $[CpRh(CO)]_2$-μ-CO will react with SO_2 to give $[CpRh(CO)]_2$-μ-SO_2 in quantitative yield. The molecular structure of this compound has been reported and shows the bridging SO_2 to have approxi-

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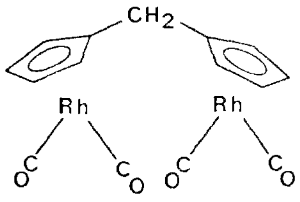
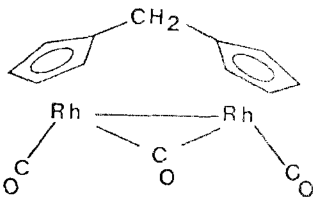


(1)



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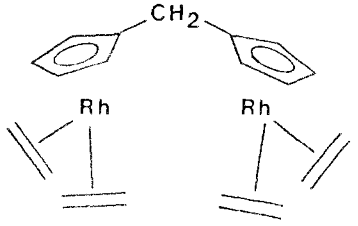


(3)

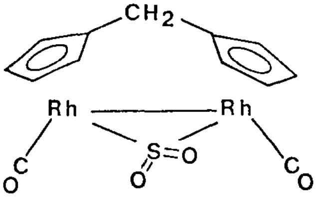
mately tetrahedral geometry. The cyclopentadienyl rings (and carbonyl groups) were found to be *trans* to one another relative to the Rh–S–Rh plane.

Cramer has reported [4] that the reaction between SO_2 and $CpRh(ene)_2$ yields a mononuclear complex, $CpRh(ene)SO_2$, in which one ethylene has been replaced by the SO_2. Ryan, Eller and Kubas [5] have determined the molecular structure of this compound and have confirmed the mononuclear identity of the compound and have shown that the $M–SO_2$ moiety is planar. The nature of the bond between the rhodium atom and the SO_2 has been discussed in detail.

We have found that when SO_2 is bubbled into benzene solutions of **2**, an immediate color change is observed in which the initially orange solution darkens to a deep red. After 30 min, the solvent is removed and the solid residue is taken up in methylene chloride and chromatographed on an alumina column. A small amount of **2** is eluted from the column followed by a light orange band, **4**, and a scarlet main band, **5**. In larger batches, **5** precipitates from the reaction mixture and may be recovered directly.

Removal of solvent from the scarlet band and recrystallization from methylene chloride yielded a red crystalline solid whose elemental analysis and spectral features are consistent with its formulation as a dinuclear μ-SO_2 complex. Chemical ionization mass spectroscopy has been conducted on this compound and a single cluster of ions corresponding to the expected isotopic pattern of the parent mass has been observed. An IR spectrum of this compound shows two bands in the terminal carbonyl region whose intensity pattern (strong, weak) is characteristic of *cis* dicarbonyl species. Similar intensity patterns are observed for $CH_2[CpRh(CO)]_2$-μ-CO [1,2] and $CH_2[CpRh(CO)]_2$-μ-CH_2 [6]. Bands at 1216 and 1067 cm^{-1} which are associated with bridging SO_2 groups are also observed. Virtually identical positions for the SO_2 absorptions are found (1214 and 1067 cm^{-1}) when the spectrum of an authentic sample of $[CpRh(CO)]_2$-μ-SO_2 is recorded in methylene chloride. ^{1}H

NMR spectra of **5** show four distinct resonances for ring protons and an AB quartet for the CH_2 group. These features suggest that the molecular conformation of this species is relatively fixed in solution. The analogous μ-CH_2 complex also appears to have a fixed geometry, but the μ-CO derivative is apparently free to undergo rearrangement on the NMR time scale which averages the environments of the CH_2 protons and the protons in the 2,5 and 3,4 ring positions, respectively. An electronic spectrum of **5** in methylene chloride shows two prominent bands at 267.5 and 372.0 nm and two smaller bands at 217.0 and 466.0 nm.



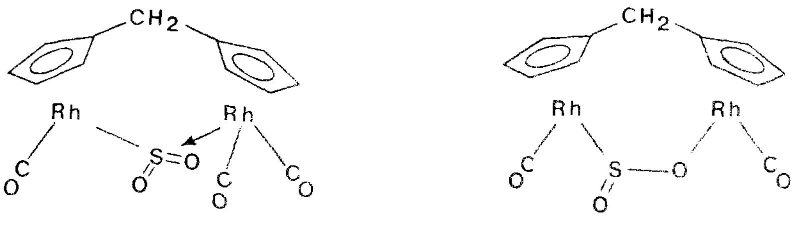
(**5**)

The light orange band yielded a small quantity of an orange oil, **4**. The IR spectrum of this compound is nearly identical to that of **5** except that there is a new terminal carbonyl band at 1976 cm^{-1}. The two higher energy terminal carbonyl bands are of about equal intensity. The ^1H NMR spectrum of this compound has a complex set of resonances in the ring proton region and a singlet for the CH_2. The electronic spectrum of this compound has a strong band at 336.0 nm and a weak band at 449.5 nm. There is evidence for a shoulder at 374.0 nm.

Thermolysis of **4** in refluxing xylene for 2 h gives **5** as the sole product. It is possible that **4** is a previously unobserved intermediate in the formation of μ-SO_2 rhodium complexes. To test this possibility, we have repeated the synthesis of $[CpRh(CO)]_2$-μ-SO_2 described by Herrmann et al., in an effort to isolate and identify a product analogous to **4**. Careful workup of this reaction yielded no evidence for such a species.

The ^1H NMR spectra of compound **4** requires that the compound be asymmetric with free rotation, or at least free torsional twisting, about the CH_2 group. The IR spectrum is consistent with the presence of a bridging SO_2. The chemical evidence from thermolysis shows that **4** cleanly transforms into **5** upon heating. We believe that it is likely that **4** is an intermediate product in SO_2 insertion (Fig. 1a) in which an unsupported, bridging SO_2 has been formed by formal insertion into the Rh–Rh bond, accompanied by slippage of the bridging carbonyl to a terminal position. In this species, one rhodium is acting as a Lewis base and is bound to the SO_2 in a dative bond. Loss of a carbon monoxide from this species would result in reformation of the Rh–Rh bond as found in **5**. Although the infrared spectral evidence appears to support a bridging SO_2, we cannot rule out the isomeric structure (Fig. 1b) in which an Rh–S(O)–O–Rh bridge couples the metals. This bridging mode has been observed by Mingos and his coworkers in $[Rh_2Cl(SO_2)_2(PPh_3)_4]_2(SO_4)$ [6].

By analogy with our syntheses of several metal carbonyl derivatives of the CH_2Cp_2 ligand, reaction of $CH_2(CpTl)_2$ with $[ClRh(ene)_2]_2$ in refluxing benzene gives $CH_2[CpRh(ene)_2]_2$ (3) in excellent yield. The ^1H NMR spectrum of this compound is similar to that of its mononuclear analog with two broad resonances



(a) (b)

Fig. 1. Possible structures of IV.

being observed for the ethylene ligands [7]. Cramer and Mrowca [7] attribute these resonances in the spectrum of CpRh(ene)$_2$ to the slow rotation of the ethylene ligands which does not average the environments of the "inner" and "outer" hydrogens (Fig. 2). The simple AA′BB′ pattern of the ring protons and the singlet resonance for the CH$_2$ in **3** indicate that the molecule has considerable rotational freedom in solution.

When SO$_2$ was bubbled through a benzene solution of **3**, an immediate color change from yellow to red occurred. When the reaction was judged to be complete, the reaction mixture was stripped and chromatographed as described previously, except that the bright red product, **6**, required acetone for elution. In some large scale preparations **6** precipitated from the reaction mixture in almost analytical purity. Analysis of this compound (C, H and S) revealed that two sulfur dioxide units have been incorporated into the molecule, while two ethylene groups have been lost. Two attempts to obtain a chemical ionization mass spectra of this compound were unsuccessful apparently due to its extensive decomposition under the solid inlet conditions. Attempts to prepare a derivative with only one SO$_2$ unit by addition of a stoichiometric amount of SO$_2$ have been uniformly unsuccessful.

The ^{1}H NMR spectrum of **6** was very similar to that of **5** discussed above except that a broad resonance attributable to freely rotating ethylene ligands was observed. As in the case of **5**, the observation of four well-resolved ring resonances and an AB quartet for the CH$_2$ group indicates that the solution conformation of the cyclopentadienyl portion of the molecule is relatively fixed. Cramer and Mrowca [7] reported a very similar ethylene resonance for CpRh(ene)$_2$ at 108°C which suggests

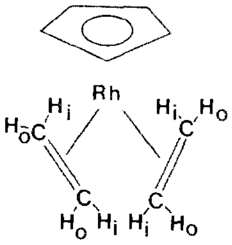


Fig. 2. Molecular geometry of CpRh(ene)$_2$ complexes. The different magnetic environments of the "inner" and "outer" ethylene protons give rise to the two resonances observed for the ethylene protons at room temperature.

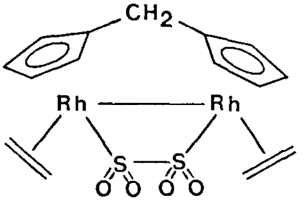


Fig. 3. Possible structure for compound VI.

that the energy barrier for ethylene rotation in **6** must be lower than it is for CpRh(ene)$_2$. The IR spectrum of **6** has bands at 1219 and 1051 cm^{-1} which are in the typical range for metal bridging SO$_2$ groups, but are quite different from the absorbances for planar terminal SO$_2$ species (1258 and 1105–1093 cm^{-1}) which were reported by Cramer. The electronic spectrum of **6** is very similar to that of **5** indicating that the Rh–Rh bond is intact.

The spectral and analytical data summarized above are entirely consistent with the proposed structure of **6** which is presented in Fig. 3. The framework of this species is analogous to that of **5** except that the metals are bridged by a dithionite, S_2O_4, group. Wojcicki and his coworkers [9] have reported the synthesis of the analogous dithionite compounds $[CpFe(CO)_2]_2S_2O_4$, $[Mn(CO)_2S_2O_4$, and $[Re(CO)_5]_2S_2O_4$, and recently Kubas, et al. [10], have reported the synthesis of $[(C_5Me_5)M(CO)_3]_2S_2O_4$, where M = Mo and W. The infrared absorptions of the dithionite groups in these compounds are in the same regions (1224–1207 and 1040–1027 cm^{-1}) as those of **6**. Further, it might be expected that a bridging dithionite group might cause **6** to assume a relatively fixed conformation in solution as required by the NMR spectrum.

Solutions of **6** are unstable to decomposition giving ill-defined solids, and all attempts to prepare crystals suitable for X-ray crystallography have been unsuccessful. Kubas et al. [10], have also noted that dithionite compounds appear to be unstable toward auto-redox reactions.

The formation of **6** from **3** may proceed through a μ-SO$_2$ intermediate which inserts a second SO$_2$ to give the observed dithionite product. A similar reaction has been observed by Wojcicki and his coworkers for the formation of $[CpFe(CO)_2]_2$-μ-S_2O_4 from $[CpFe(CO)_2]_2$-μ-SO$_2$. We believe that our failure to isolate a simple μ-SO$_2$ derivative of **3** reflects the instability of this species under the conditions of the work-up.

Efforts in this laboratory are now being directed toward development of techniques to grow suitable crystals of **6**, and toward the examination of other aspects of the chemistry of **3**.

Experimental

$CH_2[CpRh(CO)]_2$-μ-CO (**2**) and $CH_2(CpTl)_2$ were prepared as previously reported [1,2]. $[ClRh(ene)_2]_2$ was prepared from RhCl$_3$ hydrate by literature procedures. Sulfur dioxide was purchased from Columbia Organic Chemical Company, Inc. and used as received. Benzene was dried over sodium and distilled under nitrogen. All reactions were conducted after a nitrogen purge of the reaction vessels, but all compounds are air-stable. Both compounds **5** and **6** decompose at room temperature and should be stored in the cold where they are stable indefinitely.

^{1}H NMR spectra were recorded on a Varian FT-80A NMR Spectrometer operating at 79.542 MHz and are referenced to tetramethylsilane. Infrared spectra were recorded on a Perkin–Elmer 1750 FT-IR Spectrometer. Electronic spectra were recorded on a Beckman DU-7 Spectrophotometer. Elemental analyses were conducted by Galbraith Laboratory, Inc. of Knoxville, TN.

Reaction of 2 with SO_2

Into a 100 ml round bottom flask equipped with a spin bar was placed 0.2 g (0.4 mmol) **2**. After purging the flask with nitrogen, 50 ml of dry benzene was added, and the flask was fitted with a septum. Sulfur dioxide was bubbled through the solution through a teflon cannula for about 2 h, at which time a considerable amount of a red precipitate had formed. The reaction was halted and the red precipitate was collected by filtration. This solid was shown to be almost analytically pure **5**. Recorded 0.10 g, 50% yield. Found: C, 33.64; H, 2.22. $C_{13}H_{10}O_4Rh_2S$ calc: C, 33.33; H, 2.14%. Color change but no melting up to 250°C. IR (CH_2Cl_2): 2046s [carbonyl], 2013w [carbonyl], 1351w, 1216m [SO_2], 1067m [SO_2], 819m. NMR ($CDCl_3$): 6.18 (2H, s, Cp), 5.86 (2H, s, Cp), 5.76 (2H, s, Cp), 4.81 (2H, s, Cp), 3.93 (1H, AB quartet, J_{AB} 14.7 Hz, CH_2), 3.77 (1H, AB quartet, J_{AB} 14.7 Hz, CH_2). UV-VIS (CH_2Cl_2): 267.5 (14,500), 317.0 (6,624), 372.0 (11,140), 466 (1,958). Chemical ionization MS: $M^+ = 468$.

The benzene filtrate was stripped to give a small amount of a red oil which was taken up in methylene chloride and chromatographed on alumina. In some preparations a small amount of **2** was removed with methylene chloride. Elution with 3/1 methylene chloride/acetone permitted an orange band to be cleanly eluted from the column, followed by a scarlet band. After solvent removal, the orange band yielded an orange oil, **4**, and the scarlet band gave a small additional sample of **5**. The sample of **4** was insufficient for analysis, but spectral measurements were conducted. IR (CH_2Cl_2); 2042s [carbonyl], 2014s [carbonyl], 1976s [carbonyl], 1211m [SO_2], 1064m, [SO_2], 809m. NMR: ($CDCl_3$) 5.79 (1H, s, Cp), 5.62 (1H, s, Cp), 5.48 (3H, s, Cp), 5.38 (3H, s, Cp), 3.50 (2H, s, CH_2). UV-VIS (CH_2Cl_2): 288.5 sh (11,000), 336.0 (9,900), 374.0 sh (5,600), 449.5 (1,400). *Note*: extinction coefficients are approximate.

Preparation of $CH_2[CpRh(ene)_2]_2$ (3)

Into a 100 ml round bottom flask equipped with a spin bar were placed 2.7 g (6.9 mmol) $[ClRh(ene)_2]_2$ and 3.8 g (6.9 mmol) $CH_2(CpTl)_2$. The flask was evacuated and back flushed with nitrogen. About 50 ml of dry benzene was added to the flask against a nitrogen counterflow. A reflux condenser was fitted to the flask and the mixture refluxed under nitrogen for 5 h. The reaction mixture was filtered through Celite using a glass fritted filter to give a brown solution which was stripped using a rotary evaporator. The resulting brown oil was chromatographed on alumina using petroleum ether containing about 5% THF. A yellow band was eluted. After solvent removal, 1.76 g of **3** as a yellow solid was obtained; 55% Yield. Found: C, 49.64; H, 5.75. $C_{19}H_{26}Rh_2$ calc: C, 49.57; H, 5.65%. Mp. 103.0–104.5°C. IR (CH_2Cl_2): 30.17m, 2997m, 2962m, 2931m, 2899s, 1505s [ethylene], 1496s, 1474m, 1199s, 968s, 865m, 809s. NMR: ($CDCl_3$) 5.24 (4H, m, Cp), 5.05 (4H, m, Cp), 2.87 (2H, s, CH_2).

2.62 (8H, br m, ethylene outer), 1.19 (8H, br m, ethylene inner). UV-VIS (CH_2Cl_2): 279.0 sh (7,296).

Reaction of 3 with SO_2

3 was reacted with SO_2 exactly as described for **2**, above. In several cases it was possible to recover **6** as a red precipitate directly from the reaction. **6** an also be recovered by chromatography of the reaction mixture on alumina using acetone as an elutant. Found: C, 33.89; H, 3.40; S, 12.52. $C_{15}H_{18}O_4Rh_2S_2$ calc: C, 33.83; H, 3.38; S, 12.03%. Color change, but no melting up to 250°C. IR (CH_2Cl_2); 3049w, 3007w, 2978w, 2907w, 1219m [SO_2], 1180m, 1051s, [SO_2], 817m. NMR (DMSO-d_γ): 6.69 (2H, s, Cp), 6.00 (2H, s, Cp), 4.90 (2H, s, Cp), 4.78 (2H, s, Cp), 3.83 (1H, AB quartet, J_{AB} 14.46 Hz, CH_2), 3.30 (1H, AB quartet, J_{AB} 14.46 Hz, CH_2), 2.52 (8H, br s, ethylene). UV-VIS (CH_2Cl_2): 268.5 sh (13,260), 368.5 (7,300), 489.5 (2,630).

Acknowledgements

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