Journal of Organometallic Chemistry, 293 (1985) C15—C18
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

AN "ADDUCT" BETWEEN $CpRh(S_2C_2Z_2)$ AND $ZC{\equiv}CZ$ (Z = $COOCH_3$) AS AN INTERMEDIATE IN $CpRh^I$-CATALYZED SYNTHESIS OF TETRAMETHYL-2,3,4,5-THIOPHENETETRACARBOXYLATE FROM ELEMENTAL SULFUR AND $ZC{\equiv}CZ$

MASATSUGU KAJITANI*, TOSHIO SUETSUGU, RYOKO WAKABAYASHI, ATSUSHI IGARASHI, TAKEO AKIYAMA, and AKIRA SUGIMORI

Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioi-cho 7-1, Chiyoda-ku, Tokyo 102 (Japan)

(Received February 15th, 1985; in revised form May 28th, 1985)

Summary

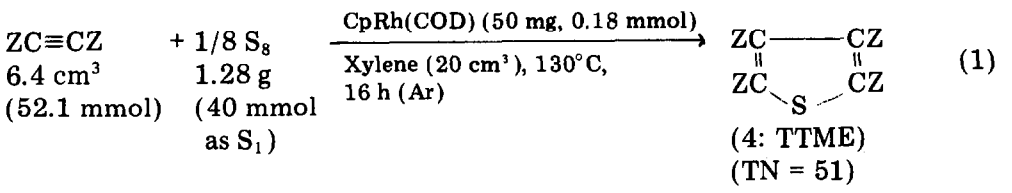
A novel rhodiadithiolene complex, η^5-cyclopentadienyl(1,2-dicarbomethoxy-1,2-ethylenedithiolato-*S,S*)rhodium, $CpRh(S_2C_2Z_2)$, which is formed by the reaction of CpRh(COD) with elemental sulfur (S_8) and $ZC{\equiv}CZ$ (Z = $COOCH_3$; DMAD = dimethyl acetylenedicarboxylate) reacts further with DMAD to form a 1/1 adduct between $CpRh(S_2C_2Z_2)$ and DMAD. This adduct which upon pyrolysis gives 2,3,4,5-tetramethylthiophenetetracarboxylate (TTME) is a key intermediate for the synthesis of TTME in the reaction of S_8 and DMAD catalyzed by CpRh(COD).

A number of novel substituted cyclopentadienylcobalt dithiolene complexes ($RCpCo(S_2C_2X,Y)$) having a variety of substituents R, X, and Y have been prepared by one-pot reactions of $RCpCo(CO)_2$ or RCpCo(COD) (COD = 1,5-cyclooctadiene) with elemental sulfur (S_8) and $XC{\equiv}CY$ [1]. These dithiolene complexes have been detected as intermediates for the synthesis of 2,3,4,5-tetramethylthiophenetetracarboxylate (TTME) in the reaction of S_8 and $ZC{\equiv}CZ$ (Z = $COOCH_3$, DMAD) catalyzed by RCpCo(I) complexes [2].

We report now that the CpRh(COD) complex also catalyzes the formation of TTME in the reaction of DMAD with S_8, and that a novel complex consisting of one mol of the rhodiadithiolene complex, η^5-cyclopentadienyl(1,2-dicarbomethoxy-1,2-ethylenedithiolato-*S,S*)rhodium ($CpRh(S_2C_2Z_2)$, 1) and 1 mol of $ZC{\equiv}CZ$ (Z = $COOCH_3$) is a key intermediate for catalytic synthesis of TTME.

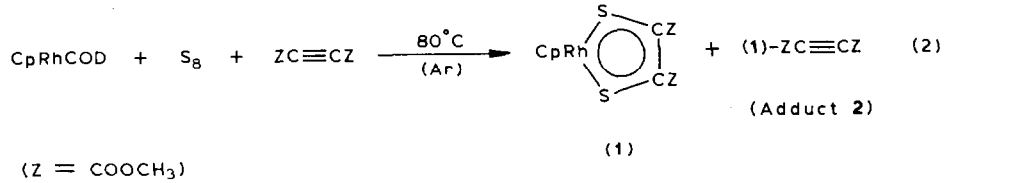
An amount of CpRh(COD) (ca. 1/150 mol based on DMAD) catalysis the formation of TTME from DMAD and elemental sulfur (S_8) in xylene at 130°C (eq. 1).

0022-328X/85/$03.30



Under similar conditions, the catalytic activity of CpRh(COD) (TN = 51) was somewhat higher than that of CpCo(COD) (TN = 47) (turnover number (TN) = amount of TTME/amount of complex).

From the reaction mixture, we isolated two kinds of sulfur-containing rhodium complexes, which are considered to be intermediates in the catalytic reaction for the synthesis of TTME. These two novel rhodium complexes have been prepared on a larger scale and under milder conditions than those of the catalytic reaction, using 10 mmol of CpRh(COD), 12.5 mmol of S_8, and 12 mmol of DMAD at 80°C (eq. 2).



With a shorter reaction time (20 min), 1 was obtained predominantly (11% yield) and only a trace amount of 2 was formed. With a longer reaction time (13 h), the yield of 2 was 39%, while that of 1 was very low (<1%). These air-stable complexes, which have been isolated by control of the reaction time, were identified as dithiolene complex 1 and adduct 2, the elemental analyses and spectroscopic analyses are given below.

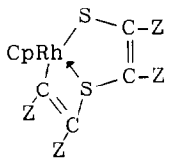
(1) (red brown crystals): m.p. 208—208.5°C; Found: C, 34.4; H, 2.9. $C_{11}H_{11}O_4S_2Rh$ calcd.: C, 35.4; H, 2.9%; IR (KBr): 1732(s), 1691(s), 1521(m), 1430(m), and 1243(s) cm^{-1}; UV-vis (CH_2Cl_2) 283.2 (ϵ 2700) and 487.2 nm (ϵ 1400); ^1H NMR (DMSO-d_6); δ 5.98 (5H, s, Cp) and 3.80 (6H, s, OCH_3) ppm; ^{13}C NMR ($CDCl_3$); δ 165.15(s), 133.97(s), 88.52 (d, J(Rh—C) 4.4 Hz), and 53.43(s) ppm; MS (70 eV) m/e (rel. intensity) 374 (M^+; 56), 343 ($M - OCH_3^+$; 11), 232 ($CpRhS_2^+$; 100), 200 ($CpRhS^+$; 7), and 168 ($CpRh^+$, 34).

(2) (red brown crystals); m.p. 153—159°C (dec.); Found: C, 39,43; H, 3.29; S, 12.34. $C_{17}H_{17}O_8S_2Rh$ calcd. (as a 1/1 adduct); C, 39.55; H, 3.22; S, 12.42%; IR(KBr): 1735(s), 1727(s), 1710(s), 1691(s), 1595(m), 1490(s), 1430(m), 1261(s), and 1213(s) cm^{-1}; UV-vis (CH_2Cl_2): 262.0 (ϵ 14600) and 353.6 nm (ϵ 5200); ^1H NMR (DMSO-d_6): δ 5.79 (5H, s, Cp), 3.75 (3H, s, OCH_3), 3.71 (3H, s, OCH_3), 3.68 (3H, s, OCH_3), and 3.59 (3H, s, OCH_3) ppm; ^{13}C NMR ($CDCl_3$): δ 178.6(s), 169.9(s), 166.5(s), 164.3 (d, J(Rh—C) 27.8 Hz), 162.6(s), 157.9(s), 126.1(s), 107.4(s), 88.5 (d, J(Rh—C) 4.4 Hz), 53.2(s), and 52.4(s) ppm; MS (70 eV); m/e (rel. intensity) 374 (M – ZC≡CZ = $CpRh(S_2C_2Z_2)^+$; 42), 316 ($TTME^+$; 17), 285 (TTME – OCH_3^+; 100), 232 ($CpRhS_2^+$; 61), 200 ($CpRhS^+$; 5), 168 ($CpRh^+$; 22), and 111 (ZC≡CZ – OCH_3^+; 4).

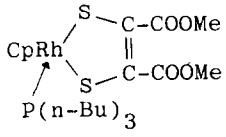
The elemental analysis and ^1H NMR results show that the latter air-stable red-brown complex 2 has a composition corresponding to a 1/1 adduct of complex 1

and DMAD. By ^1H NMR and ^{13}C NMR it was found that adduct **2** has four non-equivalent OCH_3 groups, while the Rh—C carbon signal appears as a doublet at δ 164.3 ppm (J(Rh—C) 27.8 Hz).

The above spectral data suggest that the adduct **2** has the structure shown in Fig. 1. This structure results from insertion of ZC≡CZ into the Rh—S bond of $CpRh(S_2C_2Z_2)$. Adduct **2** reacts with P-n-Bu_3 to form the phosphine adduct complex **5**; during this reaction one molecule of DMAD is eliminated.



(2)



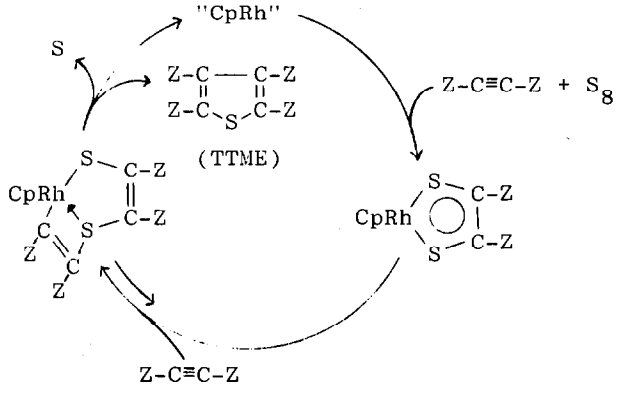
(5)

Fig. 1. Possible structure of the adduct 2 and compound 5.

Such an insertion of alkyne into a metal—S bond is unusual in the chemistry of thiolato complexes, for only a few examples have been reported of alkyne insertion into Rh—S [3], Mo—S [4], and Mn—S [5] bonds.

The pyrolysis results of adduct **2** established that it is a key intermediate for the catalytic formation of TTME, and that **2** is readily pyrolyzed (at ca. 120°C) in the solid state or in mesitylene solution (under reflux) to give the dithiolene complex **1** (56%) and TTME (41%).

The analysis of the relationship between the product yields and reaction times (by means of ^1H NMR) indicates that during pyrolysis TTME is formed directly from adduct **2** and not via the liberated complex **1**.



SCHEME 1. Possible mechanism for the catalytic cycle.

The above results suggest that the mechanism of TTME synthesis catalyzed by CpRh(COD) is that shown in Scheme 1. In TTME synthesis catalyzed by CpCo(COD), TTME formation may proceed mainly via a Diels—Alder type reaction, which results in the formation of 1,4-dithiin. Intermediate **2** in TTME synthesis catalyzed by CpRh(COD) may nevertheless be distinct from that catallyzed by CpCo(COD) with regard to the structure of the adduct. The formation

of TTME from adduct 2 seems to be achieved by reductive elimination of 1,4-dithiin, followed by desulfurization leading to thiophene.

A single-crystal X-ray diffraction study is being carried out by Drs. H. Yamazaki and K. Aoki of the Institute of Physical and Chemical Research (Japan) to determine unambiguously the structure of the adduct.

The authors wish to express their thanks to Professor Doctor Helmut Bönnemann of the Max-Planck-Institut für Kohlenforschung for his helpful information.

References

1 (a) H. Bönnemann, 2nd Intern. Symp. Homogeneous Catal. (ISHC), September 1—3, 1983, Düsseldorf, West Germany; (b) M. Kajitani, A. Igarashi, T. Suetsugu, R. Endo, H. Fujisawa, Y. Yoshida, T. Akiyama, A. Sugimori, and H. Bönnemann, 30th Symp. Organomet. Chem., Kyoto, Japan, November 1—2, 1983, Abstr. A205.

2 (a) H. Bönnemann, W. Brijoux, R. Brinkmann, M. Kajitani, G. Natarajan, and H. Samson, 3rd ISHC, August 30—September 3, 1982, Milano, Italy; (b) M. Kajitani, T. Suetsugu, A. Igarashi, T. Akiyama, A. Sugimori, and H. Bönnemann, 30th Symp. Organomet. Chem., Kyoto, Japan, November 1—2, 1983, Abstr. A206.

3 Y. Wakatsuki, H. Yamazaki, and H. Iwasaki, J. Am. Chem. Soc., 95 (1973) 5781.

4 T.R. Halbert, W.-H. Pan, and E.I. Stiefel, J. Am. Chem. Soc., 105 (1983) 5476.

5 E. Lindner, I.P. Butz, S. Hoehne, W. Hiller, and R. Fawzi, J. Organomet. Chem., 259 (1983) 99.