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Formation of stable cationic (cyclooctadiene)Rhodium(I) complexes containing thiophene ligands

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Abstract

A new series of cationic (cyclooctadiene)Rh^I complexes containing π-bound thiophene ligands has been prepared by allowing the tetrafluoroborate salt of either Rh(COD)(acetone)$_2^+$ or Rh(COD)(methanol)$_2^+$ to react with various thiophene derivatives in $CHCl_3$. The cationic Rh(COD)$^+$ monomer was prepared from the chloro-bridged dimer, [RhCl(COD)]$_2$, by halide abstraction using $AgBF_4$ in either acetone or methanol solvent. Stable 1:1 cationic complexes containing thiophene, 2-methylthiophene, and 2,5-dimethylthiophene were obtained following reaction with Rh(COD)(acetone)$_2^+$, whereas complexes containing benzothiophene and dibenzothiophene complexes were prepared in good yield using Rh(COD)(methanol)$_2^+$.

Key words: Rhodium; Thiopenes; Cyclotadiene

1. Introduction

Studies involving the interaction of thiophenes with small, well-characterized, transition metal complexes provide solution-soluble models by which to examine some of the possible binding modes of thiophenes to the surface of the catalyst in the commercially important process of catalytic hydrodesulfurization (HDS) [1]. Little is known regarding the actual mechanisms involved during the HDS process; important features that are not well defined include the mode of binding of thiophene to the catalyst surface, as well as how the mode of binding correlates with the patterns of reactivity that are observed. Previous studies involving the interactions of thiophenes and various thiophene derivatives with the platinum group metals have provided detailed examples of thiophene coordination involving the S atom [2–8,22] and, more frequently, π-bonding modes involving all of the atoms of the thiophene framework [9–18]. Less frequently observed coordination modes include an η^4 mode in which the thiophene ligand acts as a four electron donor [19–23], as well as an η^2 mode where it acts as a two electron donor [24–27]. In some instances ring opening reactions have also been observed during the process of oxidative-addition reactions following thiophene coordination, as for example, when various thiophenes are reacted with (pentamethylcyclopentadienyl)Rh^I complexes [28–30].

In our investigations involving cationic (cyclooctadiene)Rh^{I+} systems, we found that stable π-bound thiophene complexes could be prepared in good yield by a facile route involving use of the easily prepared chloro-bridged (cyclooctadiene)Rh^I dimer, [RhCl(COD)]$_2$. Cyclooctadiene complexes of the platinum group metals containing, *inter alia*, 2,5-dimethylthiophene and 2,3,4,5-tetramethylthiophene have been reported, however, the syntheses of Rh(COD)$^+$ complexes containing thiophenes others than those mentioned above have, to date, been unsuccessful [11]. We have extended the scope of this earlier work, and in this paper describe the synthesis of a new series of cationic Rh(COD)$^+$ complexes containing thiophene (T), 2-methylthiophene (2-MT), 2,5-dimethylthiophene (2,5-DMT), benzothiophene (BT), and dibenzothiophene (DBT) involving improved synthetic procedures.

2. Results and discussion

The use of $AgBF_4$ in acetone or methanol to remove the bridging halide ligands from [RhCl(COD)]$_2$ affords

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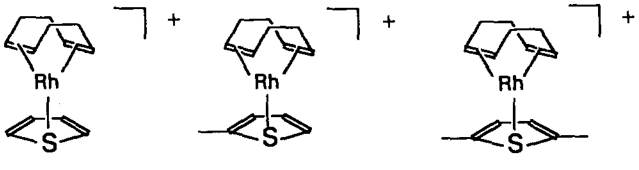
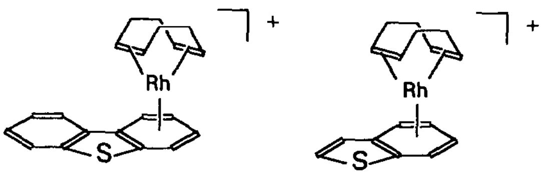
a convenient way of generating cationic complexes having the general formula Rh(COD)(solvent)$_2^+$ containing two easily displaced molecules of solvent. The ^{1}H and ^{13}C data show the presence of coordinated solvent indicating that the chloro-bridged dimer has been cleaved to produce two equivalents of the Rh(COD)(solvent)$_2^+$ monomer. Redissolving the acetone complex in $CHCl_3$ along with a stoichiometric amount of the appropriate thiophenic ligand and allowing the mixture to reflux for 24 h affords, in all cases, the desired product. We find in each instance that thiophene (**1**), 2-methylthiophene (**2**), and 2,5- dimethylthiophene (**3**) completely displace acetone from the coordination sphere of the Rh(COD)$^+$ cation. The chemical shifts observed in the ^{1}H and ^{13}C spectra indicate that these compounds possess π-bound thiophene ligands, consistent with structures shown in Fig. 1.

With benzothiophene and dibenzothiophene, the presence of two or more available ring sites affords the opportunity for the transition metal to coordinate either to the five-membered ring containing the S-atom, or to the arene ring containing the six C-atoms. Attempts to grow crystals suitable for an X-ray crystal structure determination for any of these complexes were unsuccessful. However, based on the pattern of chemical shifts associated with cationic Rh(COD)$^+$ complexes of both benzothiophene and dibenzothiophene, it appears that in both cases coordination involves the six carbon atoms of the benzene ring. Similar results have been observed by others, and in no instances have the structures of complexes containing a transition metal coordinated to the five-membered ring in an η^5 manner been reported for either benzothiophene or dibenzothiophene. A plausible explanation may be found in CNDO molecular orbital calculations which indicate that the regions of highest electron density are located on the outer 4 atoms of the benzene rings and the sulfur, thus favoring coordination to the benzene rings in these molecules [31]. Although coordination to the S-atom has been established in a number of cases, these complexes are frequently quite labile with downfield shifts observed in the ^{13}C NMR spectra. For benzothiophene and dibenzothiophene complexes **4** and **5**, respectively, the strong upfield shifts observed in the NMR spectra of both suggests that complexes having the structures shown in Fig. 2 are being formed.



(1) (2) (3)

Fig. 1. Structures proposed for the complexes obtained following the reaction of [Rh(COD)(acetone)$_2$][BF$_4$] with thiophene (1), 2-methylthiophene (2) and 2,5-dimethylthiophene (3).



(4) (5)

Fig. 2. Structures proposed for the complexes obtained following the reaction of [Rh(COD)(methanol)$_2$][BF$_4$] with benzothiophene (4), dibenzothiophene (5).

Owing to the presence of two benzene rings in dibenzothiophene, however, it should be possible to prepare complexes in which two transition metals are coordinated. Indeed, examples of complexes containing both a 1:1 and 2:1 metal:ligand stoichiometry are known. A crystal structure of the 2:1 adduct, (CpRu)$_2$(DBT), shows that the two RuCp fragments coordinate to the six-membered rings above and below the plane of the dibenzothiophene molecule [16]. With the cationic [Rh(COD)(methanol)$_2$][BF$_4$] complex used in these investigations, however, we find that only complexes bearing a 1:1 metal:ligand stoichiometry were obtained when the Rh(COD)(methanol)$_2^+$ cation was allowed to react with dibenzothiophene, even when a two-fold excess of the transition metal was used. The reasons underlying the preferential formation of a complex bearing a 1:1 metal ligand stoichiometry in the reaction of Rh(COD)$^+$ with dibenzothiophene, even when allowed to react with a two-fold excess of the metal, however, remain uncertain. It may be that binding of the metal to the dibenzothiophene ligand occurs in a stepwise fashion, and that coordination to one of the benzene rings deactivates the other arene ring with respect to coordination of a second transition metal center. Alternately, it may be that complexes possessing a 2:1 metal ligand stoichiometry are obtained only when a very large excess of the transition metal is used, or perhaps under more forcing reaction conditions than those used in the syntheses described here.

Cationic [(cyclooctadiene)Rh^I]$^+$ complexes containing 2,5-dimethylthiophene and 2,3,4,5-tetramethylthiophene have been previously described; however, the preparation of Rh(COD)$^+$ complexes containing other thiophene ligands in acetone solution were reported to be unsuccessful [11]. Increasing the number of methyl groups on the thiophene ring increases the Lewis basicity of the thiophene. As a result, both 2,5-dimethyl thiophene and 2,3,4,5-tetramethylthiophene are able to displace acetone from the coordination sphere of the transition metal, even when the reaction is carried out in acetone solvent. Isolating the cationic Rh(COD)(acetone)$_2^+$ complex as the tetrafluoroborate salt and conducting the reaction in a non-coordinating solvent such as $CHCl_3$, however, constitutes an improved synthetic route for the preparation of complexes containing thiophene ligands. Problems associated with competition between coordination of the solvent and the thiophene are obviated, thus enabling the reaction to take place in the presence of a stoichiometric amount of ligand. The cationic Rh(COD)(acetone)$_2^+$ complex can also be used in reactions involving benzothiophene and dibenzothiophene, although improved yields of products possessing these ligands are obtained if these complexes are prepared in methanol using the Rh(COD)(methanol)$_2^+$ cation. Conversely, use of the Rh(COD)(methanol)$_2^+$ complex proved to be less effective in reactions involving thiophene, 2-methylthiophene and 2,5-dimethylthiophene, giving lower product yields compared with the use of Rh(COD)(acetone)$_2^+$ in $CHCl_3$ solvent. The reasons underlying these differences are uncertain. Repeating these reactions using the cationic Rh(COD)(tetrahydrofuran)$_2^+$ complex in THF proved entirely unsuccessful.

3. Experimental section

All manipulations were carried out using standard Schlenk techniques under oxygen-free nitrogen or an inert atmosphere glove box. Solvents were distilled from suitable drying agents prior to use. Thiophene, 2-methylthiophene, 2,5-dimethylthiophene, benzothiophene, and dibenzothiophene were purchased (Aldrich), and used as received. Rhodium chloride hydrate was obtained from Engelhard. NMR spectra were recorded on a Bruker AM-250 spectrometer using $CDCl_3$ solvent dried over molecular sieves and referenced to TMS. Elemental analyses were performed by Texas Analytical Laboratories, Inc.

3.1. *Preparation of starting materials*

The chloro-bridged dimer, $[(COD)RhCl]_2$, was prepared according to the literature procedure [32]. Rh(COD)(acetone)$_2^+$ was prepared as previously described using $AgBF_4$ and isolated as the tetrafluoroborate salt [33].

Reactions involving Rh(COD)(methanol)$_2^+$ were carried out in methanol solvent. This complex was prepared by dissolving 100 mg (0.20 mmol) of $[(COD)RhCl]_2$ in 10.0 ml of freshly distilled methanol to which was then added a slight excess (89 mg 0.45 mmol) of $AgBF_4$. The reaction appeared to be instantaneous, as evidenced by the immediate formation of a precipitate of AgCl, but was allowed to continue to stir at room temperature for 30 min prior to being used in subsequent reactions. ^{1}H and ^{13}C data for this complex are consistent with the presence of two coordinated molecules of methanol and one COD ligand. ^{1}H NMR ($CDCl_3$)δ, 4.32(b, 4H), 2.44(s, 8H) (COD); 3.97(s, 6H), 3.26(s, 2H) (CH_3OH). ^{13C} NMR ($CDCl_3$)δ, 78.4, 30.8 (COD); 53.45 (CH_3OH).

3.2. *[(η^5-thiophene)(cyclooctadiene)Rh^I][BF$_4$]*

To a solution of 0.40 mmol (167 mg) of $[Rh(COD)(acetone)_2][BF_4]$ in 10.0 ml of $CHCl_3$ was added 1.0 ml (1.05 g, 125 mmol) of thiophene. The mixture was refluxed for 24 h during which time the solution color changed from light yellow to a dark brown. The solvent fraction was separated and transferred to a second Schlenk flask where the $CHCl_3$ was removed under reduced pressure. The product, in the form of a brown powder, was isolated in 61% yield. Anal. Calc.: C 37.50, H 4.16; Found: C 37.41, H 4.14%. ^{1}H NMR ($CDCl_3$)δ, 6.48(m, 2H), 4.98(m, 2H) (T); 4.57(b, 4H), 2.52(s, 8H) (COD). ^{13}C NMR ($CDCl_3$)δ, 108.0, 93.6 (T); 81.0, 31.2 (COD).

3.3. *[(η^5-2-methylthiophene)(cyclooctadiene)Rh^I][BF$_4$]*

0.5 ml (0.51 g, 52 mmol) of 2-methylthiophene was added to 0.40 mmol (167 mg) of the freshly prepared RhCOD(acetone)$_2^+$ cation and the mixture refluxed for 24 h in 10.0 ml of $CHCl_3$. The solvent fraction was separated and transferred to a new Schlenk flask where the $CHCl_3$ was removed under reduced pressure. The product was isolated in 78% yield as a brown powder. Anal. Calc.: C 39.19, H 4.52; Found: C 39.31, H 4.59%. ^{1}H NMR ($CDCl_3$)δ, 7.02(m, 1H) 6.27(m, 1H), 4.87(m, 1H), 1.84(m, 3H) (2-MT); 4.62(b, 4H), 2.44(s, 8H) (COD). ^{13}C NMR ($CDCl_3$)δ, 112.0, 108.4, 107.4, 91.6, 13.3 (2-MT); 81.8, 32.1 (COD).

3.4. *[(η^5-2,5-dimethylthiophene)(cyclooctadiene)Rh^I][BF$_4$]*

In this preparation, the reaction was carried out by a modification of the literature procedure [11]. 0.5 ml (0.49 g, 44 mmol) of 2,5-dimethylthiophene was added to 0.40 mmol (167 mg) of $[Rh(COD)(acetone)_2][BF_4]$ dissolved in 10.0 ml of $CHCl_3$. The reaction mixture was refluxed under N_2 for 24 h, although in this case, the reaction appeared to be complete in less than an hour as evidenced by the change in solution color. The solvent fraction was separated and transferred to a second Schlenk flask and was removed under reduced pressure yielding a brown powder in 85% yield. Anal. Calc.: C 40.77, H 4.85; Found: C 40.82, H 4.88%. ^{1}H NMR ($CDCl_3$)δ, 6.04(m, 2H), 1.96(s, 6H) (2,5-DMT); 4.50(b, 4H), 2.16(s, 8H) (COD). ^{13}C NMR ($CDCl_3$)δ, 109.7, 107.3, 13.0 (2,5-DMT); 82.6, 31.1 (COD).

3.5. *[(η^6-benzothiophene)(cyclooctadiene)Rh^{I}][BF_4]*

A stoichiometric amount of benzothiophene (54 mg, 0.40 mmol) was weighed and transferred to a solution containing 0.40 mmol of [Rh(COD)(methanol)$_2$][BF_4] generated *in situ* using 100 mg (0.20 mmol) of [Rh(COD)Cl]$_2$ in 10.00 ml of methanol as described above. The solution was refluxed under N_2 for 24 h during which time the solution color changed from yellow to dark brown. The reaction mixture was filtered to remove the AgCl precipitate and the solvent was removed under reduced pressure. The product was isolated as a yellow powder in 71% yield based on the amount of [RhCl(COD)]$_2$ dimer used. Anal. Calc.: C 44.44, H 4.16; Found: C 43.98, H 4.16%. ^{1}H NMR ($CDCl_3$)δ, 7.95(m, 1H), 7.80(m, 1H), 7.48(m, 1H), 7.25(m, 1H), 6.90(m, 1H), 6.70(m, 1H) (BT); 4.60(b, 4H), 2.41(s, 8H) (COD). ^{13}C NMR ($CDCl_3$)δ, 136.3, 122.3, 102.5, 101.5, 97.3, 97.21, 81.3, 81.2 (BT); 78.8, 31.8 (COD).

3.6. *[(η^6-dibenzothiophene)(cyclooctadiene)Rh^{I}][BF_4]*

74 mg (0.40 mmol) of dibenzothiophene was weighed and transferred to a Schlenk tube containing a stoichiometric amount (0.40 mmol) of the Rh(COD)(methanol)$_2^+$ cation in 10.00 ml of methanol, prepared as described above in the synthesis of the cationic Rh(COD)$^+$ complex containing benzothiophene. The reaction mixture was refluxed for 24 h under an atomosphere of N_2 after which the reaction mixture was filtered to remove the AgCl precipitate. The solvent was removed under reduced pressure and the product, in the form of a yellow powder, was isolated in 70% yield based on the amount of the [RhCl(COD)]$_2$ dimer used. This reaction was repeated with a two-fold excess (80 mmol) of the [Rh(COD)(methanol)$_2$][BF_4] complex. Identical ^{1}H and ^{13}C spectra were obtained indicating that the same product bearing a 1:1 metal:ligand stoichiometry was obtained. Anal. Calc.: C 49.79, H 4.14; Found: C 49.43, H 4.21%. ^{1}H NMR ($CDCl_3$)δ, 8.25(m, 1H) 8.09(m, 1H), 7.70(m, 1H), 7.50(m, 1H), 7.40(m, 1H), 7.25(m, 1H), 7.00(m, 1H), 6.87(m, 1H) (DBT); 4.03(b, 4H), 2.05(s, 8H) (COD). ^{13}C NMR ($CDCl_3$)δ, 130.5, 126.6 124.3, 122.5, 120.6, 117.0, 102.6, 101.1, 98.6, 96.7, 82.2, 81.6 (DBT); 81.9, 31.2 (COD).

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