Organometallics **2003,** *22,* 1585−1587 1585

Reactivity of [Ru$_3$(CO)$_{12}$] with Dibenzothiophene, Methylbenzothiophene, and Methyldibenzothiophene

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Received January 29, 2003

Summary: The reaction of dibenzothiophene (DBT) with [Ru$_3$(CO)$_{12}$] in heptane affords the dinuclear complex [Ru$_2$(C$_{12}$H$_8$)(μ-CO)(CO)$_5$], derived from a double C−S bond activation−desulfurization process. The reaction of this complex with H$_2$ under very mild conditions leads to the release of biphenyl.

In recent years the study of hydrodesulfurization (HDS) has been the target of high interest because of the need to improve the process used to remove sulfur from organosulfur molecules present in petroleum feedstocks.[1] The commercial HDS process uses a cobalt- or nickel-doped molybdenum sulfide catalyst supported on alumina; however, the highest activity has been shown by platinum metals, such as Ru, Os, Rh, Ir, Pd, and Pt, in model reactor studies, but they are not used due to their increased expense.[2] Thus, a variety of organometallic compounds contaning these metals has been studied in homogeneous HDS reactions with thiophenes.[3] There are comparatively few reports of C−S bond cleavage in complexes containing multiple metal centers.[4−6] Although the use of metal carbonyl clusters in HDS modeling reactions has been known for more than 40 years,[7] to the best of our knowledge, even after all this time, no cluster system has been reported to ring open either one or two C−S bonds in dibenzothiophene to give a well-characterized complex. Though very few reactions have been documented for the interaction of DBT with a cluster, Suzuki[8] et al. have found that the cluster [(Cp*Ru)$_3$(μ-H)$_3$(μ$_3$-H)$_2$] is capable of reacting with DBT in toluene at 110 °C, thus yielding biphenyl and [(Cp*Ru)$_3$(μ-H)$_3$(μ$_3$-S)], the mechanistic details of this reaction still being unclear. Angelici et al. have found that DBT can interact with [Co$_4$(CO)$_{12}$] to give η^6-DBT complexes,[9] which can further react with [Cr(CO)$_3$(NCCH$_3$)$_3$] to produce the desulfurized species [(η^6-benzene)Co$_4$(CO)$_9$]. Once again, the mechanistic details for this reaction have not been disclosed, and no other intermediates have been isolated; moreover, the same group found that DBT can photochemically react with [Re$_2$(CO)$_{10}$] to produce the compound [Re$_2$(CO)$_8$(μ-C$_{12}$H$_7$S)(μ-H)], derived from a C−H activation.[10] Arce et al. have found that [Os$_3$(CO)$_{10}$(NCCH$_3$)$_2$] can react with DBT to yield a C−H activation product of the type [Os$_3$(μ-H)$_2$(CO)$_9$(μ$_3$-C$_{12}$H$_6$S)].[6c]

We report here that [Ru$_3$(CO)$_{12}$] breaks two C−S bonds of DBT to give a sulfur-free product having a coordinated biphenylic moiety with the formulation [Ru$_2$(C$_{12}$H$_8$)(μ-CO)(CO)$_5$] (**1**), which we believe is the first structurally characterized complex of such a reaction; moreover, this compound is readily cleaved by hydrogen gas to give biphenyl.

The ruthenium cluster [Ru$_3$(CO)$_{12}$] reacts with an excess of DBT (refluxing heptane) to yield **1** (10%)[11] (Scheme 1, eq 1). The molecular structure of **1** was determined by X-ray diffraction (Figure 1),[12] thereby confirming that the dibenzothiophene molecule was activated to yield a biphenyl moiety coordinated to two different ruthenium centers, one of which was coordinated in an η^2 manner within a five-membered ruthenacycle system and the second of which is above the plane of both phenyl rings η^4 coordinated to the carbons of the ruthenacycle system. Both rutheniums are bridged by a metal−metal bond and a bridging carbonyl. This complex was also characterized by NMR, IR, MS-EI, and elemental analysis determinations.[13]

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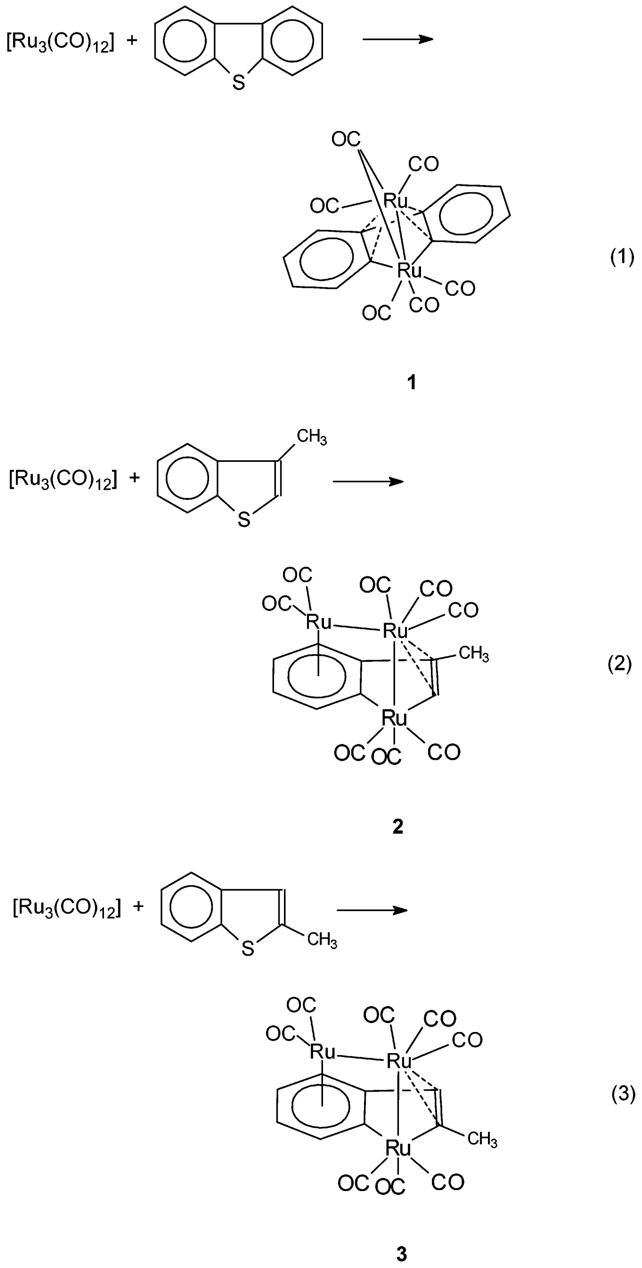
(11) [Ru$_3$(CO)$_{12}$] (0.209 g, 0.326 mmol) and DBT (0.187 g, 1.017 mmol) were reacted in refluxing heptane (15 mL) under argon for 7 days; after this time the black mixture was concentrated to dryness, suspended in hexane, and prepurified on a silica gel column with hexane to hexane/acetone (5/3 v/v) as eluent. The fraction eluted with 5/3 hexane/acetone was collected and repurified on a silica gel TLC plate, using the same order of eluents. The third band was separated, extracted with acetone, concentrated to dryness, and dried (4 h, 0.001 mmHg) to yield **1** in high purity (0.021 g, 10%).

(12) Crystal data for the X-ray structural determination of **1**: C$_{18}$H$_8$O$_6$Ru$_2$, M_r = 522.38, monoclinic, a = 7.4126(7) Å, b = 29.775(3) Å, c = 8.4638(9) Å, β = 110.262(7)°, V = 1752.4(3) Å^3, T = 293 K, space group $P2_1/c$, Z = 4, Mo Kα (λ = 0.710 73 Å), 3981 reflections measured, 3071 (R_{int} = 5.19%) of which were used in calculations. The final R1 = 8.96% and wR2 = 11.41% (all data).

10.1021/om030069q CCC: $25.00
Publication on Web 03/15/2003

Scheme 1



After a hexane solution of complex **1** was treated with H_2 (25 °C, 1 atm) to release biphenyl (20%, 12 h), the yield was increased to 90% at 6 atm.[14] Complex **1** might represent a missing key intermediate related to the systems reported by Suzuki[8] and Angelici,[9] since we have just demonstrated that such a complex can release biphenyl; however, it can also be envisaged as a potential intermediate to release benzene via C−C bond cleavage. During the synthesis of **1** other byproducts were obtained, all of which produced small amounts in order to be fully characterized.

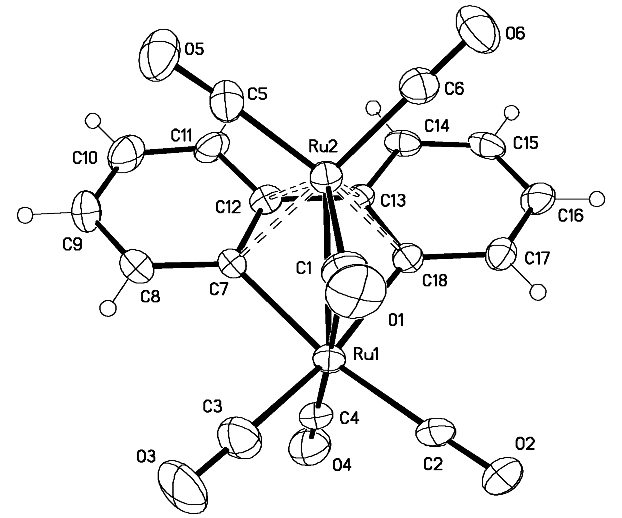


Figure 1. Molecular structure of complex **1** with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)−Ru(2) = 2.6965(9), Ru(1)−C(1) = 2.363(10), Ru(2)−C(1) = 1.936(8); Ru(2)−C(1)−Ru(1) = 77.0(3).

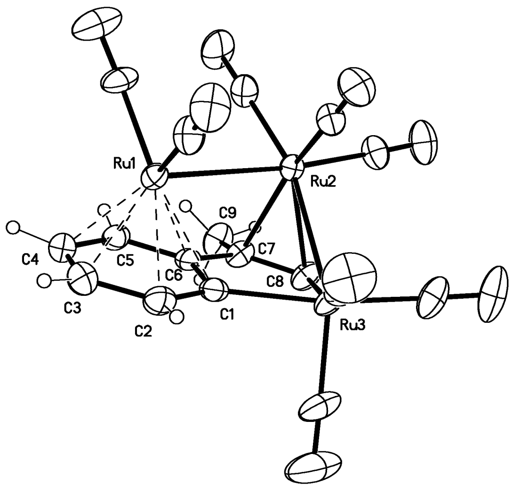


Figure 2. Molecular structure of complex **2** with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)−Ru(2) = 2.9531(10), Ru(2)−Ru(3) = 2.7751(11); Ru(3)−Ru(2)−Ru(1) = 85.19(3).

Despite several attempts, we have not succeeded in isolating any complex derived from the interaction of $[Ru_3(CO)_{12}]$ with 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene; however, methyl derivatives of benzothiophene, such as 3-methyldibenzothiophene (3-MeBT) and 2-methyldibenzothiophene (2-MeBT), do react to produce the ring-opened and desulfurized trinuclear complexes $[Ru_3(C_9H_8)(CO)_8]$ (**2** (27% yield) and **3** (19% yield), respectively)[15] (Scheme 1, eqs 2 and 3).

An X-ray study using a single crystal revealed that product **2** is a trinuclear species (Figure 2).[16] Compounds **2** and **3** are closely related to the ruthenium

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[13] NMR spectra of **1** in acetone-d_6: ^1H δ 7.3 (td, CH, $^3J(H-H)$ = 8 Hz, $^4J(H-H)$ = 1 Hz), 7.7 (td, CH, $^3J(H-H)$ = 8 Hz, $^4J(H-H)$ = 1 Hz), 8.0 (dd, CH, $^3J(H-H)$ = 8 Hz, $^4J(H-H)$ = 1 Hz), 8.6 (dd, CH, $^3J(H-H)$ = 8 Hz, $^4J(H-H)$ = 1 Hz); $^{13}C\{^1H\}$ δ 126.9 (s, CH), 127.3 (s, CH), 131.2 (s, CH), 132.8 (s, C), 138.3 (s, C), 152.6 (s, CH), 205.0 (s, CO), 205.8 (s, CO), 206.3 (s, CO), 209.9 (s, CO). IR spectrum of **1** in hexane: ν (cm^{-1}) 2086 (s), 2032 (vs), 2018 (vs), 1977 (s), 1876 (m). MS-EI: m/z 522. Anal. Calcd for $C_{18}H_8O_6Ru_2$: C, 41.44; H, 1.55. Found: C, 41.40; H, 1.56.

[14] Identified and quantified by GC-MS.

[15] Similarly to **1**, the preparation of both complexes was basically the same: in the case of **2** $[Ru_3(CO)_{12}]$ (0.202 g, 0.316 mmol) and 3-MeBT (0.208 g, 1.40 mmol) were reacted in refluxing heptane (15 mL) for 24 h; in the case of **3** $[Ru_3(CO)_{12}]$ (0.200 g, 0.320 mmol) and 2-MeBT (0.2822 g, 1.904 mmol) were reacted in refluxing heptane (15 mL) for 48 h. This complex was very sensitive to air and sunlight.

species obtained from the reaction of benzothiophene and $[Ru_3(CO)_{12}]$ by Arce et al.[6b] and for the same substrate in the case of iron by Rauchfuss et al.[17] Preliminary data indicate that like **1**, compounds **2** and **3** react with H_2 to release the corresponding sulfur-free organic moiety (isopropylbenzene and *n*-propylbenzene, respectively).

To sum up, we have demonstrated that the trinuclear complex $[Ru_3(CO)_{12}]$ can effectively activate dibenzothiophene under mild conditions to cleave all C−S bonds totally, stabilizing a missing key intermediate, complex **1**, which can further react with hydrogen to release biphenyl. Clearly, this may serve as a structural model for the coordination of thiophenic molecules in heterogeneous HDS catalysts.

Acknowledgment. We thank CONACYT for grant 34322-E and the DGAPA-UNAM grant IN-208101 for support.

Supporting Information Available: Text giving experimental details and tables of complete crystallographic data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030069Q

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(16) Crystal data for the X-ray structural determination of **2**: $C_{17}H_8O_8Ru_3$, $M_r = 643.44$, triclinic, $a = 8.2086(12)$ Å, $b = 8.5820(10)$ Å, $c = 15.9425(18)$ Å, $\alpha = 102.708(9)°$, $\beta = 90.403(11)°$, $\gamma = 117.640(9)°$, $V = 962.8(2)$ Å^3, $T = 293$ K, space group $P\bar{1}$, $Z = 2$, Mo Kα ($\lambda = 0.710\,73$ Å), 5282 reflections measured, 4371 ($R_{int} = 2.17\%$) of which were used in calculations. The final R1 = 6.64% and wR2 = 13.51% (all data).

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