Organometallics **2004,** *23,* 2194−2196

Notes

Reaction of Diaryl Disulfides with RuTp(COD)Cl in *N,N′*-Dimethylformamide: Formation of 2-(Arylmercapto)aryl Mercaptan Complexes

Christina M. Standfest-Hauser,[†] Kurt Mereiter,[‡] Roland Schmid,[†] and
Karl Kirchner*[,†]

*Institute of Applied Synthetic Chemistry and Institute of Chemical Technologies and Analytics,
Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria*

Received December 17, 2003

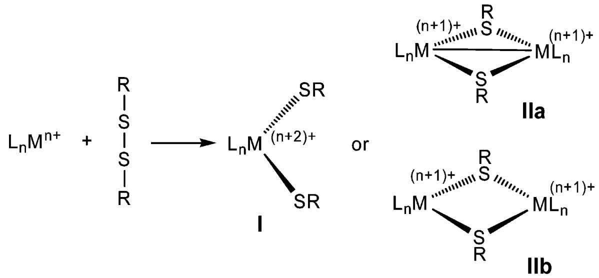
Summary: The reaction of RuTp(COD)Cl with 1 equiv of $RC_6H_4SSC_6H_4R$ (R = H, Me) in boiling DMF affords the complexes $[RuTp(\kappa^2(S,S')\text{-}S{-}C_6H_3R{-}S{-}C_6H_4R)(CO)]$ containing 2-arylmercapto−arylmercaptan and CO ligands. The formation of this unusual product involves decomposition of the solvent DMF with release of the base $HNMe_2$ acting as HCl scavenger. This outcome contrasts sharply with an otherwise similar reaction of disulfides with cationic $[RuCp(CH_3CN)_3]^+$, investigated previously, generating dinuclear Ru(III)-Ru(III) complexes with bridging thiolate ligands.

Introduction

It is still an interesting issue to compare the hydridotris(pyrazolyl)borate anion (Tp)[1,2] with cyclopentadienyl (Cp) as ligands in transition-metal chemistry.[3] On one hand, there are the same charges and number of electrons donated, as well as the facial geometry typically adopted. On the other hand, there are dramatic differences in size and electronic properties. Thus, Tp provides a large steric shielding of the metal center and serves as a reliable spectator ligand. Furthermore, because of the different geometries of the orbitals involved in constructing the complexes, Cp is a π donor, but Tp is a good σ donor. For instance, in the presence of Tp, π ligands such as COD are often substitutionally inert, in contrast to its lability in the neighborhood of Cp. Actually, the substitution of COD in RuTp(COD)Cl needs boiling DMF solutions, while in RuCp(COD)Cl this takes place at ambient temperature. Similarly, π-accepting coligands such as CO are more strongly bound at the RuTp fragment.

In the present contribution we are concerned with thiolate complexes made available through oxidative addition of alkyl or aryl disulfides to transition-metal complexes in low oxidation states. In this way either mononuclear bis-thiolate (**I**) or dinuclear complexes with bridging thiolate ligands of types **IIa** and **IIb** are generated according to Scheme 1.[4] In a recent paper[5] we have investigated the potential of the labile complex $[RuCp(CH_3CN)_3]^+$ in this respect. As a result, we obtained various dinuclear RuCp thiolate complexes of the type **IIa** in high yields.

Scheme 1



So far, RuTp complexes containing thiolate ligands are hardly known.[6,7] As a matter of fact, dinuclear RuTp complexes of type **IIb** have been reported recently to appear as mere side products in extremely low yields, <0.1%.[8] In this context we will react RuTp(COD)Cl with aryl and alkyl disulfides in boiling DMF and report the results.

Experimental Section

General Information. Manipulations were performed under an inert atmosphere of purified argon by using Schlenk

---

* To whom correspondence should be addressed. E-mail: kkirch@mail.zserv.tuwien.ac.at.

[†] Institute of Applied Synthetic Chemistry.

[‡] Institute of Chemical Technologies and Analytics.

(1) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (b) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497. (c) Trofimenko, S. *Scorpionates−The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

(2) Slugovc, C.; Schmid, R.; Kirchner, K. *Coord. Chem. Rev.* **1999**, *185−186*, 109.

(3) Rüba, E.; Simanko, W.; Mereiter, K.; Schmid, R.; Kirchner, K. *Inorg. Chem.* **2000**, *39*, 382.

(4) (a) Liaw, W.-F.; Hsieh, C.-H.; Peng, S.-M.; Lee, G.-H. *Inorg. Chim. Acta* **2002**, *332*, 153. (b) Lee, C.-M.; Lin, G.-Y.; Hsieh, C.-H.; Hu, C.-H.; Lee, G.-H.; Peng, S.-M.; Liaw, W.-F. *J. Chem. Soc., Dalton Trans.* **1999**, 2393. (c) Liaw, W.-F.; Chen, C.-H.; Lee, G.-H.; Peng, S.-M. *Organometallics* **1998**, *17*, 2370. (d) Lang, R. F.; Ju, T. D.; Kiss, G.; Hoff, C. D.; Bryan, J. C.; Kubas, G. J. *Inorg. Chem.* **1994**, *33*, 3899. (e) Haines, R. J.; de Beer, J. A.; Greatrex, R. *J. Organomet. Chem.* **1975**, *85*, 89. (f) Zanella, R.; Ros, R.; Graziani, M. *Inorg. Chem.* **1973**, *12*, 2736. (g) Lam, C. T.; Senoff, C. V. *Can. J. Chem.* **1973**, *51*, 3790. (f) Köpf, H.; Block, B. *Z. Naturforsch.* **1968**, *23b*, 1536.

(5) Becker, E.; Mereiter, K.; Schmid, R.; Kirchner, K. Submitted for publication in *Organometallics*.

(6) Mizobe, Y.; Hosomizu, M.; Hidai, M. *Inorg. Chim. Acta* **1998**, *273*, 238.

(7) Slugovc, C.; Gemel, C.; Shen, J.-Y.; Doberer, D.; Schmid, R.; Kirchner, K.; Mereiter, K. *Monatsh. Chem.* **1999**, *130*, 363.

10.1021/om034375f CCC: $27.50

techniques and/or a glovebox. All chemicals were standard reagent grade and were used without further purification. The solvents were purified according to standard procedures.[9] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. RuTp(COD)Cl (**1**) was prepared according to the literature.[10] ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AVANCE-250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to $SiMe_4$.

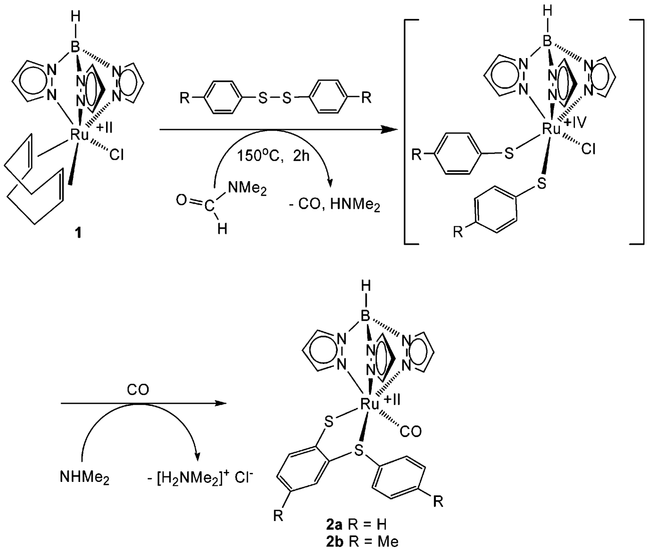
Synthesis. RuTp(κ^2(*S,S′*)-S−C_6H_4−S−C_6H_5)(CO) (2a). A suspension of RuTp(COD)Cl (200 mg, 0.437 mmol) and C_6H_5−S−S−C_6H_5 (95 mg, 0.437 mmol) was stirred in DMF (3 mL) at 150 °C for 3 h. After removal of the solvent under vacuum the crude product was redissolved in CH_2Cl_2 and purified by column chromatography (CH_2Cl_2/neutral Al_2O_3). The first red band was collected, the solvent was evaporated, and the residue was dried under vacuum. Yield: 150 mg (61%). Anal. Calcd for $C_{22}H_{19}BN_6OS_2Ru$: C, 47.23; H, 3.42; N, 15.02. Found: C, 47,12; H, 3.49; N, 15.10. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.81−7.77 (m, 2H), 7.77−7.74 (m, 1H), 7.72−7.63 (m, 4H), 7.53−7.38 (m, 4H), 7.37−7.30 (m, 1H), 7.16−7.07 (m, 2H), 6.93−6.83 (m, 1H), 6.22−6.18 (m, 1H), 6.18−6.14 (m, 1H), 6.14−6.08 (m, 1H). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 201.9 (1C, CO), 144.5, 143.2, 141.0, 137.0, 135.8, 134.9, 131.1, 130.6, 129.9, 129.5, 129.4, 129.1, 129.0, 128.5, 127.5, 127.2, 122.2, 106.3, 106.0 (21C, Ph, Tp). IR (diffuse reflection, cm^{-1}): 1960 (s, ν_{CO}).

RuTp(κ^2(*S,S′*)-S−C_6H_3Me−S−C_6H_4Me)(CO) (2b). This compound was prepared analogously to **2a** using RuTp(COD)-Cl (200 mg, 0.437 mmol) and MeC_6H_4−S−S−C_6H_4Me (107 mg, 0.437 mmol) as the starting materials. Yield: 0.172 g (67%). Anal. Calcd for $C_{24}H_{23}BN_6OS_2Ru$: C, 49.07; H, 3.95; N, 14.30. Found: C, 49.20; H, 4.02; 14.22. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.82 (d, J_{HH} = 1.72 Hz, 1H, Tp), 7.75−7.65 (m, 4H), 7.48−7.34 (m, 4H), 7.31−7.21 (m, 1H), 7.16 (d, J_{HH} = 7.14 Hz, 1H, Ph), 7.01−6.91 (m, 2H), 6.23−6.15 (m, 2H), 6.13 (t, J_{HH} = 1.83 Hz, 1H, Tp), 2.42 (s, 3H, CH_3), 2.21 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 202.2 (1C, CO), 149.5, 144.5, 143.2, 141.0, 140.3, 137.5, 135.7, 134.8, 133.9, 131.9, 131.3, 130.9, 130.3, 130.1, 129.9, 128.6, 106.3, 106.0, 105.9 (21C, Ph, Tp), 21.5 (1C, CH_3), 20.5 (1C, CH_3). IR (diffuse reflection, cm^{-1}): 1964 (s, ν_{CO}).

X-ray Structure Determination for 2a. Well-developed pink prisms of **2a** were obtained by diffusion of diethyl ether into CH_2Cl_2 solutions. X-ray data were collected on a Bruker Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å, 0.3° ω-scan frames covering an entire sphere of the reciprocal space) equipped with a Bruker Kryoflex cooling unit. The data were corrected for absorption.[11] The structure was solved with direct methods using program SHELXS97, and structure refinement on F^2 was carried out with the program SHELXL97.[12] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding on the atoms to which they were bonded.

2a: $C_{22}H_{19}BN_6ORuS_2$, M_r = 559.43, orthorhombic, space group *Pbca* (No. 61), T = 100(2) K, a = 14.422(1) Å, b = 17.366(1) Å, c = 18.593(1) Å, V = 4656.5(3) Å^3, Z = 8, μ = 0.881 mm^{-1}. Of 62 117 reflections collected, 6765 were independent; R_{int} = 0.0192. Final R indices: R1 = 0.022 (all data), wR2 = 0.056 (all data).

Scheme 2



Results and Discussion

Treatment of RuTp(COD)Cl (**1**) with ≥1 equiv of $RC_6H_4SSC_6H_4R$ (R = H, Me) in boiling DMF for 2 h affords after workup the complexes [RuTp(κ^2(*S,S′*)-S−C_6H_3R−S−C_6H_4R)(CO)] (**2a**,**b**) in 61 and 67% isolated yields, respectively (Scheme 2). If only 0.5 equiv of the disulfide was used, the yield of **2** diminished dramatically (<20%). In contrast to the case for the CpRu fragment, in the present case no monodentate or bridging thiolate ligands were obtained; instead, a 2-(arylmercapto)aryl mercaptan and CO ligands resulted. Both **2a** and **2b** are thermally robust pink solids which are air-stable in both solution and the solid state. As another difference, neither aryl diselenides nor alkyl disulfides reacted cleanly with **1**, under otherwise identical conditions, but gave intractable materials. Ultimately, the solvent DMF seems to take actively part in the reaction, since in other solvents with high boiling points such as toluene only complete decomposition occurred.

The products **2a**,**b** were characterized by elemental analysis and ^{1}H and ^{13}C{^{1}H} NMR and IR spectroscopy. The ^{1}H and ^{13}C{^{1}H} solution NMR spectra of **2** give rise to the expected three distinct sets of pyrazol-1-yl resonances, due to the nonequivalency of the pyrazol-1-yl rings. The ^{13}C{^{1}H} NMR spectra exhibit characteristic singlets at 201.9 and 202.2 ppm, respectively, assignable to the CO ligand. In the IR spectrum the CO stretching frequencies are observed at 1960 and 1964 cm^{-1}.

In the absence of detectable intermediates, the underlying reaction mechanism of the formation of **2** is highly speculative, of course. It is clear, however, that the transformation of the aryl disulfides to 2-(arylmercapto)aryl mercaptans is effected in the coordination sphere of the metal center, since heating of aryl disulfides in the absence of **1** or **2** under otherwise identical conditions left the disulfide essentially unchanged.[13] In view of the structure of the product and the relatively clean reaction (>60% isolated yields), it seems likely that the conversion proceeds via the intermediacy of a

---

[8] Shiu, K.-B.; Chen, J.-Y.; Yu, S.-J.; Wang, S.-L.; Liao, F.-L.; Wang, Y.; Lee, G.-H. *J. Organomet. Chem.* **2002**, *648*, 193.

[9] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988.

[10] Gemel, C.; Trimmel, G.; Slugovc, C.; Kremel, S.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 3998.

[11] Bruker AXS, 2001: programs SMART, version 5.626; SAINT, version 6.36A.; SADABS, version 2.05; XPREP, version 6.12. Bruker AXS Inc., Madison, WI.

[12] Sheldrick, G. M. SHELX97: Program System for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1997.

[13] Killops, S. D.; Knox, S. A. R.; Riding, G. H.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1978**, 486.

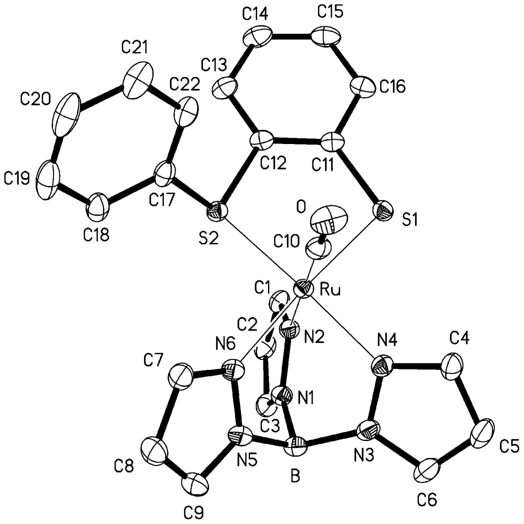


Figure 1. Structural view of RuTp(κ^2(*S,S′*)-S−C_6H_4−S−C_6H_5)(CO) (**2a**) (hydrogen atoms omitted, 50% ellipsoids). Selected bond lengths (Å) and angles (deg): Ru−S(1) = 2.355(1), Ru−S(2) = 2.325(1), Ru−C(10) = 1.845(1), Ru−N(2) = 2.132(1), Ru−N(4) = 2.086(1), Ru−N(6) = 2.123(1); S(1)−Ru−S(2) = 87.6(1), N(2)−Ru−N(4) = 84.3(1), N(4)−Ru−N(6) = 85.2(1), N(2)−Ru−N(6) = 87.5(1).

Ru(IV) bis-thiolate complex of type **I** bearing either Cl and/or CO coligands (Scheme 2), and not that of type **II** with two bridging thiolate ligands, as formed with the related RuCp system. The conversion of the two thiolate ligands to afford the 2-(arylmercapto)aryl mercaptan ligand mediated by the Ru(IV) metal center acting as oxidizing agent has a parallel in the oxidation of the bis-thiolate complex $Cp_2Mo(SPh)_2$ by $AgBF_4$, generating the 2-(phenylmercapto)phenyl mercaptan complex [Cp_2Mo(κ^2(*S,S′*)-S−C_6H_5−S−C_6H_5)]BF_4.[14] It is not clear, however, whether at some stage of this reaction an ortho metalation takes place or whether one arene ring is merely deprotonated by $HNMe_2$. Finally, it is safe to assume that the CO ligand in the product stems from the decomposition of the solvent DMF with the leaving chloride, forming [H_2NMe_2]Cl from released $HNMe_2$ (Scheme 2).

The solid-state structure of **2a** could be resolved by single-crystal X-ray diffraction, confirming the presence of a CO ligand and the κ^2(S,S′) coordination of the 2-(phenylmercapto)phenyl mercaptan ligand (Figure 1). Selected bond distances and angles are given in the caption. The coordination geometry around ruthenium is slightly distorted octahedral. Due to the strong trans influences of CO and the thiolate sulfur atom, the Ru−N(Tp) bond distance trans to CO and the thiolate atom (Ru−N(2) = 2.132(1) Å and Ru−N(6) = 2.123(1) Å) are elongated remarkably relative to that in the cis position (Ru−N(4) = 2.086(1) Å), i.e., the bond that is trans to the sulfur atom of the thioether moiety. The Ru−S bond distances Ru−S(1) and Ru−S(2) are 2.355(1) and 2.325(1) Å, respectively, comparable to those in the RuCp analogue RuCp(κ^2(*S,S′*)-S−C_6H_3Me-S−C_6H_4Me)(CO).[13]

In summary, the peculiar behavior of the starting material RuTp(COD)Cl in the present case can be interpreted as originating from two facts. First, great steric shielding of the metal center by the Tp ligand prevents the formation of binuclear complexes with bridging thiolate ligands, as found in the reaction of cationic [RuCp(CH_3CN)$_3$]$^+$, and second, there is a high affinity of the RuTp fragment for strong π-acceptor ligands, to the extent of decomposing DMF.

Acknowledgment. Financial support by the “Fonds zur Förderung der wissenschaftlichen Forschung” is gratefully acknowledged (Project No. P16600-N11).

Supporting Information Available: Listings of atomic coordinates, anisotropic temperature factors, and all bond lengths and angles for complex **2a**; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034375F

---

(14) Dias, A. R.; Garcia, M. H.; Minas da Piedade, M. F.; Carrondo, M. A. A. F. d. C. T. *J. Organomet. Chem.* **2001**, *632*, 107.