



Note

C–S bond cleavage of 2-methoxythiophene by Ir–TMEDA complex (TMEDA = *N,N,N',N'*-tetramethylethylenediamine). Formation of novel dinuclear iridathiacyclohexenyl complex

Kentaro Iwasa, Hidetake Seino, Yasushi Mizobe *

Institute of Industrial Science, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8505, Japan

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ABSTRACT

The Ir–TMEDA complex $[\text{Ir}(\text{C}_2\text{H}_4)_2(\text{TMEDA})(\text{MeCN})][\text{BF}_4]$ (TMEDA = $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$) was treated with 2-methoxythiophene in MeCN at 70 °C in the presence of H_2O to afford the novel dinuclear iridathiacyclohexenyl complex $[\text{Ir}_2\{\text{C}(\text{OMe})\text{CHCHCH}(\text{CMe}=\text{NH})\text{S}\}(\text{MeCONH})(\text{TMEDA})_2][\text{BF}_4]_2$ in 42% yield, in which two Ir(TMEDA) fragments, one 2-methoxythiophene, and two MeCN molecules are incorporated together with one H_2O molecule. The mechanism that involves the insertion of the Ir center into the thiophenic S–C(OMe) bond followed by the π -coordination of the second Ir center to the thiametallacycle has been proposed.

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1. Introduction

Hydrodesulfurization of petroleum feedstocks is one of the most important industrial processes catalyzed by transition metals. Cobalt-modified molybdenum sulfide supported on alumina is used most commonly as catalyst and certain Co–Mo–S cluster generated at the edge of the layered MoS_2 phase is suggested to be the active site of desulfurization, but details are yet unknown [1]. Among various organo-sulfur compounds included in the crude oils, thiophenes are of particular interest because removal of their S atoms is relatively difficult. Reactivities of thiophenes with transition metal complexes [2], especially with those of Group 9 metals [3] and Group 6 metals [4], are therefore attracting much attention in this context.

Now we have found that the reaction of the Ir–TMEDA complex (TMEDA = $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$) with 2-methoxythiophene affords the novel dinuclear iridathiacyclohexenyl complex via the insertion of one Ir center into the thiophenic C–S bond. In this paper, details of the characterization of this product are reported. Although related C–S bond cleaving reactions of thiophenes using certain Ir as well as Rh and Co complexes have been reported already [2,3], these are mostly conducted by the use of phosphine and cyclopentadienyl complexes, and those promoted by the complexes with N-

donor ligands are still rare except for the Rh-hydrotris(pyrazolyl)borate complexes [3a] and Rh-diiminato species [3b].

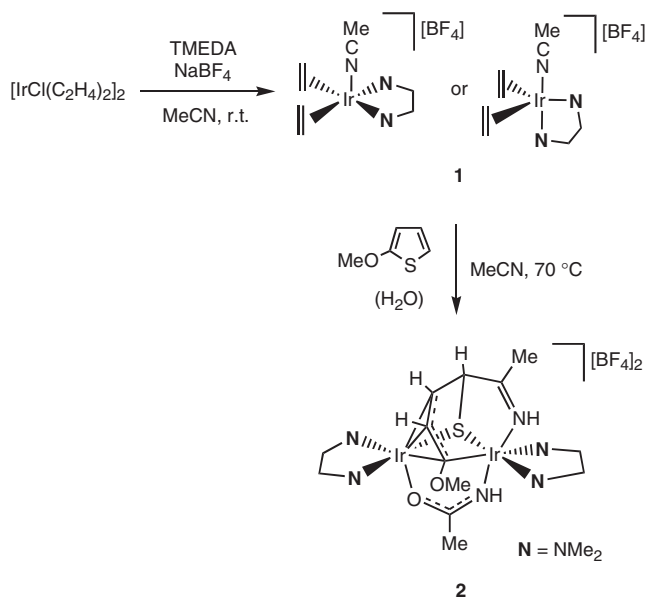
2. Results and discussion

Monomeric Ir–TMEDA complex $[\text{Ir}(\text{C}_2\text{H}_4)_2(\text{TMEDA})(\text{MeCN})][\text{BF}_4]$ (**1**) was obtained by treatment of $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ with TMEDA and NaBF_4 in MeCN at room temperature (Scheme 1). Complex **1** has been tentatively formulated by ^1H NMR spectrum in acetone- d_6 , showing characteristic signals including four doublets of doublets of doublets at δ 3.31, 3.11, 2.56, and 1.93 with the intensities of 2H each due to the ethylene protons, together with two singlets at δ 3.23 and 2.13 with the intensities of 6H each assignable to TMEDA methyl protons and one singlet at δ 2.68 with the intensity of 3H for coordinated MeCN. These ^1H NMR data suggest the square-pyramidal or trigonal-bipyramidal structure with two equatorial ethylene ligands. However, since **1** is extremely air-sensitive, isolation and full characterization was not successful.

When **1** generated in situ was treated with excess 2-methoxythiophene in MeCN at 70 °C, dinuclear iridathiacyclohexenyl complex $[\text{Ir}_2\{\text{C}(\text{OMe})\text{CHCHCH}(\text{CMe}=\text{NH})\text{S}\}(\text{MeCONH})(\text{TMEDA})_2][\text{BF}_4]_2$ (**2**) was isolated in 26% yield from the reaction mixture. Single crystals were available for the PF_6 analogue, **2'**, obtained from **2** after the anion metathesis with KPF_6 , and the X-ray analysis of **2'** was undertaken. However, refinements of the structure were unable to be completed to the satisfactory level due to the severe disorder observed for the dimetallacyclic core. Nevertheless, preliminary

* Corresponding author. Fax: +81 3 5452 6361.

E-mail address: ymizobe@iis.u-tokyo.ac.jp (Y. Mizobe).



Scheme 1.

results revealed unambiguously the atom connecting scheme in the cation, as shown in Scheme 1.

The cation consists of two Ir(TMEDA) fragments, one Ir center of which inserts into the S–C(OMe) bond of 2-methoxythiophene selectively to form the six-membered ring, while the other Ir center binds to the C(OMe)CHCH moiety of this six-membered ring in an η^3 -manner together with the S atom. Furthermore, two MeCN molecules are incorporated into this cation with concurrent hydrolysis: one is connected with the 5-C atom of the thiophene ring at the cyanide C atom to form iminoacyl group and the other is converted to the bridging amidate ligand. Insertion of the metal center into the thiophenic C–S bonds is well demonstrated for many transition metal complexes including Group 9 metal (Ir^I, Rh^I, and Co^I) complexes [3]. Selective C(OMe)–S bond scission is also precedent for, e.g. [Cp* Rh(C₂H₄)₂] (Cp* = η^5 -C₅Me₅) [3c], but the successive coordination of the second metal center to the generated thiametallacycle accompanied by the coupling to the nitrile is the finding distinctive to this Ir–TMEDA system. It is to be noted that the reactions of [Cp* Co(C₂H₄)₂] [3d,3e] and [Rh(coe){XyNC(Me)CHC(Me)N-Xy}] (coe = *cis*-cyclooctene; Xy = 2,6-Me₂C₆H₃) [3b] with thiophene result in the formation of dicobalt and dirhodium complexes in which the cobalt- or rhodathiacyclohexadiene ring binds to the other Co or Rh atom in a κ^4 form at the S–M–C=C moiety.

The spectroscopic data for **2** are consistent with this solid-state structure. Thus, the IR spectrum shows the sharp bands at 3368 and 3289 cm⁻¹ that are characteristic of ν (NH), while these NH protons resonate at δ 11.12 and 6.34 as broad signals, which disappeared by the H/D exchange using D₂O as the deuterium source. The CH protons of the iridathiacycle are observed at δ 4.89, 4.56, and 4.18 as one triplet and two doublets with J = 5.8 Hz. In addition, eleven signals due to the methyl protons appeared, indicating that all methyl groups in **2** are inequivalent as expected from its structure in a solid form.

Reactions of other thiophenes with **1** under similar conditions were also attempted. Unfortunately, all systems did not afford the products isolable in a pure form, but it has turned out from ¹H NMR criteria that for the reaction with 2-methylthiophene the scission of not the C–S bond but the C–H bond takes place. On the other hand, both products resulting from the C–S and C–H bond cleavages are obtained for the reaction with 2-acetylthiophene in a ratio of ca. 5:3.

The mechanism proposed for the formation of **2** is depicted in Scheme 2. It has been demonstrated previously that decreasing the electron density of the thiophene ring facilitates the insertion of the metal center into the C–S bond [5]. Since the insertion of Ir center to the C–S bond takes place for the thiophenes with both the electron-donating methoxy group and the electron-withdrawing acetyl group among the thiophenes examined but not for methylthiophene, it might be presumed in this Ir^I–TMEDA system that the insertion to the C–S bond is not controlled by the difference in the electron density of the thiophenes but is initiated for the thiophenes that can coordinate to Ir in a κ^2 fashion. After the insertion of Ir^I into the C–S bond to generate the iridathiacyclohexadiene species, the binding of the second Ir^I center to the S–Ir–C=C array, as demonstrated for the other Co and Rh complexes (*vide supra*), occurs with concurrent nucleophilic attack of the 5-C atom to the cyano C atom to give the Ir^{III}–Ir^{III} iminato species. Hydrolysis of this intermediate by the adventitious water finally gives **2**. Thus, as expected, addition of an almost stoichiometric amount of water to the reaction mixture resulted in the significant increase in the yield of **2** to 42%. The unique reactivity observed in this reaction system might be ascribable to the quite electron-rich nature of the Ir(TMEDA) moieties.

3. Experimental

3.1. General

All manipulations were carried out under N₂ using standard Schlenk techniques. Solvents were dried by common methods and distilled under N₂ before use. Complex [IrCl(C₂H₄)₂] [6] was prepared according to the literature method, while chemicals were obtained commercially and used as received except for TMEDA, which was treated with KOH and distilled under N₂.

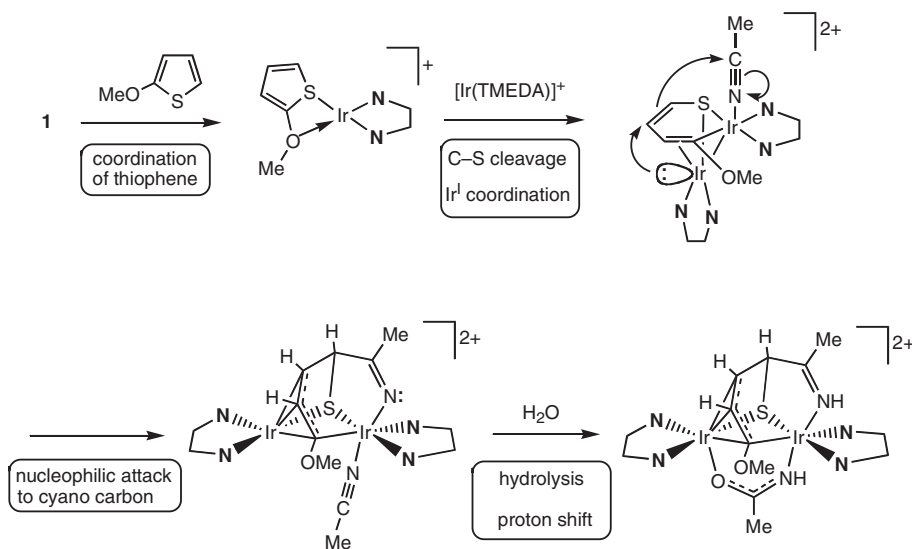
IR and NMR spectra were recorded on a JASCO FT/IR-420 and a JEOL alpha-400 spectrometer, respectively. Elemental analyses were done with a Perkin-Elmer 2400 series II CHN analyzer.

3.2. Preparation of **1**

Complex [IrCl(C₂H₄)₂] (115 mg, 0.203 mmol) was dissolved in MeCN (10 mL) and TMEDA (60 μ L, 0.40 mmol) was added to this solution at room temperature. After stirring for 1 h, finely powdered NaBF₄ (45 mg, 0.41 mmol) was added and the mixture was stirred continuously at room temperature for 3 h. The resultant yellow solution was filtered and the filtrate was evaporated to dryness in vacuo to give the yellow oily solid containing **1** (189 mg). Further purification to isolate analytically pure **1** failed since **1** was highly air-sensitive. ¹H NMR data for **1** (acetone-*d*₆): δ 3.31 (ddd, J = 11.1, 8.7, 2.4 Hz, 2H, C₂H₄), 3.23 (s, 6H, NMe), 3.11 (ddd, J = 10.4, 9.5, 2.4 Hz, 2H, C₂H₄), 2.98, 2.87 (m, 2H each, NCH₂), 2.68 (s, 3H, MeCN), 2.56 (ddd, J = 10.4, 8.7, 1.6 Hz, 2H, C₂H₄), 2.13 (s, 6H, NMe), 1.93 (ddd, J = 11.1, 9.5, 1.6 Hz, 2H, C₂H₄).

3.3. Preparation of **2**

Into a solution of [IrCl(C₂H₄)₂] (570 mg, 1.00 mmol) in MeCN (50 mL) was added TMEDA (300 μ L, 2.01 mmol) at room temperature. After stirring for 1 h, NaBF₄ (225 mg, 2.05 mmol) was added and the mixture was stirred continuously at room temperature for 20 h. Then, 2-methoxythiophene (0.50 mL, 5.0 mmol) and H₂O (20 μ L, 1.1 mmol) were added and the mixture was stirred at 70 °C for 24 h. The resulting mixture was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was purified by chromatography using the column packed with



Scheme 2.

neutral alumina. Complex **2** was obtained as yellow needles by adding ether (50 mL) to the concentrated yellow fraction eluted by MeCN (429 mg, 42% yield).

From the reaction conducted analogously but in the smaller scale without addition of H₂O, **2** was isolated in 26% yield. ¹H NMR (acetone-*d*₆): δ 11.12, 6.34 (br s, 1H each, NH), 4.89 (t, *J* = 5.8 Hz, 1H, CH), 4.56 (d, *J* = 5.8 Hz, 1H, CH), 4.18 (d, *J* = 5.8 Hz, 1H, CH), 3.82 (s, 3H, OMe), 3.63 (s, 3H, Me), 3.46 (m, 2H, CH₂), 3.27 (ddd, 1H, CH₂), 3.14 (ddd, 1H, CH₂), 3.0–2.6 (m, total 4H, CH₂, overlapping with Me resonances), 2.94, 2.93, 2.86, 2.71, 2.61, 2.45, 2.43 (s, 3H each, Me), 2.42 (d, *J* = 2.0 Hz, 3H, Me), 2.34 (s, 3H, Me). IR (KBr): 3368, 3289 cm⁻¹ (ν(NH)). Anal. Calc. for C₂₁H₄₆B₂F₈N₆O₂Ir₂S: C, 25.10; H, 4.62; N, 8.36. Found: C, 25.39; H, 4.59; N, 8.59%.

3.4. Preparation of 2'

A mixture of **2** (51 mg, 0.050 mmol) and KPF₆ (28 mg, 0.15 mmol) in MeCN (5 mL) was stirred for 2 days and the resulting mixture was filtered. Addition of ether (20 mL) to the filtrate gave **2'**·MeCN as yellow crystals (32 mg, 55% yield). Anal. Calc. for C₂₃H₄₉F₁₂N₇O₂P₂Ir₂S: C, 23.77; H, 4.25; N, 8.44. Found: C, 23.46; H, 4.09; N, 8.03%.

3.5. Reactions of 1 with 2-methylthiophene and 2-acetylthiophene

Reactions of **1** with these thiophenes were carried out analogously to that with 2-methoxythiophene. However, these reactions did not proceed so cleanly as compared to that forming **2**, so that the isolation of the analytically and spectroscopically pure products were unsuccessful. Characteristic ¹H NMR signals of the crude products indicated that the reaction with 2-methylthiophene underwent the C–H bond cleavage to give the hydrido-thienyl complex exhibiting the hydrido resonance at δ –23.14 (s, 1H) and the thienyl protons at δ 6.52 (d, *J* = 3.4 Hz, 1H, 4-thienyl H) and 7.02 (dq, *J* = 3.4 and 1.2 Hz, 1H, 3-thienyl H), while that with 2-acetylthiophene gave a mixture of the C–S and C–H bond scission in ca. 5:3 ratio, where the signals assignable to former are observed at δ 11.54 (br, 1H, NH), 6.58 (br, 1H, NH), 5.92 (dd, *J* = 7.8, 0.4 Hz, 1H, CH), 5.70 (dd, *J* = 5.2, 0.4 Hz, 1H, CH), and 4.15 (dd, *J* = 7.8, 5.2 Hz, 1H, CH) and those to the latter at δ –23.06 (s, 1H, IrH), 7.54 (d, *J* = 4.0 Hz, 1H, thienyl), and 7.02 (d, *J* = 4.0, 1H, thienyl), respectively.

3.6. X-ray crystallography for 2'

Single crystal of **2'** was sealed in a glass capillary under argon and mounted on a Rigaku Mercury-CCD diffractometer equipped with a graphite-monochromatized Mo Kα source. All diffraction studies were done at 23 °C. Data collections were performed by using the CRYSTALCLEAR program package [7]. All data were corrected for Lorentz and polarization effects as well as absorption.

Structure solution and refinements were conducted by using the CRYSTALSTRUCTURE program package [8]. The positions of non-hydrogen atoms were determined by Patterson methods (SHELX97) [9] and subsequent Fourier synthesis (DIRDIF99) [10], which were refined by full-matrix least-squares techniques using isotropic thermal parameters for all C atoms as well as the two O atoms and with anisotropic thermal parameters for other non-hydrogen atoms. However, since the C(OMe)CHCHCH(S) moiety of **2'** is severely disordered over two positions in a ratio of ca. 6:4, the structure could not be refined to the satisfactory level. Crystal data: formula, C₂₃H₄₉N₇O₂F₁₂P₂SiR₂; *F*_w = 1160.10; space group, *P*2₁; *a* = 14.013(1), *b* = 9.0391(7), *c* = 15.250(1) Å, β = 99.250(1)°, *V* = 1906.5(3) Å³; *Z* = 2; ρ_{calc} = 2.021 g cm⁻³; crystal size, 0.20 × 0.20 × 0.20 mm³; no of unique reflections, 8039; no of variables, 393; *R*₁ and *wR*₂ values with all data, 0.061 and 0.127; GOF, 1.023.

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References

- [1] (a) T. Kabe, A. Ishihara, W. Qian, Hydrodesulfurization and Hydrodenitrogenation, Kodansha/WILEY-VCH, Tokyo-Weinheim, Japan, 1999; (b) A.N. Startsev, J. Mol. Catal. A 152 (2000) 1.
- [2] (a) R.A. Sánchez-Delgado, Organometallic Modeling of the Hydrodesulfurization and Hydrodenitrogenation Reactions, Kluwer, Dordrecht, Netherland, 2002; (b) M. Brorson, J.D. King, K. Kiriakidou, F. Prestopino, E. Nordlander, in: P. Braunstein, L.A. Oro, P.R. Raithby (Eds.), Metal Clusters in Chemistry, WILEY-VCH, Weinheim, 1999, pp. 741–781. Chapter 2.6; (c) R.J. Angelici, Organometallics 20 (2001) 1259.

- [3] (a) M. Paneque, S. Taboada, E. Carmona, *Organometallics* 15 (1996) 2678;
(b) S.T.H. Willems, P.H.M. Budzelaar, N.N.P. Moonen, R. de Gelder, J.M.M. Smits, A.W. Gal, *Chem. Eur. J.* 8 (2002) 1310;
(c) W.D. Jones, M. Chin, *J. Am. Chem. Soc.* 114 (1992) 9851;
(d) W.D. Jones, R.M. Chin, *Organometallics* 11 (1992) 2698;
(e) W.D. Jones, R.M. Chin, *J. Organomet. Chem.* 472 (1994) 311;
(f) W.D. Jones, D.A. Vicic, R.M. Chin, J.H. Roache, A.W. Myers, *Polyhedron* 16 (1997) 3115;
(g) C. Bianchini, J.A. Casares, M.V. Jiménez, A. Meli, S. Moneti, F. Vizza, V. Herrera, R.A. Sánchez-Delgado, *Organometallics* 14 (1995) 4850;
(h) C. Bianchini, A. Meli, V. Patinec, V. Sernau, F. Vizza, *J. Am. Chem. Soc.* 119 (1997) 4945;
(i) J. Chen, R.J. Angelici, *Coord. Chem. Rev.* 106–207 (2000) 63.
- [4] (a) D.G. Churchill, B.M. Bridgewater, G. Parkin, *J. Am. Chem. Soc.* 122 (2000) 178;
(b) R.C. Mills, K.A. Abboud, J.M. Boncella, *Chem. Commun.* (2001) 1506.
- [5] (a) M. Hernández, G. Miralrio, A. Arévalo, S. Bernes, J.J. García, C. López, P.M. Maitlis, F. de Rio, *Organometallics* 20 (2001) 4061;
(b) K. Yu, H. Li, E.J. Wateon, K.L. Virkaitis, G.B. Carpenter, D.A. Sweigart, *Organometallics* 20 (2001) 3550.
- [6] A.L. Onderdelinden, A. van der Ent, *Inorg. Chim. Acta* 6 (1972) 420.
- [7] CrystalClear 1.3.5: Rigaku Corporation, 1999. *CRYSTALCLEAR Software User's Guide*, Molecular Structure Corporation, (c) 2000. J.W. Pflugrath, *Acta Cryst. D* 55, (1999) 1718.
- [8] CrystalStructure 3.8.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MS, 2000–2006.
- [9] SHELX97 G.M. Sheldrick, Program for Crystal Structure Calculations, University of Göttingen, Germany, 1997.
- [10] DIRDIF99: P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, and J.M.M. Smits, The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory: University of Nijmegen, Nijmegen, The Netherlands, 1999.