Oxidative Reaction of 1,5-Dithioniabicyclo[3.3.0]octane Bis(trifluoromethanesulfonate) with Diene Complexes of Zirconium and Tantalum: Synthesis of $Cp_2Zr(OTf)_2(thf)$ and $Cp(\eta^4\text{-}1,3\text{-butadiene})Ta(OTf)_2$

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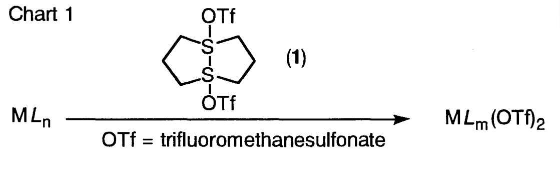
Oxidative addition of a hypervalent organosulfur compound, 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) (**1**), to diene complexes of zirconium and tantalum, $Cp_2Zr(\eta^4\text{-}1,3\text{-butadiene})$ and $CpTa(\eta^4\text{-}1,3\text{-butadiene})_2$, in THF resulted in the almost quantitative formation of bis(triflate) complexes of zirconium, $Cp_2Zr(OTf)_2(thf)$ (**3**), and tantalum, $CpTa(\eta^4\text{-}1,3\text{-butadiene})(OTf)_2$ (**5**), respectively.

Hypervalent compounds such as organosilicates[1] and organoiodanes[2] have been utilized as highly reactive reagents in organic synthesis. It is recent trend that hypervalent compounds have been used to add oxidatively to organometallic complexes of late transition metals: *e.g.*, organoiodanes for the oxidative vinylation and alkynylation of Vaska's complex[3-5] and trithiapentalene derivatives for the oxidative reactions with $Pd(PPh_3)_4$ and $Rh(Cl)(PPh_3)_3$ resulting in the formation of palladium and rhodium carbene complexes.[6] In contrast to the extensive investigations for late transition metals, to the best of our knowledge, oxidative reaction of hypervalent compounds to organometallic complexes of early transition metals has not been reported to date.[7] Herein we report on the reaction of a hypervalent organosulfur compound, 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) (**1**),[8-10] with low valent early transition metal complexes such as diene complexes of zirconium and tantalum,[11] resulting in the formation of bis(trifluoromethanesulfonate) complexes (Chart 1).

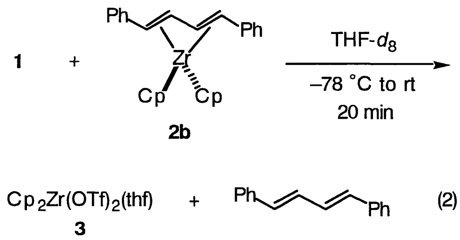
Chart 1



Treatment of $Cp_2Zr(1,3\text{-butadiene})$ (**2a**: a mixture of *cis*- and *trans*-1,3-butadiene isomers)[12,13] (Cp = cyclopentadienyl) with an equimolar amount of **1** in THF resulted in the formation of a colorless solution, from which the colorless crystals of $Cp_2Zr(OTf)_2(thf)$ (**3**) (96%) along with 1,5-dithiacyclooctane (95%) were obtained, respectively (equation. 1).[14] The product **3** was identified by comparison of its spectral data with the previously reported ones.[15] Thewalt and Lasser reported the preparation of **3** in 43% yield by metathesis reaction of Cp_2ZrCl_2 with 2 equiv of AgOTf in THF.[15,16]

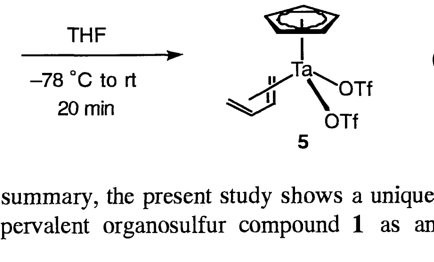
$$\underset{}{\mathbf{1}} + \underset{\mathbf{2a}}{Cp_2Zr(1,3\text{-butadiene})} \xrightarrow[\substack{-78\ ^\circ C\ \text{to rt} \\ 20\ \text{min}}]{\text{THF}} \underset{\mathbf{3}}{Cp_2Zr(OTf)_2(thf)} \qquad (1)$$

In the reaction course, the butadiene ligand was liberated. In order to make sure of it, we examined a similar reaction of **1** with $Cp_2Zr(s\text{-}trans\text{-}1,4\text{-diphenyl-}1,3\text{-butadiene})$ (**2b**)[12] in THF-d_8; the formation of the complex **3** (66%) accompanied with the liberated (*E*,*E*)-1,4-diphenyl-1,3-butadiene (81%) detected by ^{1}H-NMR spectroscopy (equation. 2).



This synthetic method can be applied to the preparation of a tantalum bis(triflate) complex. We have recently reported that a CpTa(diene) fragment is isoelectronic and isolobal to the well-known metallocene fragment of group 4 metals, Cp_2M; both of these 14 electron fragments stabilize various reactive species such as benzyne,[17] carbene,[18] and alkyl cation.[19,20] Thus, a bis(diene) complex of tantalum, $CpTa(cis\text{-}1,3\text{-butadiene})_2$ (**4**),[21] is also expected to react with **1**. Actually, the reaction of **4** with **1** proceeded smoothly to give purple solids of $CpTa(OTf)_2(\eta^4\text{-}cis\text{-}1,3\text{-butadiene})$ (**5**) in 95% yield, which was characterized by spectroscopic as well as elemental analysis (equation. 3).[14] The ^{1}H NMR spectrum of **5** in C_6D_6 displayed a singlet at δ 5.89 due to cyclopentadienyl ring protons together with a set of multiplets at δ 0.08, 1.40, and 6.80 due to the s-*cis*-butadiene ligand bound to the tantalum center, these resonances being comparable to those reported for $CpTaCl_2(\eta^4\text{-}cis\text{-}1,3\text{-butadiene})$, while the triflate ligands bound to the tantalum atom were confirmed by the ^{19}F NMR and the IR spectroscopic data.[21]

$$\mathbf{1} + \underset{\mathbf{4}}{CpTa(1,3\text{-butadiene})_2}$$



In summary, the present study shows a unique capability of the hypervalent organosulfur compound **1** as an excellent reagent for preparing transition metal trifluoromethanesulfonates. We are in the process of investigating the scope and the limitation of this type of reaction for a variety of transition metals.[22]

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† Research Fellow of the Japan Society for the Promotion of Science,1996–1997.

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14 **3**: colorless crystals, 96% yield, mp 97—100 °C (decomp). ^{1}H NMR ($CDCl_3$, 35 °C): δ 1.85 (m, 4H, THF), 3.74 (m, 4H, THF), 6.54 (s, 10H, Cp); ^{19}F NMR ($CDCl_3$, 35 °C): δ –78.5 (s, OSO_2CF_3); IR (Nujol/KBr): 1273, 1171, 1023, 764, 632 cm^{-1}. The ^{1}H NMR and IR spectral data are identical to those of the literature.[15]
5: purple powder, 95% yield, mp 122—126 °C (decomp). ^{1}H NMR (C_6D_6, 35 °C): δ 0.08 (m, 2H, $H^1{}_{anti}$ and $H^4{}_{anti}$), 1.40 (m, 2H, $H^1{}_{syn}$ and $H^4{}_{syn}$), 5.89 (s, 5H, Cp), 6.80 (m, 2H, H^2 and H^3); ^{19}F NMR (C_6D_6, 35 °C): δ –78.6 (s, OSO_2CF_3); IR (Nujol/KBr): 1200, 1004, 854, 721, 626, 505 cm^{-1}. Anal. Found: C, 22.81; H, 1.99%. Calcd for $C_{11}H_{11}O_6S_2F_6Ta$: C, 22.08; H, 1.85%.

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22 We already found that the compound **1** reacted with $IrCl(CO)(PPh_3)_2$ to give a bis(triflate) complex, $IrCl(OTf)_2(CO)(PPh_3)_2$, and furthermore **1** reacted with metallic samarium to give a bis(triflate) compound of samarium(II); the manuscript in preparation.