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[9] ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): $\delta = 8.21$ (d, 12 H, $^3J_{H,H} = 6$ Hz; *ortho*), 7.23 (m, 18 H; *meta* and *para*), 1.09 (m, 27 H, $^3J_{Pt,H} = 43$, $^4J_{Pt,H} = 25$ Hz; PCH$_3$); ^{31}P{^{1}H} NMR (160 MHz, [D$_6$]benzene, 25 °C, relative to 85 % H$_3$PO$_4$): $\delta = 27.0$ ($^1J_{P,Pt} = 2959$, $^2J_{P,Pt} = 418$, $^3J_{P,P} = 86$ Hz); ^{13}C{^{1}H} NMR (100 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 152.5$ (*ipso*, $^2J_{C,Pt} = 48$ Hz), 136.4 (*ortho*), 128.4 (*para*), 128.0 (*meta*), 21.9 (m, $^2J_{Pt,C} = 82$ Hz); ^{195}Pt{^{1}H} NMR (64.1 MHz, [D$_6$]benzene, 25 °C): $\delta = -3980$ relative to K$_2$[PtCl$_4$]; ^{29}Si{^{1}H} NMR (79 MHz, [D$_6$]benzene, 25 °C): $\delta = 279.4$ ($J_{Si,Pt} = 945$ Hz); elemental analysis calcd for C$_{45}$H$_{57}$Si$_3$P$_3$Pt$_3$ (%): C 39.73, H 4.22; found: C 39.67, H 4.03.

[10] Complex **2** gave satisfactory elemental analyses, NMR data, and X-ray crystallographic results. Analogous complexes [(dppe)Pt(R$_2$SiO-SiR$_2$)] (R = Me, *i*Pr) were prepared by reaction of O$_2$ with disilene Pt complexes [(dppe)Pt(R$_2$SiSiR$_2$)] (dppe = 1,2-bis(diphenylphosphanyl)ethane): E. K. Pham, R. West, *J. Am. Chem. Soc.* **1989**, *111*, 7667; E. K. Pham, R. West, *Organometallics* **1990**, *9*, 1517.

[11] Crystallographic data for **1**: C$_{45}$H$_{57}$P$_3$Si$_3$Pt$_3$, $M_r = 1360.69$; triclinic, space group $P\bar{1}$ (no. 2), $a = 12.914(3)$, $b = 17.632(4)$, $c = 12.830(4)$ Å, $\alpha = 111.01(2)$, $\beta = 116.59(2)$, $\gamma = 87.36(2)°$, $V = 2416$ Å^3, $Z = 2$, $\mu = 8.834$ mm^{-1}, $F(000) = 1296$, $\rho_{calcd} = 1.870$ g cm^{-3}. The final R factor was 0.044 ($Rw = 0.035$) for 4183 reflections with $I > 3\sigma(I)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141185. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] Pt^{II} and Pd^{II} complexes with a stable metal–metal bond are unknown. X-ray photoelectron spectroscopy (XPS) was applied to **1** and related Pt complexes to obtain more direct evidence for the valency of the metal centers. Complex **1** shows peaks at 72.3 and 75.6 eV (due to 4f$_{7/2}$ and 4f$_{5/2}$ states, respectively). The peak positions, however, are negligibly different to those of the triangular Pt^0 complex [Pt$_3$(2,6-Me$_2$-C$_6$H$_3$CN)$_6$] (72.2 and 75.5 eV) and the mononuclear Pt^{II} complex [Pt(SiHPh$_2$)$_2$(PMe$_3$)$_2$] (72.3 and 75.7 eV). These data and the NMR data of the complexes did not provide additional useful information for determining the valence of Pt in **1**.

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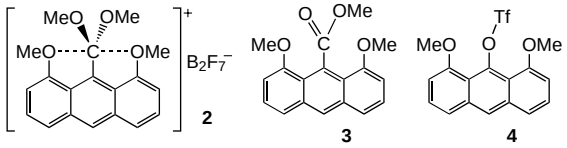
[15] The molecular orbital diagram is available as Supporting Information.

Synthesis of a Versatile Tridentate Anthracene Ligand and its Application for the Synthesis of Hypervalent Pentacoordinate Boron Compounds (10-B-5)**

Makoto Yamashita, Yohsuke Yamamoto, Kin-ya Akiba,* and Shigeru Nagase

Hypervalent pentacoordinate boron compounds (10-B-5)[1] have been postulated as transition states in S_N2-type reactions at a boron atom. For example, the reaction of the [BH$_3$-CO] complex with NMe$_3$[2] as well as the intramolecular bond switch at the boron atom in compounds bearing a van Koten type ligand[3] have been reported. There has been only one report of isolable hypervalent boron compounds (10-B-5 and 12-B-6),[4] but the compounds bearing tridentate pyridine diol ligand(s) were characterized by ^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectra in solution. The X-ray analysis of the compounds has not been reported. Here we report the synthesis and X-ray structures of 1,8-dimethoxy-9-borylanthracene (**1a–c**, see Scheme 2): the first fully characterized hypervalent 10-B-5 compounds.

Recently, we reported the synthesis and the X-ray structure of the hypervalent five-coordinate carbon compound (10-C-5) **2** through the use of an 1,8-dimethoxy-9-anthracenyl ligand.[5] Ester **3** was synthesized from the 9-OTf derivative **4** (OTf = trifluoromethanesulfonate) by carbon monoxide insertion in



methanol mediated by [Pd(PPh$_3$)$_4$]. However, several attempts to synthesize **1** from **4** were not successful. Thus, we designed a novel versatile precursor 1,8-dimethoxy-9-bromoanthracene (**8**). The synthetic pathway for **8** is illustrated in Scheme 1. After conversion of 1,8-dimethoxy-9-hydroxyanthracene (**5**)[6] into the corresponding phosphate (**6**), reaction conditions for the reduction of **6** and the subsequent treatment of the resulting anion **7** with BrCF$_2$CF$_2$Br to yield **8** were examined (Table 1). Only the 9-H compound was obtained using Birch reduction conditions (entry 1) and only a trace amount of **8** was obtained by using lithium naphthalenide (entry 2). Fortunately, the reduction of **6** with lithium 4,4′-di-

[*] Prof. K.-y. Akiba, M. Yamashita, Prof. Y. Yamamoto
Department of Chemistry, Graduate School of Science
Hiroshima University, 1-3-1 Kagamiyama
Higashi-Hiroshima 739-8526 (Japan)
Fax: (+81) 824-24-0723
E-mail: akiba@sci.hiroshima-u.ac.jp
Prof. S. Nagase
Department of Chemistry, Graduate School of Science
Tokyo Metropolitan University, 1-1 Minami-Osawa
Hachioji, Tokyo 192-0397 (Japan)

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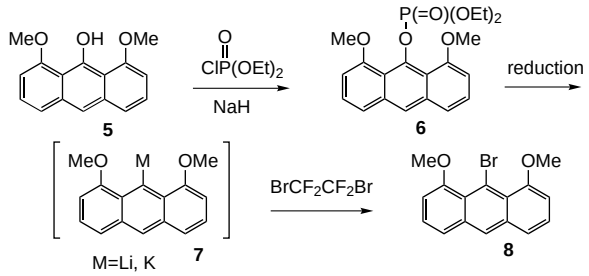


Scheme 1. Synthesis of bromoanthracene **8**.

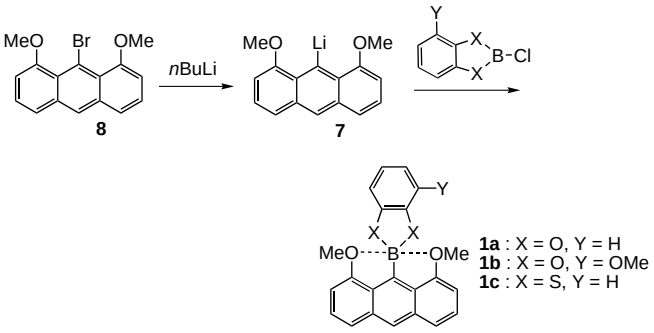
Table 1. Reaction conditions for the reduction of **6**.

Entry	Metal (equivalent)	Electron carrier	Solvent	T [°C], t [h]	Yield of **8** [%]
1	K (2.2)	–	liq. NH_3	– 78, 2	0
2	Li (2.5)	naphthalene	THF	0 → 25, 3.5	trace
3	Li (2.5)	DTBB	THF	0, 1	14
4	Li (2.5)	DTBB	THF	– 20, 2	20
5	Li (2.5)	DTBB	THF	– 30, 12	30
6	Li (4)	DTBB	THF	– 20, 12	28
7	Li (10)	DTBB	THF	– 20, 2	trace

DTBB = 4,4′-di-*tert*-butylbiphenyl

tert-butylbiphenylide (LDBB) gave **8**, albeit in low yields (up to 30 %, entry 5).

Compound **8** was lithiated at – 100 °C in a dilute solution of THF and then the *B*-chlorocatecholateborane derivatives added at the same temperature (Scheme 2). Catecholborane derivatives **1a**–**c** were obtained in acceptable yields (47 % for **1a**, 25 % for **1b**, and 32 % for **1c**). These compounds were stable to atmospheric moisture and chromatographic treatment (SiO_2).



Scheme 2. Synthesis of hypervalent boron **1**.

Crystals of **1a**–**c** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/*n*-hexane (Figure 1; Table 2).[7] The sum of the bond angles around the central boron atom of **1a**–**c** are 360.0°, which indicates that the central boron atom is planar with sp^2 hybridization. Thus, one of the lone pairs on the oxygen atoms at the 1,8-positions in **1** interacts with the empty p orbital of the central boron atom at position 9 to form a three-center four-electron bond. Therefore, the structure around the central boron atom can be regarded as a slightly distorted trigonal bipyramid. The two B–O bond lengths (B1–O1, B1–O2) are 2.379(2) and 2.441(2) Å in **1a**, 2.398(4) and 2.412(4) Å in **1b**, and are

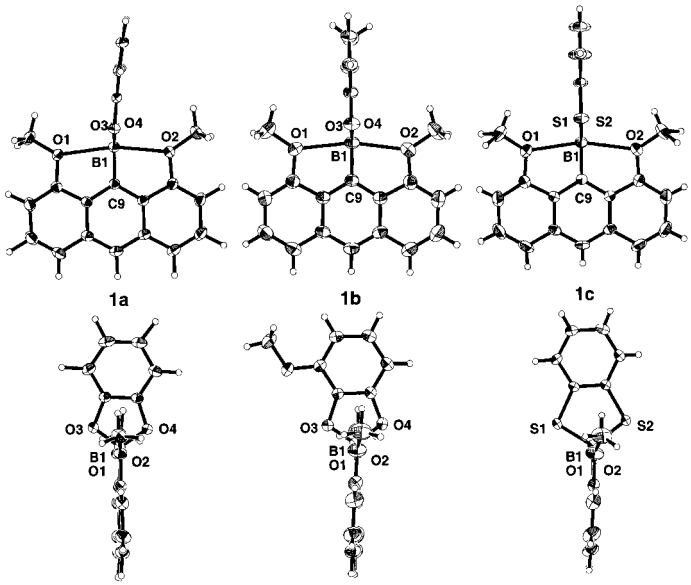


Figure 1. Crystal sructures (30 % thermal ellipsoids) of **1a**–**c**.

Table 2. Selected bond lengths [Å] and angles [°] of **1a**–**c**.

	O1–B1	O2–B1	O1-B1-O2	O1-C1-C11	O2-C8-C14
1a	2.379(2)	2.441(2)	167.10(7)	113.2(1)	113.7(1)
1b	2.398(4)	2.412(4)	166.3(2)	113.2(2)	112.9(2)
1c	2.436(2)	2.436(2)	164.0(3)	113.5(2)	113.5(2)

identical (2.436(2) Å) in **1c**. The bonds are longer than those of the B1–O3 and B1–O4 bonds (1.397(2) and 1.403(2) Å in **1a**, 1.394(3) and 1.400(3) Å in **1b**) but shorter than the sum of the van der Waals radii (3.48 Å).[8] The small difference in the B1–O1/2 bond lengths observed in **1a** may be a consequence of a packing effect or may be related to the electrophilicity of the central boron atom since **1b**, which bears a more electron-donating OMe substituent, showed a more symmetrical structure.

The ^{11}B NMR chemical shifts for **1a**–**c** are in the range of normal catecholborane derivatives (phenylcatecholborane: $\delta = +32.1$ (THF)),[9] which indicates that the interaction between the central boron atom and the oxygen atoms at the 1,8-positions is weak. In contrast, upfield shifts were observed in the spectra of the boron compounds prepared by Lee and Martin (– 20 to – 41 ppm).[4] The difference in the chemical shifts between the compounds of Lee and Martin and **1a**–**c** may be a consequence of the charge difference (the former being anionic systems, while **1a**–**c** are electronically neutral systems), and hence further investigation on the synthesis and chemical shifts of boron compounds bearing anionic oxygen atoms (O^-) at the 1,8-positions is in progress.

However, an attractive interaction between the central boron atom and the oxygen atoms at the 1,8-positions, even though weak, is confirmed by hybrid nonlocal density functional theory (DFT) at the B3LYP/6-31G* level using the Gaussian 98 program.[10] The optimized geometry of **1a** is the symmetrical structure. The two B–O bond lengths are identical (2.447 Å) and are slightly longer than the experimental data (2.379(2) and 2.441(2) Å). The bond path is found between the central boron atom and the two oxygen

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atoms, which indicates that these atoms are bonded.[11] The B–O bond is weak and slightly ionic as shown by the small value of the electron density ($\rho(r)$: 0.021 e a_0^{-3}; a_0 = 0.529177 Å)[11] and small positive Laplacian value ($\nabla^2\rho(r)$: 0.057 e a_0^{-5})[11] at the bond critical points (BCP). These values, which include a large value of the ellipticity (ε = 0.220),[11] are very similar to the values for the C–O bond in our hypervalent five-coordinate carbon compound **2** ($\rho(r)$: 0.022 e a_0^{-3}, $\nabla^2\rho(r)$: 0.078 e a_0^{-5}, ε: 0.220).[5]

Experimental Section

6: Dry THF (10 mL) was added in an argon atmosphere at 0 °C to a mixture of **5** (509 mg, 2.00 mmol) and NaH (48.6 mg, 2.2 mmol; oil dispersion). After stirring the mixture for 15 min at 0 °C, diethyl chlorophosphate (0.32 mL, 2.2 mmol) was added dropwise and the mixture heated to reflux at 80 °C for 4 h. The solvent was then removed under reduced pressure, and the residue was poured into water, followed by extraction with CH_2Cl_2. The organic layer was collected and dried over K_2CO_3. Solvents were removed under reduced pressure to give a crude product, which was purified by cooled column chromatography (CH_2Cl_2/diethyl ether = 1/0–3/1, –10 °C) to give **6** (505 mg, 65 %) as a yellow solid. M.p. 115.8–117.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, $CHCl_3$): δ = 1.13 (dt, ^4J(P,H) = 1 Hz, ^3J(H,H) = 7 Hz, 6H; CH_3CH_2), 3.94–4.09 (m, 4H; CH_3CH_2), 4.02 (s, 6H; OCH_3), 6.75 (d, ^3J(H,H) = 8 Hz, 2H; aromatic CH), 7.33 (t, ^3J(H,H) = 8 Hz, 2H; aromatic CH), 7.47 (d, ^3J(H,H) = 8 Hz, 2H; aromatic CH), 8.12 (s, 1H; aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): δ = 15.54 (d, ^3J(C,P) = 8.7 Hz, CH_3CH_2), 54.88 (s, OCH_3), 63.31 (d, ^2J(C,P) = 6.6 Hz, CH_3CH_2), 103.21 (d, J(C,P) = 1.6 Hz, aromatic CH), 117.28 (d, J(C,P) = 4.2 Hz, quaternary C), 119.38 (d, J(C,P) = 5.8 Hz, aromatic CH), 122.57 (d, J(C,P) = 3.3 Hz, aromatic CH), 125.37 (d, J(C,P) = 12.4 Hz, aromatic CH), 133.45 (d, J(C,P) = 2.5 Hz, quaternary C), 141.40 (d, J(C,P) = 9.1 Hz, quaternary C), 155.79 (d, J(C,P) = 1.7 Hz, quaternary C); ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = –6.89 (s); elemental analysis calcd for $C_{20}H_{23}O_6P$: C 61.54, H 5.94; found: C 61.22, H 5.92.

8: THF (4 mL) was added to a mixture of 4,4′-di-*tert*-butylbiphenyl (668 mg, 2.5 mmol) and Li (17.8 mg, 2.5 mmol) under argon at 0 °C. The mixture was stirred for 4 h at 0 °C with a glass-coated stirring bar to give a solution of LDBB. A solution of **6** (390.5 mg, 1 mmol) in THF (5 mL) was added to the LDBB solution at –78 °C and the mixture stirred at that temperature for 1 h. The mixture was then allowed to warm to –30 °C and was stirred at the temperature for 12 h. $BrCF_2CF_2Br$ (0.36 mL, 3 mmol) was added dropwise into the reaction mixture at –30 °C. The mixture was then allowed to warm to room temperature and was stirred for 1 h. Solvents were removed under reduced pressure. The crude product was dissolved in CH_2Cl_2 and was washed with CH_2Cl_2/H_2O. The organic layer was collected and was dried over K_2CO_3. Solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography (CH_2Cl_2/*n*-hexane 0/1–1/15) to give **8** (99.1 mg, 30 %) as a pale yellow solid. M.p. 141–149 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, $CHCl_3$): δ = 4.04 (s, 6H; OCH_3), 6.90 (d, ^3J(H,H) = 8 Hz, 2H; aromatic CH), 7.37 (t, ^3J(H,H) = 8 Hz, 2H; aromatic CH), 7.54 (d, ^3J(H,H) = 8 Hz, 2H; aromatic CH), 8.29 (s, 1H; aromaic CH) ; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): δ = 55.75 (OCH_3), 101.78 (aromatic CH), 116.19 (aromatic CH), 119.63 (aromatic CH), 121.33 (quaternary C), 124.75 (quaternary C), 127.37 (aromatic CH), 131.68 (quaternary C), 155.77 (quaternary C); MS (FAB+): *m*/*z*: 316/318 [M^+]; elemental analysis calcd for $C_{16}H_{13}O_2Br$: C 60.59, H 4.13; found: C 60.50, H 3.88.

1a: A solution of *n*BuLi in *n*-hexane (0.35 mL, 0.55 mmol) was added dropwise to a mixture of **8** (159 mg, 0.5 mmol) and THF (20 mL) at –100 °C. The reaction mixture was then stirred for 1.5 h at –100 °C. The solution of *B*-chlorocatecholborane (87.3 mg, 0.57 mmol) and THF (10 mL) was transferred to the reaction mixture at –100 °C. The mixture was stirred for 7.5 h at –100 °C and 9 h at room temperature. The reaction was quenched with aqueous 1N HCl (50 mL) and the mixture extracted with CH_2Cl_2. The organic layer was collected and dried over $MgSO_4$. The crude product was purified by HPLC to give **1a** (84.7 mg, 47 %) as a pale blue-green fraction (retention time = 74 min; Lc 908-C60. Column (Japan Analytical Industry), $ClCH_2CH_2Cl$ eluent, 15 mL min^{-1} flow rate): m.p. 278–288 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, $CHCl_3$): δ = 3.67 (s, 6H; OCH_3), 6.71 (d, ^3J(H,H) = 7 Hz, 2H; aromatic CH), 7.12 (dd, ^3J(H,H) = 6 Hz, ^4J(H,H) = 2 Hz, 2H; aromatic CH), 7.30 (dd, ^3J(H,H) = 6 Hz, ^4J(H,H) = 2 Hz, 2H; aromatic CH), 7.38 (dd, ^3J(H,H) = 7 Hz, ^3J(H,H) = 8 Hz, 2H; aromatic CH), 7.64 (d, ^3J(H,H) = 8 Hz, 2H; aromatic CH), 8.45 (s, 1H); ^{11}B NMR (128 MHz, $CDCl_3$, 25 °C, $BF_3 \cdot OEt_2$): δ = 28–39 (br); elemental analysis calcd for $C_{22}H_{17}O_4B$: C 74.19, H 4.81; found: C 73.78, H 4.67. A similar procedure was employed for **1b** and **1c**. **1b**: yield 25 %; pale blue fraction (retention time = 70 min): m.p. 262–273 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, $CHCl_3$): δ = 3.69 (s, 6H; OCH_3), 4.00 (s, 3H; OCH_3), 6.69 (d, ^3J(H,H) = 8 Hz, 2H; aromatic CH), 6.76 (d, ^3J(H,H) = 8 Hz, 1H; aromatic CH), 6.97 (d, ^3J(H,H) = 8 Hz, 1H; aromatic CH), 7.06 (t, ^3J(H,H) = 8 Hz, 1H; aromatic CH), 7.38 (t, ^3J(H,H) = 8 Hz, 2H; aromatic CH), 7.62 (d, ^3J(H,H) = 8 Hz, 2H; aromatic CH), 8.44 (s, 1H; aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$) δ = 56.57 (OCH_3), 56.66 (OCH_3), 102.66 (aromatic CH), 105.20 (aromatic CH), 106.74 (aromatic CH), 121.17 (aromatic CH), 121.64 (aromatic CH), 125.39 (aromatic CH), 127.77 (aromatic CH), 128.81 (quaternary C), 132.30 (quaternary C), 137.25 (quaternary C), 145.36 (quaternary C), 150.35 (quaternary C), 155.29 (quaternary C); ^{11}B NMR (128 MHz, $CDCl_3$, 25 °C, $BF_3 \cdot OEt_2$): δ = 30–37 (br); elemental analysis calcd for $C_{23}H_{19}O_5B$: C 71.53, H 4.96; found: C 71.18, H 4.68. **1c**: yield 32 %; pale blue fraction (retention time = 75 min): m.p. 240–250 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, $CHCl_3$): δ = 3.62 (s, 6H; OCH_3) 6.67 (d, ^3J(H,H) = 7 Hz, 2H; aromatic CH), 7.25 (dd, ^3J(H,H) = 6 Hz, ^4J(H,H) = 3 Hz, 2H; aromatic CH), 7.39 (dd, ^3J(H,H) = 7 Hz, ^3J(H,H) = 8 Hz, 2H; aromatic CH), 7.61 (d, ^3J(H,H) = 8 Hz, 2H; aromatic CH), 7.70 (dd, ^3J(H,H) = 6 Hz, ^4J(H,H) = 3 Hz, 2H; aromatic CH) 8.45 (s, 1H; aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$) δ = 54.50 (OCH_3), 103.24 (aromatic CH), 121.15 (aromatic CH), 124.34 (aromatic CH), 125.31 (aromatic CH), 125.53 (aromatic CH), 127.98 (quaternary C), 128.13 (quaternary C), 132.65 (quaternary C), 140.76 (quaternary C), 155.81 (quaternary C); ^{11}B NMR (128 MHz, $CDCl_3$, 25 °C, $BF_3 \cdot OEt_2$) δ = 55–68 (br); elemental analysis calcd for $C_{22}H_{17}O_2S_2B$: C 68.05, H 4.41; found: C 67.69, H 4.29.

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[7] Crystal data for **1a**: monoclinic system, space group $P2_1/a$ (no. 14), a = 11.9620(4), b = 7.2280(1), c = 20.2810(7) Å, β = 100.490(1)°, V = 1724.21(7) Å^3, Z = 4, ρ_{calcd} = 1.372 g cm^{-3}; R = 0.0560 (Rw = 0.1103) for 3446 observed reflections (244 parameters) with $I > 3\sigma(I)$; GOF = 1.367. Crystal data for **1b**: orthorhombic system, space group *Pca*21 (no. 29), a = 9.8670(4), b = 14.2920(6), c = 14.0810(4) Å, V = 1985.7(1) Å^3, Z = 4, ρ_{calcd} = 1.292 g cm^{-3}; R = 0.0570 (Rw = 0.0820) for 2132 observed reflections (262 parameters) with $I > 3\sigma(I)$; GOF = 0.847. Crystal data for **1c**: orthorhombic system, space group *Pnma* (no. 62), a = 8.4930(2), b = 14.3130(6), c = 15.9540(8) Å, V = 1939.4(1) Å^3, Z = 4, ρ_{calcd} = 1.330 g cm^{-3}; R = 0.0428 (Rw = 0.0933) for 1125 observed reflections (275 parameters) with $I > 3\sigma(I)$; GOF = 1.438. Data were collected at 298 K on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Unit cell parameters were determined by autoindexing several images in each data set separately with the program DENZO. For each data set, rotation images were collected in 3° increments with a total rotation of 180° about ϕ. Data were

processed by using SCALEPACK. The structure was solved using the teXsan system and refined by full-matrix least-squares. (The programs DENZO and SCALEPACK are available from Mac Science Co., Z. Otwinowski, University of Texas, Southwestern Medical Center. The program teXsan is available from Rigaku Co.) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-141764, -141765, and -141766. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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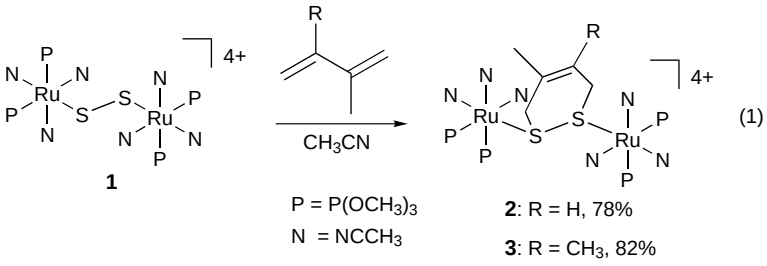
Diels–Alder Type Addition of 1,3-Dienes to a Disulfide Bridging Ligand in Diruthenium Complexes**

Hiroyasu Sugiyama, Yong-Shou Lin, and Kazuko Matsumoto*

Carbon–sulfur bond formation and C–S bond cleavage reactions have been the focus of research for several years because of their relevance to the biologically related metallo-sulfide proteins, the industrially important hydrodesulfurization (HDS) process, and the organic synthesis of sulfur-containing compounds.[1] Reactions of transition metal sulfides with unsaturated organic substrates, such as alkynes, alkenes, and nitriles, have been reported, in which [2+3] cycloadditions occur between $M(S)_2$ and C–X double or triple bonds (X = C or N) to give metalacycles.[2] The addition of olefins to a bridging sulfide ligand in the dimolybdenum complex has also been reported.[3] Nevertheless, to the best of our knowledge, the reaction of transition metal sulfides with dienes has not been reported. It is well known that in the HDS process thiophene is converted into butadiene and hydrogen sulfide.[3d, 4] As a reverse reaction of the HDS process, the treatment of dienes with sulfur is especially noteworthy on transition metal centers. In our recent studies on the Ru_2S_2 core chemistry in the disulfide-bridged diruthenium complexes,[5] we found that $[\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}_2(\mu\text{-}S_2)]^{4+}$ (**1**, as CF_3SO_3 salt) reacts with unsaturated organic molecules, such as ketones and terminal olefins, to form C–S bonds on the disulfide ligand via the C–H bond activation reaction.[6] These are very rare processes and only one analogous C–S bond formation reaction can be found in the literature: The reaction of acetone with a terminal sulfide ligand,[7] which, however, seems to have been found by chance and no systematic study was carried out. Through our recent study of new reactions, we have found that the S_2 ligand in the electron-deficient Ru^{III} complex **1** and its analogues is activated to achieve C–H bond splitting both through electronic and steric effects. In our previous reports, we suggested that the addition of a C–H bond to the S=S double bond is the key step in the C–H bond activation process of acetone and monoolefins.[6b,c] In the present report, we demonstrate directly the double bond character of the S=S bond between the two Ru centers by isolating the [2+4] cycloaddition products from the reaction of **1** with dienes.

Treatment of **1** with a conjugated diene, such as isoprene or 2,3-dimethylbutadiene in CH_3CN at room temperature, resulted in the formation of a pale yellow solution, from which $[\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}_2\{\mu\text{-}SCH_2C(R)=C(CH_3)\text{-}CH_2S\}]^{4+}$ (**2**, as CF_3SO_3 salt, R = H, 78%; **3**, as CF_3SO_3 salt, $R = CH_3$, 82%) was obtained after standard work-up [Eq. (1)]. When the complex **1** was treated with 1,3-pentadiene, a similar color change was observed, however, the product was a mixture according to the ^1H NMR spectrum. Separation of these products was not successful. Furthermore, the reaction of **1** with 2,4-hexadiene was also examined but no sign of the C–S bond formation was observed: Only $[\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}_2(\mu\text{-}S_2)](CF_3SO_3)_3$[5a] was recovered. Therefore, it seems that the C–S bond formation reaction of **1** needs at least one of the two double bonds at the terminal position. The structure of **3** was determined by X-ray diffraction, as shown in Figure 1.[8, 10]



1 (1)

Analogously, the reaction of the dicationic complex $[\{Ru[P(OCH_3)_3]_2(CH_3CN)\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]^{2+}$ (**4**, as CF_3SO_3 salt) with 2,3-dimethylbutadiene gave $[\{Ru[P(OCH_3)_3]_2(CH_3CN)\}_2\text{-}\{\mu\text{-}SCH_2C(CH_3)=C(CH_3)CH_2S\}(\mu\text{-}Cl)_2]^{2+}$ (**5**, as CF_3SO_3 salt)

[*] Prof. Dr. K. Matsumoto, H. Sugiyama, Dr. Y.-S. Lin
Department of Chemistry
Advanced Research Center for Science and Engineering
Waseda University
3-4-1, Ohkubo, Shinjuku, Tokyo 169-8555 (Japan)
Fax: (+81) 3-5273-3489
E-mail: kmatsu@mn.waseda.ac.jp

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