[9] F. Jérôme, C. P. Gros, C. Tardieux, J. M. Barbe, R. Guilard, *New J. Chem.* **1998**, *22*, 1327–1329.

[10] S. Licoccia, R. Paolesse in *Metal Complexes with Tetrapyrrole Ligands III, Vol. 84* (Ed.: J. W. Buchler), Springer, Berlin, **1995**, pp. 71–133.

[11] J. L. Sessler, S. J. Weghorn, *Tetrahedron Organic Chemistry Series, Vol. 15* (Eds.: J. E. Baldwin, P. D. Magnus), Pergamon, Oxford, **1997**, pp. 11–125.

[12] Z. Gross, N. Galili, I. Saltsman, *Angew. Chem.* **1999**, *111*, 1530–1533; *Angew. Chem. Int. Ed.* **1999**, *38*, 1427–1429.

[13] T. Boschi, S. Licoccia, R. Paolesse, P. Tagliatesta, M. Azarnia Tehran, G. Pelizzi, F. Vitali, *J. Chem. Soc. Dalton Trans.* **1990**, 463–468.

[14] R. Guilard, C. P. Gros, F. Bolze, F. Jérôme, Z. Ou, J. Shao, K. M. Kadish, unpublished resustls.

[15] T. Ohta, H. Takaya, R. Noyori, *Inorg. Chem.* **1988**, *27*, 566–569.

[16] Physical data: M.p. >350 °C; ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 8.78$ (s, 1H; H-10), 8.67 (s, 2H; H-5, H-15), 3.95 (m, 4H; H-2a, H-18a), 3.83 (q, 4H; H-3a, H-17a), 3.65 (m, 4H; H-8a, H-12a), 1.87 (t, 6H; H-2b, H-18b), 1.74 (t, 6H; H-3b, H-17b), 1.71 (s, 6H; H-7a, H-13a), 1.64 (t, 6H; H-8b, H-12b); ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 140.1$, 138.O, 136.8, 136.0, 134.9, 131.5, 129.9, 129.1, 95.6 (C-10), 93.2 (C-5, 15), 21.1, 20.2, 20.1, 19.3, 17.8, 11.9; MALDI/TOF MS (%) m/z: 1186.53 (100), calcd for $C_{66}H_{78}N_8{}^{102}Ru_2$: 1186.45; IR (KBr): $\tilde{\nu} = 2962$ (CH), 2927 (CH), 2896 (CH), 1610, 1450, 1059, 822 cm^{-1}; UV/Vis (CH$_2$Cl$_2$) : λ_{max}[nm](ε) = 336 (103295), 393 (59071), 521 (15481); elemental analysis calcd (%) for $C_{66}H_{78}N_8Ru_2$: C 66.87, H 6.63, N 9.45; found: C 66.93, H 6.69, N 9.50.

[17] X-ray data: $C_{66}H_{78}Ru_2N_8$, crystals were obtained by slow diffusion of methanol in dichloromethane; crystal dimensions 0.40 × 0.38 × 0.10 mm, monoclinic $P2_1/c$, $a = 14.2080(8)$, $b = 13.6160(8)$, $c = 16.1907(7)$ Å, $\beta = 113.322(3)°$, $V = 2876.3(3)$ Å^3, $Z = 2$; $\rho_{calcd} = 1.369$ g cm^{-3}, μ(Mo) = 5.73 cm^{-1}. The measurement of the reflection intensities was carried out on a Enraf-Nonius Kappa-CCD diffractometer ($T = 112(2)$ K, Mo$_{K\alpha}$ radiation $\lambda = 0.71073$ Å); ϕ and ω scans with κ offsets; $2\theta_{max} = 55°$; 15324 measured reflections ($R_{int} = 0.053$). The structure was solved with direct methods and refined with F^2 against all independently observed reflections (4507); heavy atoms with anisotropic, H atoms with isotropic temperature factors); $R1 = 0.0957$, $wR2 = 0.2476$ (for $I > 2\sigma(I)$; total number of parameters 351, $\Delta\rho_{max} = 1.051$ e Å^{-3}, $\Delta\rho_{min} = -0.553$ e Å^{-3}. The programs used for solving and refinement of the structure were SHELXS-97 and SHELXL-97 (G. M. Sheldrick, University of Göttingen) respectively. 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-141388. 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).

[18] V. Schumaker, K. N. Trueblood, *Acta Crystallogr. Sect. B* **1968**, *24*, 63.

[19] X. E. He, B. M. Craven, *Acta Crystallogr. Sect. A* **1993**, *49*, 10.

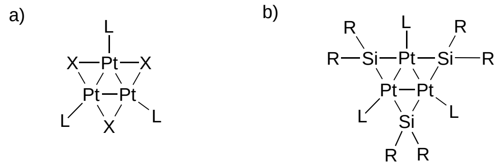
[20] J. P. Collman, S. T. Harford, *Inorg. Chem.* **1998**, *37*, 4152–4153.

[21] B. Billier, F. Jérôme, J. M. Barbe, R. Guilard, unpublished results.

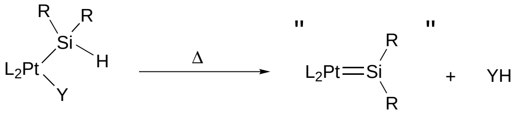
A Triangular Triplatinum Complex with Electron-Releasing SiPh$_2$ and PMe$_3$ Ligands: [{Pt(μ-SiPh$_2$)(PMe$_3$)}$_3$]**

Kohtaro Osakada,* Makoto Tanabe, and Tomoaki Tanase

Triangular complexes composed of three zerovalent transition metal centers are among the most extensively studied cluster compounds. The trinuclear Pt^0 complexes reported so far contain bridging CO or CNR ligands, which have significant π-acceptor character and stabilize complexes with low-valent metal centers (Scheme 1a).[1] Organosilyl ligands have not been commonly used as ligands for these cluster compounds, partly because of the mismatched coordination of a ligand having a significant σ-donor character and negligible π-acceptor capability with electron-rich metal centers. The electronic state and structure of Pt^0 complexes with organosilyl ligands would be of significant interest, but they have not yet been prepared.[2, 3] Since the target structure in Scheme 1b is a trimeric form of a platinum–silylene complex, a synthetic approach that uses such species as precursors might be successful. Owing to their intrinsic instability,[4, 5] mononuclear platinum–silylene complexes were obtained only by using well-designed precursors; however, they were postulated to arise by α-elimination from dialkyl- or diarylsilyl complexes of platinum (Scheme 2).[6, 7] We chose a diaryl-



Scheme 1. Triangular trinuclear complexes of platinum: a) known complexes, where X = CO, CNR, or other neutral ligands; b) target complexes with organosilyl ligands.



Scheme 2. Postulated formation of mononuclear platinum–silylene complexes by α-elimination.

---

[*] Prof. Dr. K. Osakada, M. Tanabe
Research Laboratory of Resources Utilization
Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku, Yokohama 226-8503 (Japan)
Fax: (+81) 45-924-5224
E-mail: kosakada@res.titech.ac.jp

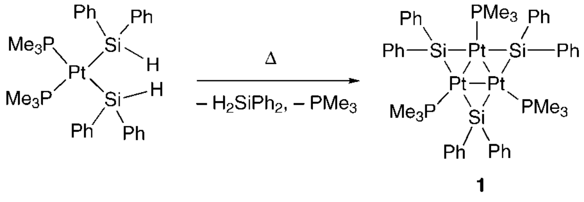
Prof. T. Tanase
Department of Chemistry, Nara Women's University
Kitauoya-higashi-machi, Nara 630-8285 (Japan)

[**] This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas, "Molecular Physical Chemistry", from the Ministry of Education, Science, Culture, and Sports, Japan (11166221). We thank Dr. Tadashi Yamaguchi and Prof. Tasuku Ito, Tohoku University, and Dr. Michikazu Hara and Prof. Kazunari Domen, Tokyo Institute of Technology, for ^{195}Pt NMR and X-ray photoelectron spectroscopy measurements, respectively, as well as for helpful discussions.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

silylplatinum complex as the precursor for a trinuclear Pt^0 cluster with bridging silylene ligands.

Heating $[Pt(SiHPh_2)_2(PMe_3)_2]$[8] at 100 °C gave **1**, which was isolated as red crystals [Eq. (1)].[9] The accompanying formation of H_2SiPh_2 and a smaller quantity of $HSiPh_3$ was observed during the reaction. The reaction mixture also contained $[(Me_3P)_2Pt(Ph_2SiOSiPh_2)]$ (**2**), which can be attributed to the reaction of adventitious oxygen with a disilene Pt complex generated in situ.[10] Figure 1 shows the molecular structure of **1**, as determined by X-ray crystallography.[11] The three Pt centers form a triangle with Pt–Pt distances of 2.697–2.716 Å and Pt-Pt-Pt angles of 59.6–60.3°. The metal–metal distances are similar to those in analogous trinuclear Pt^0 complexes with bridging CNR and CO ligands and suggest the presence of Pt–Pt bonds. Interaction between transition metals with d^{10} configurations was proposed to account for the structure and electronic state of multinuclear complexes of Pd^0, Pt^0, and Cu^I. The acute Pt-Si-Pt angles (70.0–70.4°) and the almost perpendicular orientation of the phenyl substituents with respect to the coordination plane are similar to other silylene-bridged transition metal complexes.



(1)

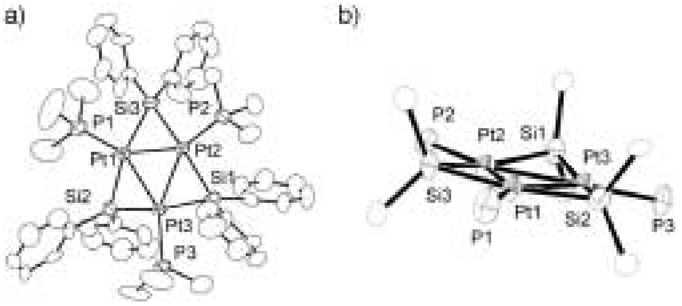


Figure 1. a) Top view and b) side view of the X-ray structure of **1**. Selected bond lengths [Å] and angles [°]: Pt1-Pt2 2.716(1), Pt1-Pt3 2.713(1), Pt2-Pt3 2.697(1), Pt1-P1 2.243(5), Pt2-P2 2.226(5), Pt3-P3 2.247(4), Pt1-Si2 2.364(5), Pt1-Si3 2.357(5), Pt2-Si1 2.355(5), Pt2-Si2 2.345(5), Pt3-Si3 2.343(5), Pt3-Si1 2.337(5); Pt1-Pt2-Pt3 60.17(3), Pt2-Pt3-Pt1 60.27(3), Pt3-Pt1-Pt2 59.57(3), Pt1-Pt2-Si2 55.1(1), Pt2-Pt1-Si2 54.5(1), Pt2-Pt3-Si1 55.2(1), Pt3-Pt2-Si1 54.6(1), Pt1-Pt3-Si3 55.0(1), Pt3-Pt1-Si3 54.5(1), Si2-Pt1-Si3 167.0(2), Si1-Pt2-Si2 163.4(2), Si3-Pt3-Si1 164.1(2), Si2-Pt1-P1 94.0(2), Si3-Pt1-P1 98.0(2), Si1-Pt2-P2 95.0(2), Si2-Pt2-P2 94.9(2), Si1-Pt3-P3 94.6(2), Si3-Pt3-P3 96.6(2), Pt1-Si2-Pt2 70.4(1), Pt2-Si3-Pt3 70.5(1), Pt2-Si1-Pt3 70.2(1).

The satellite signals of the PMe_3 hydrogen atoms in the ^1H NMR spectrum exhibit both three- and four-bond Pt–H coupling ($^3J_{Pt,H} = 43$, $^4J_{Pt,H} = 25$ Hz). The $^{31}P\{^1H\}$ NMR spectrum (Figure 2) exhibits long-range $^{31}P-^{195}Pt$ and $^{31}P-^{31}P$ coupling. The presence of significantly stable Pt–Pt bonds, confirmed from the crystallographic and spectroscopic data, seems to be more consistent with Pt^0 rather than the alternative Pt^{II} formulation.[12]

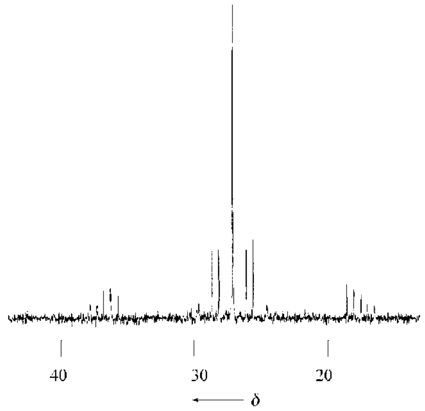


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of **1** (160 MHz at 25 °C in $[D_6]$benzene).

Complex **1** contains $SiPh_2$ and PMe_3 ligands, both of which are strongly electron donating, and is expected to have a unique electronic state. Modeling the electronic state of **1** by extended Hückel molecular orbital calculations on the C_{3v} model complex $[Pt_3(PH_3)_3(\mu\text{-}SiH_2)_3]$ (**I**) gave results that were consistent with the above structure.[13] The electronic structure of **I** was consistent with the proposed 42-valence-electron cluster in which three Pt centers are bound with metal–metal bonds, in a similar manner to that observed in $[Pt_3(PH_3)_3(\mu\text{-}CNH)_3]$ (**II**).[14, 15] The Pt–Pt bond overlap population in **I** (0.24) is comparable to that in **II** (0.20), whereas the energy of the HOMO is higher than that of the isocyanide complex **II** due to significant mixing of Si p orbitals.

Experimental Section

1: A solution of $[Pt(SiHPh_2)_2(PMe_3)_2]$ (405 mg, 0.57 mmol) in toluene (20 mL) was heated for 24 h at 100 °C. The color of the solution changed from yellow to dark red. Analysis of the solution by ^1H NMR spectroscopy showed the formation of H_2SiPh_2 and a smaller amount of $HSiPh_3$. After evaporation of the solvent, hexane was added to the residue. This resulted in separation of an orange solid, which was repeatedly recrystallized from toluene/hexane to afford **1** as red crystals (96 mg, 28 %). Cooling the hexane filtrate obtained after separation of **1** yielded **2** as pale yellow crystals (34 %).

Received: March 14, 2000
Revised: August 21, 2000 [Z14848]

---

[1] a) D. Imhof, L. M. Venanzi, *Chem. Soc. Rev.* **1994**, *23*, 185; b) G. Longoni, M. Manassero, M. Sansoni, *J. Am. Chem. Soc.* **1980**, *102*, 7973; c) R. G. Goel, W. O. Ogini, R. C. Srivastava, *J. Organomet. Chem.* **1981**, *214*, 405; d) A. Moor, P. S. Pregosin, L. M. Venanzi, *Inorg. Chim. Acta* **1981**, *48*, 153; e) A. Moor, P. S. Pregosin, L. M. Venanzi, *Inorg. Chim. Acta* **1982**, *61*, 135; f) J. C. Jeffery, I. Moore, M. Murray, F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* **1982**, 1741; g) A. Moor, P. S. Pregosin, L. M. Venanzi, A. J. Welch, *Inorg. Chim. Acta* **1984**, *85*, 103; h) C. E. Briant, D. I. Gilmour, D. M. P. Mingos, R. W. M. Wardle, *J. Chem. Soc. Dalton Trans.* **1985**, 1693; i) K. Takahashi, Y. Yamamoto, K. Matsuda, H. Yamazaki, *Electrochim. Acta* **1988**, *33*, 1489; j) G. Ferguson, B. R. Lloyd, R. J. Puddephat, *Organometallics* **1986**, *5*, 344; k) R. A. Burrow, D. H. Farrer, J. J. Irwin, *Inorg. Chim. Acta* **1991**, *181*, 65.

[2] For germylene and stannylene Pt^0 complexes, see: G. K. Campbell, P. B. Hitchcock, M. F. Lappert, M. C. Misra, *J. Organomet. Chem.* **1985**, *289*, C1; P. B. Hitchcock, M. F. Lappert, M. C. Misra, *J. Chem. Soc. Chem. Commun.* **1985**, 863.

[3] A trinuclear Pt complex with a trialkoxysilyl ligand and phosphane and bridging phosphido ligands was recently prepared and characterized by X-ray crystallography: R. Bender, P. Braunstein, S.-E. Bouaoud, N. Merabet, D. Rouag, P. Zanello, M. Fontani, *New. J. Chem.* **1999**, *23*, 1045.

[4] a) G. P. Mitchell, T. D. Tilley, *Angew. Chem.* **1998**, *110*, 2602; *Angew. Chem. Int. Ed.* **1998**, *37*, 2524; b) G. P. Mitchell, T. D. Tilley, *J. Am. Chem. Soc.* **1998**, *120*, 7635.

[5] F. Ozawa, M. Kitaguchi, H. Katayama, *Chem. Lett.* **1999**, 1289.

[6] K. Yamamoto, H. Okinoshima, M. Kumada, *J. Organomet. Chem.* **1970**, *23*, C7; K. Yamamoto, H. Okinoshima, M. Kumada, *J. Organomet. Chem.* **1971**, *27*, C31.

[7] a) Y. Uchimaru, A. Mouneer, M. E. Sayed, M. Tanaka, *Organometallics* **1993**, *12*, 2065; b) T. Kobayashi, T. Hayashi, H. Yamashita, M. Tanaka, *Chem. Lett.* **1988**, 1411.

[8] Y.-J. Kim, J.-I. Park, S.-C. Lee, K. Osakada, M. Tanabe, J.-C. Choi, T. Koizumi, T. Yamamoto, *Organometallics* **1999**, *18*, 1349.

[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$_2$SiOSiR$_2$)] (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**.

[13] a) R. Hoffman, *J. Chem. Phys.* **1963**, *39*, 1397; b) R. Hoffmann, W. N. Lipscomb, *J. Chem. Phys.* **1962**, *36*, 2179; c) R. Hoffmann, W. N. Lipscomb, *J. Chem. Phys.* **1962**, *36*, 3489; d) C. Mealli, D. Proserpio, *J. Chem. Educ.* **1990**, *67*, 399.

[14] a) D. J. Underwood, R. Hoffmann, K. Tatsumi, A. Nakamura, Y. Yamamoto, *J. Am. Chem. Soc.* **1985**, *107*, 5968; b) T. Tanase, T. Horiuchi, Y. Yamamoto, K. Kobayashi, *J. Organomet. Chem.* **1992**, *440*, 1.

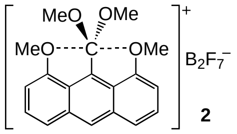
[15] The molecular orbital diagram is available as Supporting Information.

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

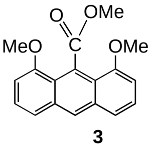
Makoto Yamashita, Yohsuke Yamamoto,
Kin-ya Akiba,[*] and Shigeru Nagase

Hypervalent pentacoordinate boron compounds (10-B-5)[1] have been postulated as transition states in S$_N$2-type reactions at a boron atom. For example, the reaction of the [BH$_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.

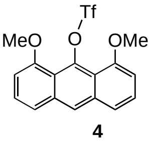
Recently, we reported the synthesis and the X-ray structure of the hypervalent five-coordinate carbon compound (10-C-5) **2** through the use of an 1,8-dimethoxy-9-anthracenyl ligand.[5] Ester **3** was synthesized from the 9-OTf derivative **4** (OTf = trifluoromethanesulfonate) by carbon monoxide insertion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



2



3



4

---

[*] 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)

[**] This work was supported by a Grant-in-Aid for Scientific Research (Nos. 09239103, 11166248, and 11304044) from the Ministry of Education, Science, Sports, and Culture of the Japanese Government.