[8] J. P. Wolfe, S. Wagaw, S. L. Buchwald, *J. Am. Chem. Soc.* **1996**, *118*, 7215–7216.

[9] For a structurally characterized example, see K. Burgess, B. F. G. Johnson, J. Lewis, P. R. Raithby, *J. Chem. Soc. Dalton Trans.* **1982**, 263–269.

[10] S. Gambarotta, M. Basso-Bert, C. Floriani, C. Gaustini, *J. Chem. Soc. Chem. Commun.* **1982**, 374–375.

[11] S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, *Inorg. Chem.* **1983**, *22*, 2029–2034.

[12] This complex was prepared in a similar fashion to **1a**. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C, TMS): $\delta = 8.52$ (pseudo q, $J = 9$ Hz, 4H), 7.88 (m, 4H), 6.65–7.45 (m, 25H), 6.44 (d, $^3J_{H,H} = 7.2$ Hz, 2H), 4.98 (br s, 1H), 4.23 (s, 1H), 4.09 (s, 1H), 3.96 (s, 1H), 3.93 (s, 1H), 3.78 (s, 1H), 3.73 (s, 1H), 3.68 (s, 1H), 2.66 (s, 3H); in addition, a ratio of 0.5 toluene molecules per **1b** molecule was determined; ^{31}P{^{1}H} NMR (122 MHz, [D$_6$]benzene, 25 °C, 85% H$_3$PO$_4$): $\delta = 27.22$ (d, $^2J_{P,P} = 30.6$ Hz), 13.97 (d $^2J_{P,P} = 30.6$ Hz); IR(Nujol) $\tilde{\nu}_{N-H} = 3224$, $\tilde{\nu}_{C=N} = 1571$, 1594 cm^{-1}.

[13] Crystal structure analysis of **1b**: space group $P\bar{1}$ (no. 2), $a = 13.36(1)$, $b = 18.30(2)$, $c = 10.04(1)$ Å, $\alpha = 103.26(9)$, $\beta = 91.85(9)$, $\gamma = 78.32(8)^\circ$, $V = 2339(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.39$ g cm^{-3}, $2\theta_{max} = 50.0^\circ$, Mo$_{K\alpha}$ ($\lambda = 0.71069$ Å), $\omega - 2\theta$, 8.0° min^{-1} (in ω), $(1.26 + 0.3\tan\theta)^\circ$, −105 °C, 8616 reflections with 8231 unique. The data were corrected for Lorentz and polarization factors. No absorption correction was applied. The structure was solved by direct methods and refined with Fourier techniques and teXan software. Number of observations ($I > 3.00\sigma(I)$) 3147 and number of variables 577. H atoms were included but not refined. $R = 0.056$, $wR = 0.64$, refined against $|F|$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101249. 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).

[14] P. A. S. Smith, *Derivatives of Hydrazone and other Hydronitrogens Having N-N Bonds*, Benjamin, Reading, MA, **1983**, p. 46.

[15] M. S. Driver, J. F. Hartwig, *J. Am. Chem. Soc.* **1996**, *108*, 4206–4207.

[16] G. Mann, J. Hartwig, *J. Am. Chem. Soc.* **1996**, *118*, 13109–13110.

[17] M. S. Driver, J. F. Hartwig, *Organometallics* **1997**, *16*, 5706–5715.

[18] This complex was prepared in similar fashion to the *p*-*t*Bu analogue.

[19] G. Mann, M. S. Driver, J. F. Hartwig, *J. Am. Chem. Soc.* **1998**, *120*, 827–828.

[20] A recent synopsis of these mechanisms and their accompanying data is included in C. Amatore, F. Pfluger, *Organometallics* **1990**, *9*, 2276–2282.

[21] J. P. Wolfe, S. L. Buchwald, *Tetrahedron Lett.* **1997**, *38*, 6359–6362.

[22] B. C. Hamann, J. F. Hartwig, *J. Am. Chem. Soc.* **1998**, in press.

[23] J. March, *Advanced Organic Chemistry*, 3rd ed., Wiley, New York, **1985**.

[24] M. Busch, S. Schäffner, *Chem. Ber.* **1923**, *56*, 1612–1616.

[25] Note added in proof (July 22, 1998). Buchwald et al. have recently reported a variety of indoles prepared by the hydrazone arylation strategy. S. Wagaw, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **1998**, *120*, 6621–6622.

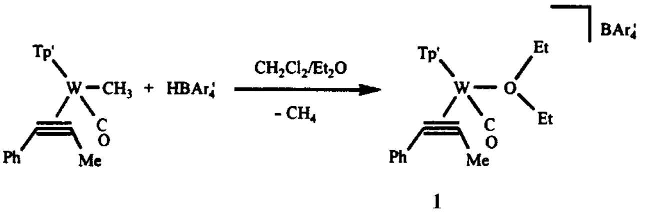
Spectra, Structure, Ligand Exchange, and Decomposition of a Tungsten(II) Ether Complex[**]

Thomas Brent Gunnoe, Jennifer L. Caldarelli, Peter S. White, and Joseph L. Templeton[*]

Ether ligands can reversibly bind to Lewis acidic metal moieties and thus stabilize reactive metal fragments and provide useful precursors for catalysts.[1–6] Ether complexes of the Group 6 elements[6–11] have been prepared from alkylidene complexes[7, 8] and by protonation of [WCp*(CO)$_3$(Me)] (Cp* = C$_5$Me$_5$) with HBAr$'_4$ in Et$_2$O.[9, 10] Addition of acid to [WCp(H)(CO)$_3$] (Cp = C$_5$H$_5$) and benzaldehyde dimethyl acetal gives the ether complex [WCp(CO)$_3$(PhCH$_2$OMe)][X] (X = CF$_3$SO$_3^-$, BAr$'_4$; Ar′ = 3,5-bis(trifluoromethyl)phenyl).[11] The synthesis of diethyl ether and dimethyl ether complexes of rhenium is also pertinent.[12]

We have now synthesized [WTp′(CO)(OEt$_2$)(PhC≡CMe)]-[BAr$'_4$] (**1**; Tp′ = hydridotris(3,5-dimethylpyrazol-1-yl)borate). To determine whether **1** is a convenient precursor for the reactive fragment [WTp′(CO)(PhC≡CMe)]$^+$,[13] we studied the substitution of the labile ether ligand by acetonitrile and the decomposition of **1** in dichloromethane.

Reaction of [WMeTp′(CO)(PhC≡CMe)][14] with HBAr$'_4$ in CH$_2$Cl$_2$/Et$_2$O (ca. 2/1) yields **1** in 70% yield [Eq. (a)].



(a)

Formation of **1** is accompanied by a color change from dark blue to light blue, and the CO stretching frequency increases from 1875 to 1923 cm^{-1}. Complex **1** is stable for days at room temperature in dichloromethane in the presence of an excess of diethyl ether. However, if no excess of diethyl ether is present, **1** decomposes rapidly (ca. 2 h, see below). In the solid state, **1** is stable for weeks in air and indefinitely under an inert atmosphere.

The ^{1}H NMR spectrum of **1** in CD$_2$Cl$_2$ at −80 °C reflects restricted rotation about the tungsten–ether bond. Thus, four multiplets are observed for the four methylene protons of the ether ligand in the range $\delta = 3-5$. Each multiplet consists of five lines, and this is consistent with nearly equal geminal and vicinal coupling constants ($^2J_{HH} \approx {}^3J_{HH} \approx 7$ Hz). Two triplets are observed for the methyl groups of the coordinated ether. The ^{13}C NMR spectrum (−80 °C) displays typical resonances for the ligands (alkyne as four-electron donor) and the

---

[*] Dr. J. L. Templeton, T. B. Gunnoe, J. L. Caldarelli, P. S. White
Department of Chemistry
University of North Carolina at Chapel Hill
Chapel Hill, NC 27599-3290 (USA)
Fax: (+1) 919-962-2388
E-mail: joetemp@unc.edu

[**] This work was supported by the National Science Foundation (grant CHE-9727500). T.B.G wishes to thank the Department of Education for support through a GAANN Fellowship.

$[\mathrm{BAr'_4}]^-$ counterion.[14] The signals of the methylene carbon atoms of the coordinated ether are at $\delta = 80.6$ and 71.9 (each a triplet, $^1J_{\mathrm{CH}} = 145$ Hz).

Recrystallization of **1** ($\mathrm{Et_2O}$/hexanes) provided a crystal suitable for an X-ray diffraction study (Figure 1).[27] The geometric features of the $[\mathrm{WTp'(CO)(PhC{\equiv}CMe)}]^+$ ion are typical of such compounds.[15] The W–O bond length (2.210(4) Å) is similar to those of $[\mathrm{WCp(CO)_3(PhCH_2OMe)}][\mathrm{OTf}]$ (2.206(11) Å) and $[\mathrm{WCp^*(CO)_3(OEt_2)}][\mathrm{BAr'_4}]$ (2.197(7) Å).[9, 11] The W-O5-C6 and W-O5-C8 bond angles are 119.9(4) and 127.4(3)°, respectively. The larger angle perhaps results from the proximity of the ethyl group to the bulky Tp′ ligand.

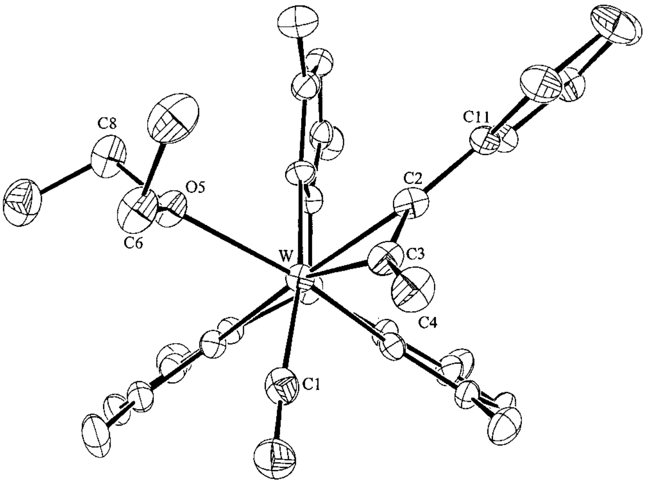


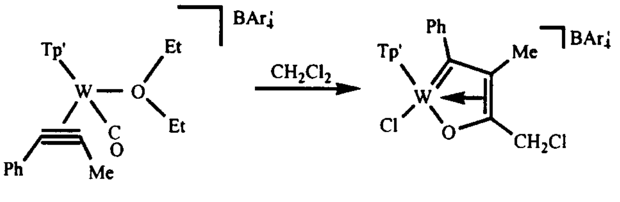
Figure 1. ORTEP diagram of the cation of **1**. Selected bond lengths [Å] and angles [°]: W–O5 2.210(4), W–C2 2.027(6), W–C3 2.073(5), W–C1 1.930(7), O5–C8 1.461(8), O5–C6 1.457(7), C2–C3 1.308(9); W-O5-C8 127.4(3), W-O5-C6 119.9(4), C6-O5-C8 112.8(5), W-C1-O1 176.8(5), W-C2-C11 145.4(4), W-C3-C4 147.3(5).

Dissolution of **1** in $\mathrm{CD_2Cl_2}$ at −78 °C followed by addition of an excess of acetonitrile and warming of the solution to room temperature results in quantitative conversion into $[\mathrm{WTp'(CO)(N{\equiv}CMe)(PhC{\equiv}CMe)}][\mathrm{BAr'_4}]$.[16] The kinetics of this substitution reaction were studied by treating **1** with various amounts of acetonitrile (10–45 equiv) and monitoring the ligand exchange under pseudo-first-order conditions by ^{1}H NMR spectroscopy at 0 °C. Rate constants for the exchange process are invariant with respect to the range of standard deviations; the reaction is zero order in acetonitrile.

In a second series of experiments with 15 equivalents of acetonitrile, the temperature was varied from −5 °C to room temperature. An Eyring plot allowed the determination of activation parameters for this exchange: $\Delta H^{\ddagger} = 74.0(4.6)\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\ddagger} = -15.5(16.3)$ eu. The large enthalpy and small entropy of activation suggest a dissociative mechanism, perhaps an interchange mechanism. Activation parameters for the dissociative exchange of dimethyl sulfide when the complex $[\mathrm{Re(O)(Ph)Tp(OSMe_2)}][\mathrm{OTf}]$ (Tp = hydridotris(pyrazol-1-yl)borate) is treated with free $\mathrm{Me_2S}$ ($\Delta H^{\ddagger} = 67.3\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\ddagger} = -10.9$ eu)[17] resemble the values for nitrile/ether exchange of complex **1**.

An important development in the application of positively charged metal fragments is the use of noncoordinating counterions.[18] Although these counterions can hinder the decomposition of electrophilic metal species, other factors can limit the synthetic application of this class of compounds. An example is the ability of highly electrophilic metal complexes to activate and react with a variety of solvents.

At room temperature in dichloromethane, **1** decomposes to the metallacycle **2** [Eq. (b)]. Monitoring the decomposition of **1** by ^{1}H NMR spectroscopy in $\mathrm{CD_2Cl_2}$ showed nearly quantitative conversion into deuterated **2**.



1 **2**

(b)

An ORTEP diagram of metallacycle **2** is shown in Figure 2.[27] The W–C6 bond length of 1.93(1) Å is consistent with a carbene complex.[19] To achieve an 18-electron count, the unsaturated C2–C4 bond must interact with the tungsten center; indeed, the ring binds to the tungsten through all four atoms. The W–C2 and W–C4 bond lengths of 2.32(1) and 2.29(1) Å, respectively, are within the range of W–C single bonds.[20] The W–O bond length of 2.01(8) Å is consistent with those of other alkoxotungsten complexes.[14] Examples of η^4 metallacycles of this type are sparse[21] relative to the more common η^2 mode of coordination.[22]

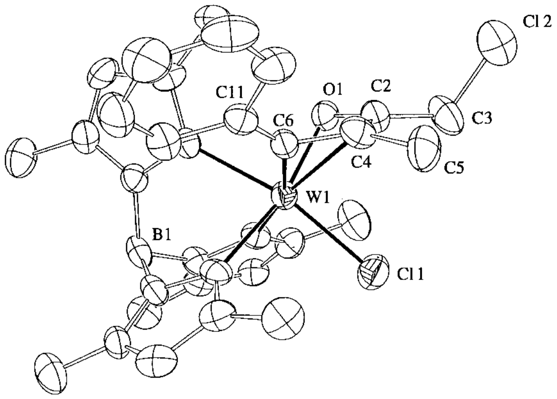
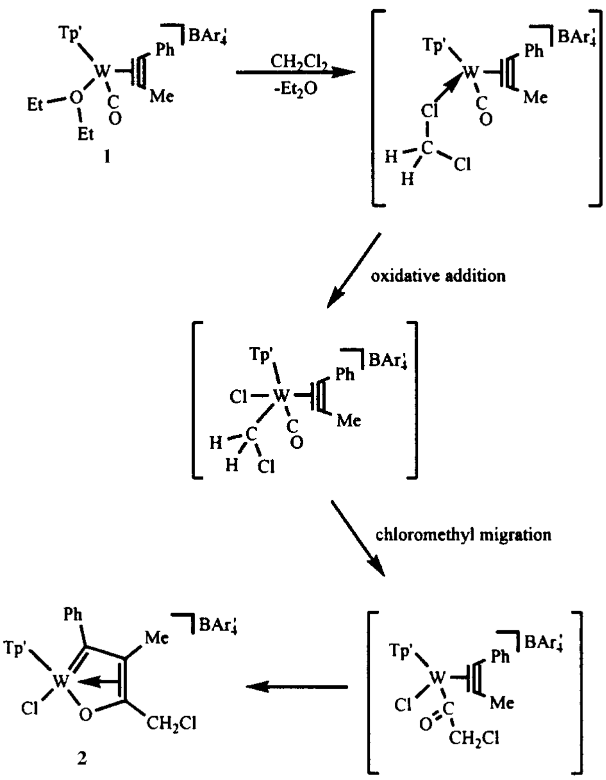


Figure 2. ORTEP diagram of the cation of **2**. Selected bond lengths [Å] and angles [°]: W–O1 2.016(8), W–Cl1 2.311(4), W–C6 1.931(13), W–C4 2.286(12), W–C2 2.321(13), C4–C6 1.392(18), C2–C4 1.437(20), O1–C2 1.379(16); W-C6-C11 147.3(9), W-O1-C2 84.0(7), W-C6-C4 85.3(8).

A plausible mechanism for the formation of **2** is shown in Scheme 1. Dissociation of $\mathrm{Et_2O}$ from **1** would open a coordination site for binding $\mathrm{CH_2Cl_2}$. Formation of an acyl complex by C–Cl bond cleavage and migration of the chloromethyl group to carbon monoxide would form an acyl intermediate. The mechanistic details of this sequence are unknown, although the process could occur by oxidative addition of a C–Cl bond (shown in Scheme 1) or a radical pathway. Since the formation of a seven-coordinate intermediate by oxidative addition is presumably sterically inhibited, such a route is unlikely.[23] However, as has been observed for other metal complexes, labilization of one arm of the Tp′



Scheme 1. Proposed mechanism for formation of metallacycle **2**.

ligand could precede oxidative addition.[24] Coupling of the alkyne and the acyl fragment, known to yield metallacycles in other systems,[21a, b, 25, 26] would form the metallacycle **2**.

In conclusion, we have structurally characterized the unusually stable ether complex [WTp'(CO)(OEt$_2$)(PhC≡CMe)][BAr'$_4$] (**1**), the ether ligand of which can be displaced by acetonitrile. In CH$_2$Cl$_2$, **1** decomposes and reacts with one equivalent of solvent to form a tungsten metallacycle.

Experimental Section

1: In a representative reaction, a dark blue solution of [WMeTp'(CO)(PhC≡CMe)] (0.3365 g) in dichloromethane was cooled to $-78\,^\circ$C and added by cannula to HBAr'$_4$ (0.532 g, 1 equiv) at $-78\,^\circ$C. At the same temperature, an excess of diethyl ether (ca. 15 mL) was added. The solution was then warmed to room temperature, and the solvent removed under reduced pressure. The remaining blue powder was washed with hexanes (2 × 20 mL) and dried under vacuum. Layering a solution of **1** in diethyl ether with hexanes yielded blue crystals in 70% yield. IR (CH$_2$Cl$_2$): $\tilde{\nu}_{CO} =$ 1923 cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 7.70$ (brs, 8H, *o*-H of Ar'), 7.55 (brs, 4H, *p*-H of Ar'), 7.29, 6.59 (m, 5H, Ph), 6.13, 5.88, 5.74 (3s, 3H, C*H* of Tp'), 4.69, 4.39, 3.42, 3.14 (each quint., 4H, $^2J_{HH} = 7$, $^3J_{HH} = 7$ Hz, [W]-O(CH_2CH$_3$)$_2$), 3.80 (3H, PhC$_2$CH_3), 2.70, 2.56, 2.52, 2.46, 1.30, 1.23 (18H, CH_3 of Tp'), 0.98, 0.82 (each t, 6H, $^3J_{HH} = 7$ Hz, [W]-O(CH$_2$CH_3)$_2$); ^{13}C NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 226.5$ (CO); 209.2, 205.0 (PhC$_2$Me), 162.1 (q, $^1J_{BC} = 49$ Hz, *ipso*-C of Ar'), 153.9, 151.8, 150.6, 147.7, 147.6, 145.6 (*C*CH$_3$ of Tp'), 135.0 (*ipso*-C of Ph), 134.3 (*o*-C of Ar'), 130.0, 128.7, 128.4 (*o*-, *m*-, and *p*-C of Ph), 128.2 (q, $^2J_{CF} = 40$ Hz, *m*-C of Ar'), 124.3 (q, $^1J_{CF} =$ 270 Hz, *C*F$_3$), 117.2 (*p*-C of Ar'), 108.2, 108.0, 107.3 (*C*H of Tp'), 80.6, 71.9 (t, $^1J_{CH} = 145$ Hz, [W]-O(*C*H$_2$CH$_3$)$_2$), 22.2, 15.6, 14.9, 14.1, 12.8, 12.7, 12.5, 11.7, 11.5 (C*C*H$_3$ of Tp', alkyne *C*H$_3$, and ether *C*H$_3$); elemental analysis: calcd: C 46.89, H 3.35, N 5.38; found: C 47.10, H, 3.46, N 5.42.

2: ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 7.73$, 7.56 (2s, 8:4, Ar'), 7.55–6.82 (m, 5H, Ph), 6.31, 6.12, 5.55 (3s, 3H, C*H* of Tp'), 5.75 (d, 1H, $^2J_{HH} = 14$ Hz, C*H*HCl), 5.53 (d, 1H, $^2J_{HH} = 14$ Hz), 2.91, 2.71, 2.52, 2.45, 2.35, 1.93, 0.84 (6s, 21H, CCH_3 of Tp', W=C(Ph)-C(CH_3)); ^{13}C NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 254.1$ (α-C of metallacycle), 162.2 (q, $^1J_{BC} = 49$ Hz, *ipso*-C of Ar'), 157.3, 154.6, 152.9, 151.9, 148.5, 147.6 (*C*CH$_3$ of Tp'), 134.6, 130.8, 128.4, 128.2 (Ph of metallacycle), 135.2 (br, *o*-C of Ar'), 129.3 (q, $^2J_{CF} =$ 31 Hz, *m*-C of Ar'), 125.0 (q, $^1J_{CF} = 271$ Hz, *C*F$_3$), 117.9 (br, *p*-C of Ar'), 111.3, 109.8, 109.3 (*C*H of Tp'), 97.8 (β-C of metallacycle), 35.9 (*C*H$_2$Cl), 17.9, 15.1, 15.0, 14.8, 13.3, 13.2, 12.5 (C*C*H$_3$ of Tp' and Me of metallacycle); the signal for the γ-C atom of the metallacycle could not be located due to likely overlap with signals in the phenyl region of the spectrum; elemental analysis: calcd: C 49.06, H 2.82, N 5.34; found: C 49.09, H 2.86, N 5.55%.

Received: October 27, 1997
Revised version: April 22, 1998 [Z11084IE]
German version: *Angew. Chem.* **1998**, *110*, 2207–2210

Keywords: Lewis acids · metallacycles · O ligands · oxidative additions · tungsten

---

[1] a) S. H. Bergens, B. Bosnich, *J. Am. Chem. Soc.* **1991**, *113*, 959–967; b) P. A. White, J. Calabrese, K. H. Theopold, *Organometallics* **1996**, *15*, 5473–5475.

[2] F. C. Rix, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 1137–1138

[3] F. C. Rix, M. Brookhart, P. S. White, *J. Am. Chem. Soc.* **1996**, *118*, 2436–2448.

[4] L. K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 267–268.

[5] L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415.

[6] E. L. Muetterties, E. Band, *J. Am. Chem. Soc.* **1980**, *102*, 6572–6574.

[7] A. S. Gamble, J. M. Boncella, *Organometallics* **1993**, *12*, 2814–2819.

[8] W. M. Vaughan, K. A. Abboud, J. M. Boncella, *Organometallics* **1995**, *14*, 1567–1577.

[9] C. S. Yi, D. Wódka, A. L. Rheingold, G. P. A. Yap, *Organometallics* **1996**, *15*, 2–4.

[10] A similar Cp compound has been reported: K. Sünkel, G. Urban, W. Beck, *J. Organomet. Chem.* **1985**, *290*, 231–240.

[11] J. Song, D. J. Szalda, R. M. Bullock, *J. Am. Chem. Soc.* **1996**, *118*, 11134–11141.

[12] S. K. Agbossou, J. M. Fernández, J. A. Gladysz, *Inorg. Chem.* **1990**, *29*, 476–480.

[13] Review on the chemistry of [WTp'(CO)(RC≡CR')]$^+$ cations: a) J. L. Caldarelli, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1992**, *114*, 10097; b) D. M. Schuster, P. S. White, J. L. Templeton, *Organometallics* **1996**, *15*, 5467; c) M. B. Wells, P. S. White, J. L. Templeton, *Organometallics* **1997**, *16*, 1857; d) T. B. Gunnoe, P. S. White, J. L. Templeton, *Organometallics* **1997**, *16*, 3794; e) T. B. Gunnoe, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1996**, *118*, 6916; f) S. G. Feng, C. C. Philipp, A. S. Gamble, P. S. White, J. L. Templeton, *Organometallics* **1991**, *10*, 3504; g) T. B. Gunnoe, P. S. White, J. L. Templeton, L. Casarrubios, *J. Am. Chem. Soc.* **1997**, *119*, 3171.

[14] J. L. Caldarelli, L. E. Wagner, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1994**, *116*, 2878–2888.

[15] See, for example, a) T. B. Gunnoe, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1996**, *118*, 6916–6923; b) L. W. Francisco, P. S. White, J. L. Templeton, *Organometallics* **1996**, *15*, 5127–5136.

[16] Synthesis of [WTp'(CO)(N≡CMe)(PhC≡CMe)][BF$_4$]: a) S. G. Feng, J. L. Templeton, *J. Am. Chem. Soc.* **1989**, *111*, 6477–6478; b) S. G. Feng, J. L. Templeton, *Organometallics* **1992**, *11*, 1295–1303.

[17] S. N. Brown, J. M. Mayer, *J. Am. Chem. Soc.* **1996**, *118*, 12119–12133.

[18] S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927–942.

[19] See, for example, a) S. G. Feng, P. S. White, J. L. Templeton, *Organometallics* **1993**, *12*, 2131–2139; b) S. G. Feng, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1992**, *114*, 2951–2960.

[20] See, for example, a) R. R. Schrock, R. M. Kolodziej, A. H. Liu, W. M. Davis, M. G. Vale, *J. Am. Chem. Soc.* **1990**, *112*, 4338–4345; b) M. B. O'Regan, A. H. Liu, W. C. Finch, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.* **1990**, *112*, 4331–4338; c) R. R. Schrock, T. E. Glassman, M. G. Vale, M. Kol, *J. Am. Chem. Soc.* **1993**, *115*, 1760–1772; d) A. H. Liu, R. C. Murray, J. C. Dewan, B. D. Santarsiero, R. R. Schrock, *J. Am. Chem. Soc.* **1987**, *109*, 4282–4291.

[21] a) M. Etienne, P. S. White, J. L. Templeton, *Organometallics* **1993**, *12*, 4010–4015; b) M. D. Curtis, J. Real, W. Hirpo, W. M. Butler,

Organometallics **1990**, *9*, 66–74; c) M. Etienne, F. Biasotto, R. Mathieu, J. L. Templeton, *Organometallics* **1996**, *15*, 1106–1112; d) W. Hirpo, M. D. Curtis, *Organometallics* **1994**, *13*, 2706–2712.

[22] J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science, Mill Valley, CA, **1987**, chap. 9, pp. 459–520, and references therein.

[23] See, for example, a) M. D. Curtis, K. Shiu, W. M. Butler, *J. Am. Chem. Soc.* **1986**, *108*, 1550; b) M. D. Curtis, K. Shiu, *Inorg. Chem.* **1985**, *24*, 1213; c) M. D. Curtis, K. Shiu, W. M. Butler, *J. Am. Chem. Soc.* **1986**, *108*, 3335.

[24] a) S. E. Bromberg, H. Yang, M. C. Asplund, T. Lian, B. K. McNamara, K. T. Kotz, J. S. Yeston, M. Wilkens, H. Frei, R. G. Bergman, C. B. Harris, *Science* **1997**, *278*, 260; b) for related chemistry, see D. D. Wick, K. I. Goldberg *J. Am. Chem. Soc.* **1997**, *119*, 10235.

[25] a) C. A. Rusik, M. A. Collins, A. S. Gamble, T. L. Tonker, J. L. Templeton, *J. Am. Chem. Soc.* **1989**, *111*, 2550–2560; b) L. W. Francisco, P. S. White, J. L. Templeton, *Organometallics* **1997**, *16*, 2547.

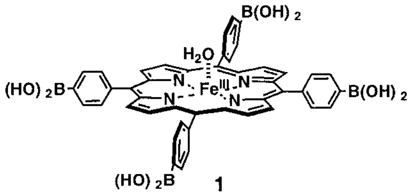
[26] a) H. G. Alt, H. E. Engelhardt, *J. Organomet. Chem.* **1985**, *288*, 165–177; b) P. L. Watson, R. G. Bergman, *J. Am. Chem. Soc.* **1979**, *101*, 2055–2062.

[27] Crystal structure analyses: a) **1**: $C_{61}H_{52}B_2F_{24}O_2N_6W$, $M_r = 1562.54$, triclinic, space group $P\bar{1}$, $a = 12.735(3)$, $b = 13.356(4)$, $c = 20.296(7)$ Å, $\alpha = 73.19(3)$, $\beta = 76.68(3)$, $\gamma = 82.63(2)°$, $Z = 2$, $V = 3208.7(17)$ A^3, $\rho_{calcd} = 1.617\ g\,cm^{-3}$, blue plates, crystal dimensions: $0.45 \times 0.40 \times 0.06\ mm^3$, Rigaku diffractometer, monochromated (graphite) $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 173$ K, $5.00 < 2\theta < 46.00°$. Of 8884 independent reflections measured, 7060 with $I > 2.5\sigma(I)$ were used in the refinement, $R_1 = 0.045$, $R_2 = 0.041$. b) **2**: $C_{58}H_{44}B_2Cl_2F_{24}ON_6W$, $M_r = 1573.35$, monoclinic, space group $C2/c$, $a = 38.016(7)$, $b = 13.562(2)$, $c = 26.329(4)$, $Z = 8$, $V = 12\,856(4)$ A^3, $\rho_{calcd} = 1.626\ g\,cm^{-3}$, blue plates, crystal dimensions: $0.25 \times 0.20 \times 0.20\ mm^3$, Rigaku diffractometer, monochromated (graphite) $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 295$ K, $5.00 < 2\theta < 45.00°$. Of 8396 independent reflections measured, 4661 with $I > 2.5\sigma(I)$ were used in the refinement, $R_1 = 0.048$, $R_2 = 0.052$. c) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101794 (**1**) and CCDC-101793 (**2**). 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).

A Strong Positive Allosteric Effect in the Molecular Recognition of Dicarboxylic Acids by a Cerium(IV) Bis[tetrakis(4-pyridyl)porphyrinate] Double Decker**

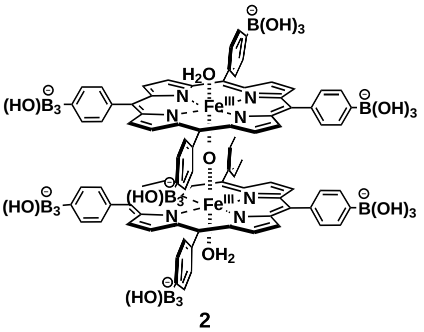
Masayuki Takeuchi, Tomoyuki Imada, and
Seiji Shinkai*

Positive and negative allosteric effects are ubiquitous in nature where biological events must be efficiently regulated in response to chemical or physical signals from the outside world. Typical examples[1–4] are the cooperative binding of dioxygen to hemoglobin,[1] the hexamerization of the arginine repressor,[2] and a cooperative effect that depends on the concentration of arachidonate-containing phospholipids in cytosolic phospholipase A_2.[3] The biomimetic design of such allosteric systems is of great significance for regulating the complexation properties or catalytic activity of artificial receptors by means of allosteric effects.[5] Furthermore, the methodology is very useful for amplifying weak chemical or physical signals and converting them into forms that can be more conveniently measured. Several allosteric systems have been reproduced.[5–7] To the best of our knowledge, however, there is only one precedent for a positive allosteric effect with a large Hill coefficient *n* which involves cooperative binding of saccharides to a cyclic tetrameric resorcinol derivative ($n = 4$).[6]



1

We previously synthesized a porphyrinatoiron(III) complex bearing four boronic acid groups (**1**).[7] The *μ*-oxo dimer **2** is formed from **1** at alkaline pH values and shows extraordinarily high affinity and selectivity for glucose and galactose. However, only one pair of boronic acid groups is used to form 1:1 complexes with saccharides, and the remaining three pairs of boronic acids do not bind saccharides.[7] The strong negative allosterism was attributed to an inclination of the two porphyrin planes, which was induced by the binding of the first saccharide guest. Hence, if the first guest could suppress the rotation of the two porphyrin planes and maintain their parallel arrangement, the second guest should be bound more efficiently, and the system should exhibit positive allosterism.



2

To construct such a porphyrin-based positively allosteric system, we chose a cerium(IV) bis(porphyrinate) double decker,[8, 9] namely, the tetrakis(4-pyridyl)porphyrin derivative **3a**.[8a, f–h] This molecule satisfies our requirements: First, slow rotation of the two porphyrin planes with respect to one another should be possible at room temperature, in analogy to similar cerium(IV) bis(diarylporphyrin) and bis(tetraarylporphyrin) complexes studied by Aida et al.;[9, 10] second, tilting of the two porphyrin planes is more difficult than in **2**; and third, the four pairs of 4-pyridyl groups are available as hydrogen-bond acceptor sites for diols, hydroxycarboxylic acids, and dicarboxylic acids. Compound **3b**, which has only one pair of pyridyl groups, was used as a reference. Compound

---

[*] Prof. S. Shinkai, Dr. M. Takeuchi, Dr. T. Imada
Department of Chemical Science and Technology
Faculty of Engineering, Kyushu University
Fukuoka 812 (Japan)
Fax: (+81) 92-642-3611
E-mail: seijitcm@mbox.nc.kyushu-u.ac.jp

[**] This work was supported by a Grant-in-Aid for COE Research "Design and Control of Advanced Molecular Assembly Systems" from the Ministry of Education, Science and Culture, Japan (#08CE2005).

1433-7851/98/3715-2096 $ 17.50+.50/0