Inorg. Chem. **2002**, *41*, 5326–5328

Inorganic Chemistry
Communication

A Tetranuclear Heterobimetallic Square Formed from the Cooperative Ligand Binding Properties of Square Planar and Tetrahedral Metal Centers

Nathan C. Gianneschi and Chad A. Mirkin*

Department of Chemistry and the Institute for Nanotechnology, Northwestern University,
2145 Sheridan Road, Evanston, Illinois 60208-3113

Lev N. Zakharov and Arnold L. Rheingold

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Received July 15, 2002

Reaction of Rh(I) and Zn(II) metal centers with a ligand containing salicylaldiminato and thioether–phosphine moieties resulted in the formation of a tetranuclear heterobimetallic molecular square. The directionality required to form these structures is imparted by both the tetrahedral and square planar metal centers acting in concert with one another.

The use of coordination chemistry to arrange molecular building blocks has evolved into one of the most useful and flexible strategies for the synthesis of supramolecular structures.[1] However, despite the variety of metals and ligands that have been used to date in the synthesis of molecular squares, there are few examples of systems in which the metals have coordination geometries other than octahedral or square planar.[2] Here, we report the first example of a Rh−Zn heterobimetallic molecular square.

In order to form the square, the novel bifunctional ligand **1** was synthesized in two steps and in 81% overall yield (Supporting Information). Initially, 1-chloro-2-diphenylphosphinoethane and 4-aminothiophenol are coupled to form 4-(2-diphenylphosphanylethylsulfanyl)phenylamine (DPEP). DPEP was further reacted with 3,5-di-*tert*-butyl-1-hydroxybenzaldehyde to form the target ligand **1**. Compound **1** contains a hemilabile thioether−phosphine functional group attached to a salicylaldiminato functional group. These functional groups provide two very different binding moieties that are known to complex a variety of main group and transition metals.[3,4]

Reactions between 2 equiv of **1** and 1 equiv of a mononuclear Rh(I) source followed by addition of a second equivalent of a Zn(II) source results in the formation of **4** in 86% isolated yield (Scheme 1). Significantly, the order of metal addition can be reversed with **4** being obtained in comparable yield. These reactions proceeded at room temperature in dry solvents under an inert atmosphere. Compound **4** was isolated as a mildly air sensitive, but thermally stable (no decomposition observed after 5 days at 80 °C in CH_2Cl_2), yellow microcrystalline solid by recrystallization from CH_2Cl_2/pentane with subsequent drying of the crystals in vacuo.[5]

Intermediates **2** and **3** have been isolated and fully characterized. Compound **2** exhibits a characteristic $^{31}P\{^{1}H\}$ NMR resonance at δ 64.6 ($J_{RhP} = 161.6$ Hz), diagnostic of

---

* Author to whom correspondence should be addressed. E-mail: CAMirkin@chem.northwestern.edu.

(1) For recent reviews, see: (a) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975−982. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853−907. (c) Swiegers, G. F.; Malefetse, T. J. *Chem Rev.* **2000**, *100*, 3483−3538. (d) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022−2043. (e) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759−771. (f) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509−518.

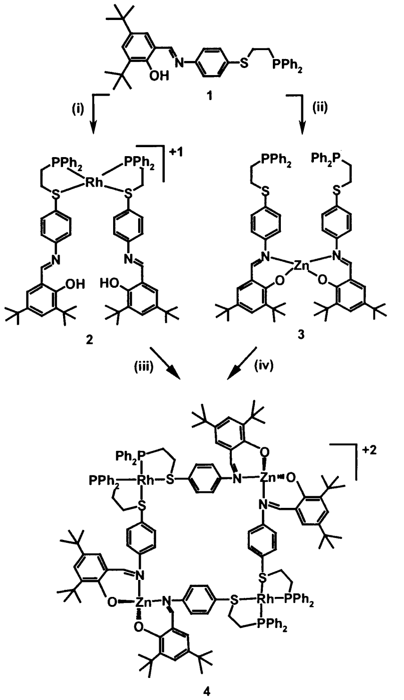
(2) Stang, P. J.; Persky, N. E. *Chem. Commun.* **1997**, 77−78.

(3) For recent examples of salicylaldiminato complexes, see: (a) Gibson, V. C.; Mastroianni, S.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2000**, 1969−1971. (b) Strauch, J.; Warren, T. H.; Erker, G.; Frohlich, R.; Saarenketo, P. *Inorg. Chim. Acta* **2000**, *300−302*, 810−821. (c) Tian, J.; Coates, G. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3626−3629. (d) Darensbourg, D. J.; Rainey, P.; Yarbrough, J. *Inorg Chem.* **2001**, *40*, 986−993. (e) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Matsukawa, N.; Takagi, Y.; Tsuru, K.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2001**, *123*, 6847−6856. (f) Emslie, D. J.; Piers, W. E.; Macdonald, R. *J. Chem. Soc., Dalton Trans.* **2002**, 293−294.

(4) (a) Farrell, J. R.; Mirkin, C. A.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1998**, *120*, 11834−11835. (b) Farrell, J. R.; Mirkin, C. A.; Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 465−467. (c) Farrell, J. R.; Eisenberg, A. H.; Mirkin, C. A.; Guzei, I. A.; Liable-Sands, L. M.; Incarvito, C. D.; Rheingold, A. L.; Stern, C. L. *Organometallics* **1999**, *18*, 4856−4868. (d) Holliday, B. J.; Farrell, J. R.; Mirkin, C. A.; Lam, K.-C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1999**, *121*, 6316−6317. (e) Dixon, F. M.; Eisenberg, A. H.; Farrell, J. R.; Mirkin, C. A.; Liable-Sands, L. M.; Rheingold, A. L. *Inorg. Chem.* **2000**, *39*, 3432−3433. (f) Eisenberg, A. H.; Dixon, F. M.; Mirkin, C. A.; Stern, C. L.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **2001**, *20*, 2052−2058.

10.1021/ic025875o CCC: $22.00

Scheme 1. The Synthesis of **2**−**4**[a]



[a] All reactions performed at 25 °C. All counterions are BF_4^-. Reagents, conditions, and yields: (i) $^1/_2$Rh(COE)$_2$BF$_4$, THF/CH$_2$Cl$_2$, 90%; (ii) $^1/_2$Et$_2$Zn, THF, 95%; (iii) Et$_2$Zn, THF, 95%; (iv) Rh(COE)$_2$BF$_4$, THF/CH$_2$Cl$_2$, 90%.

a *cis*-phosphine/*cis*-thioether complex, and compound **3** exhibits a resonance at δ −16.6, assigned as free phosphine (**1** has a resonance comparable to that of **3** at δ −16.4). The solution structure and purity of the molecular square **4** have been confirmed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, elemental analysis, and ES-MS. The ^{31}P{^{1}H}NMR spectrum of **4** exhibits the diagnostic resonance at δ 65.2 (J_{Rh-P} = 162.6 Hz) for a *cis*-phosphine/*cis*-thioether complex of Rh(I), which compares well with the ^{31}P{^{1}H} NMR resonance observed for **2**. In addition, the solid-state structure of **4** has been determined by a single-crystal X-ray diffraction study (Figure 1).[6]

The solid-state structure of **4** shows the two square planar Rh(I) centers and two distorted tetrahedral Zn(II) centers, bound by four ligands. The square is slightly distorted and is defined by a Rh−Rh distance of 11.90 Å and a Zn−Zn distance of 11.48 Å, with Rh−Zn edge distances of 8.53 Å.

The *cis*-phosphine/*cis*-thioether arrangement of the ligands around the Rh center is crucial in enforcing the directionality of the ligand. The use of this arrangement in the formation of large Rh(I) bimetallic macrocycles and homotetranuclear squares has recently been demonstrated by our group.[4,7] This approach has allowed us to synthesize large and diverse supramolecular species from a range of flexible ligands.[8] However, here the molecule's shape is facilitated by two very different types of ligand−metal interactions. The bifunctional ligand **1** is capable of specifically binding Zn(II) in the salicylaldiminato portion of the ligand and Rh(I) in the thioether/phosphine portion. Significantly, the resulting subunits (**2** and **3**) are not themselves "square" corners formed from square planar metal centers. Indeed, before the second equivalent of metal is added, the orientations of the ligands are flexible (Scheme 1). Hence, the resulting square is formed by cooperative interactions throughout the molecule rather than by any specific directional bonding effect. As opposed to assembling prefabricated corners and linkers, we are effectively constraining flexible building blocks into a rigid structure using complementary coordination geometries. Furthermore, it is likely that this approach can be used to create flexible macrocycles through the breakage of the

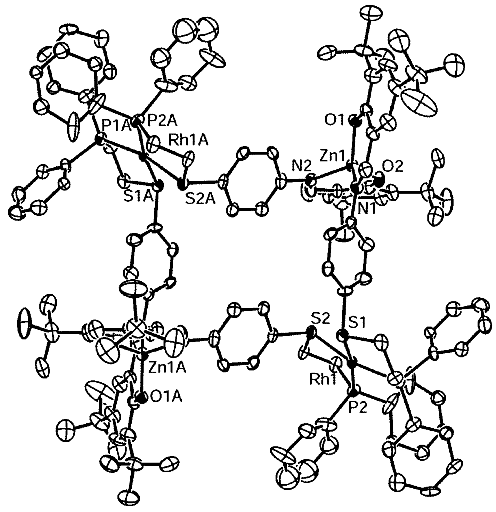


Figure 1. Thermal ellipsoid drawing of **4** showing the labeling scheme for selected atoms and ellipsoids at 30% probability. Hydrogens are omitted for clarity. Selected bond angles (deg): P(2)−Rh(1)−P(1), 98.39(7); P(2)−Rh(1)−S(2), 85.37(6); P(1)−Rh(1)−S(2), 167.30(7); P(2)−Rh(1)−S(1), 171.39(7); S(2)−Rh(1)−S(1), 92.09(6); P(1)−Rh(1)−S(1), 85.85(6); O(2)−Zn(1)−O(1), 120.7(2); O(2)−Zn(1)−N(2), 95.4(2); O(1)−Zn(1)−N(2), 118.4(2); O(2)−Zn(1)−N(1), 119.2(2); N(2)−Zn(1)−N(1), 109.7(2); O(1)−Zn(1)−N(1), 94.8(2).

---

(5) It is possible to form **4** in one pot following either path detailed in Scheme 1; however, the reactions do not proceed as cleanly as when intermediates **2** and **3** are isolated prior to addition of the second equivalent of metal. This is possibly due to the less than quantitative yield of **2** and **3** and the incompatibility of Rh(COE)$_2$BF$_4$ with Et$_2$Zn.

(6) Crystal data for **4** at 100(2) K: $C_{73}H_{84}BF_4N_2O_2P_2RhS_2Cl_2Zn$, M_r = 1615.27, triclinic, $P\bar{1}$, a = 13.0662(8) Å, b = 17.7855(10) Å, c = 18.3270(11) Å, α = 105.105(1)°, β = 95.586(1)°, γ = 105.462(1)°, V = 3898.8(4) Å^3, Z = 2, ρ_{calcd} = 1.376 g cm^{-3}, $F(000)$= 1664, μ-(Mo Kα) = 0.87 mm^{-1}. Data collection: X-ray diffraction intensities were collected on a Bruker SMART APEX CCD diffractometer (T = 100(2) K, Mo Kα radiation (λ = 0.71073 Å), crystal dimensions 0.30 × 0.20 × 0.15 mm^3, $2\theta_{max}$ = 56.5°, total number of reflections 24289, independent reflections 17239 [R_{int} = 0.0487]). In the crystal structure of **4** there are three disordered solvate CH$_2$Cl$_2$ molecules. The program SQUEEZE (Van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *A46*, 194−201) was used to treat the solvent molecules. Corrections of the X-ray data for **4** by SQUEEZE (263 electrons/cell) were close to the required values (252 electrons/cell, respectively) for the formula above. Two Ph rings at the P atoms are disordered over two positions with occupancies 0.33/0.67 and 0.51/0.49, respectively. Only one position of these rings is shown in Figure 1. The final R factors [$I > 2\sigma(I)$]: R1 = 0.0903, wR2 = 0.2092. All software and scattering factors are contained in the SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI). Crystallographic data (excluding structure factors) for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-189343. Copies of the data can be obtained free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax, +44 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

(7) Liu, X.; Stern, C. L.; Mirkin, C. A. *Organometallics* **2002**, *21*, 1017−1019.

(8) Ovchinnikov, M. V.; Holliday, B. J.; Mirkin, C. A.; Zakharov, L. N.; Rheingold, A. L. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4927−4931.

weak thioether−Rh bonds as in the weak-link approach to supramolecular complexes.[1d,4] Efforts to evaluate this chemistry are underway.

Acknowledgment. C.A.M. acknowledges the NSF (CHE-9625391) and the AFOSR for support of this research.

Supporting Information Available: Experimental procedures and spectral data for all new compounds. X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC025875O