# **Inorganic Chemistry**

# New Class of Phosphine Oxide Donor-Based Supramolecular Coordination Complexes from an in Situ Phosphine Oxidation Reaction or Phosphine Oxide Ligands

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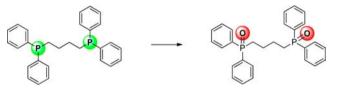
# **Supporting Information**

**ABSTRACT:** A one-pot, multicomponent, coordinationdriven self-assembly approach was used to synthesize the first examples of neutral bridging phosphine oxide donorbased supramolecular coordination complexes. The complexes were self-assembled from a fac-Re(CO)<sub>3</sub> acceptor, an anionic bridging O donor, and a neutral soft phosphine or hard phosphine oxide donor.

ver the past 3 decades, significant research interest has been shown for discrete supramolecular coordination complexes (SCCs) because of their properties and potential applications in sensors, catalysts, flasks, anticancer agents, light harvesters, and nanomaterials.<sup>1,2</sup> The synthesis of SCCs by coordination-driven self-assembly, using predesigned transitionmetal-based acceptors and organic donor precursors, is wellestablished. Because of their high importance in many fields, efforts are being directed toward making complex SCCs and SCCs with functional units and finding a one-pot strategy for multicomponent assembly. As a continuation of the research on the development of rhenium(I)-based SCCs,<sup>2</sup> which exhibit rich photophysical properties and potential applications in many fields, <sup>fb,j-1,2</sup> we envision that substituting the commonly used neutral N donors with phosphine oxide (P=O) donors would result in a SCC with different photophysical properties because of the electronic differences that exist between these coordinating units.<sup>3</sup> Although bis(P=O) ligands have been utilized as bridging ligands between the metal centers in supramolecular architecture including coordination polymers, metal-organic frameworks, and discrete lanthanide-based SCCs,  $^{4-6}$  rhenium-based SCCs with a bis(P=O)-donor building unit are scarce.<sup>7</sup> Herein, we report the first examples of neutral hard P=O-donor-bridged neutral and heteroleptic rhenium(I)-based SCCs (1-3). The multicomponent assembly of 1 and 2 was achieved by a combination of the fac-Re(CO)<sub>3</sub> acceptor, anionic O donors, and a neutral ditopic phosphine donor ligand, whereas 3 was assembled from  $fac-Re(CO)_{3}$ , anionic O donors, and a neutral tetratopic P=O donor. This report is also the first example of SCCs constructed via transforming a soft ditopic P donor to a hard ditopic O=P donor during the self-assembly process (Scheme 1).

In this study, 1,4-bis(diphenylphosphino)butane (P–P), 1,2,4,5-tetrakis(dimethylphosphoryl)benzene (tpbO), chloranilic acid (H<sub>2</sub>-CA), and tetrahydroxy-1,4-quinone hydrate (H<sub>4</sub>-

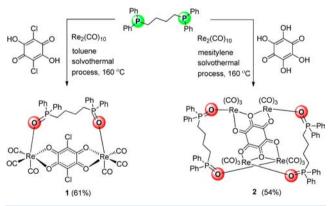
## Scheme 1. Neutral Ditopic Donors



thq·xH<sub>2</sub>O) were explored as basic building units. In the synthetic route to 1 and 2, a neutral P donor is used as the starting material, which is transformed into a P=O donor through in situ oxidation; the P=O group coordinates to the metal via the neutral O-donor atom. This approach is different from the known *fac*-Re(CO)<sub>3</sub>-directed orthogonal bonding approach, in which the neutral ligand is limited to N donors, which coordinate to the metal without any change in the donor properties.

Compounds 1 and 2 were prepared by treating  $\text{Re}_2(\text{CO})_{10}$ , P– P, and anionic O donors (H<sub>2</sub>-CA for 1 and H<sub>4</sub>-thq·xH<sub>2</sub>O for 2) in a one-pot procedure (Scheme 2). The products are air- and

Scheme 2. Synthesis of 1 and 2



moisture-stable. Complex 1 is soluble in polar organic solvents, whereas 2 is sparingly soluble. The Fourier transform infrared (FT-IR) spectrum of 1 exhibits strong bands at 2014, 1919, and 1878 cm<sup>-1</sup>, characteristic of *fac*-Re(CO)<sub>3</sub>.<sup>2a</sup> The band at 1522 cm<sup>-1</sup> indicates the presence of a bis-chelating CA<sup>2-</sup> unit in 1. A strong band at 1149 cm<sup>-1</sup> was assigned to the  $\nu$ (P=O)

**Received:** May 18, 2013 **Published:** August 28, 2013 stretching of the coordinated bis(P==O) unit.<sup>Sf</sup> The <sup>1</sup>H NMR spectrum of **1** shows signals for protons of the CH<sub>2</sub> and phenylene units, corresponding to 1,4-bis(diphenylphosphino)butane dioxide (O=P-P==O).<sup>8</sup> Further, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **1** confirms the presence of the O=P-P=O unit ( $\delta$ 30.65).<sup>8</sup> It is well-known that the highly oxophilic phosphine ligand can transform into P==O under thermal conditions.<sup>9</sup> Similar FT-IR and <sup>31</sup>P NMR patterns were observed for complex **2** (Figures S1–S3 in the Supporting Information, SI).

The structures of 1 and 2 were confirmed with a single-crystal X-ray diffraction (SC-XRD) study. Compound 1 adopts a  $M_3LL'$ -type pseudorectangular structure (Figure 1). The

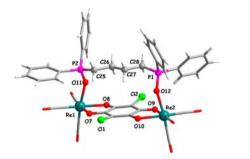
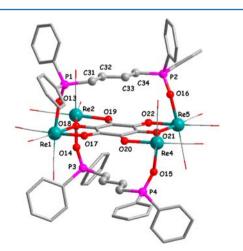


Figure 1. Molecular structure of 1 in a ball-and-stick model.

coordination geometry around the Re center is distorted octahedral with a  $C_3O_3$ -donor environment. The  $CA^{2-}$  unit is planar and acts as a symmetrical bis-chelating unit. The bond distances of  $CA^{2-}$  indicate that the  $\pi$  electrons are confined to the upper and lower halves of the  $CA^{2-}$  unit. The O=P-P=O unit adopts a syn-conformation mode with anti cofaciality. The aliphatic chain has the anti conformation and is planar with the P atoms in **1**. The crystal structure of **1** was stabilized by various intra- and intermolecular noncovalent interactions (Figures S5 and S6 in the SI).

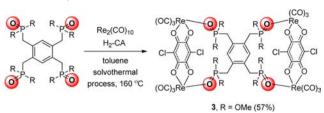
Complex **2** adopts a  $M_4LL'_2$ -type bicyclic structure (Figure 2). thq<sup>4-</sup> acts as a hexadentate 12-electron donor using six O atoms and taking two  $\mu_2:\eta^1:\eta^2:\eta^1$  modes to coordinate four Re atoms. The  $\pi$  electrons in the  $C_6O_6^{4-}$  unit are delocalized in the two chelating units, contrary to the delocalization found in the CA<sup>2-</sup> unit in **1**. The coordination mode and arrangement of the aliphatic chain of O=P-P=O in **2** are similar to those in **1**.



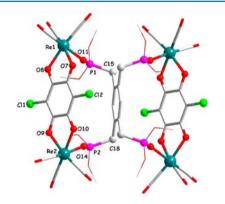
**Figure 2.** Molecular structure of **2** in a ball-and-stick view (CO units are shown as thin sticks, and H atoms are removed for clarity).

To expand further, tpbO, which has four P=O units, and H<sub>2</sub>-CA were used to create  $[(Re(CO)_3)_4(CA)_2(tpbO)]$  (3; Scheme 3). Complex 3 was air- and moisture-stable and sparingly soluble

## Scheme 3. Synthesis of 3



in polar organic solvents. Related N-donor-based SCC [(Re- $(CO)_3)_4(CA)_2(1,2,4,5$ -tetrakis(5,6-dimethylbenzimidazol-1-methyl)benzene)] is insoluble.<sup>10</sup> The FT-IR spectrum of **3** confirms the presence of *fac*-Re $(CO)_3$ , CA<sup>2-</sup>, P==O, and P–OMe units. Complex **3** adopts a M<sub>4</sub>L<sub>2</sub>L'-type double-decker structure (Figure 3). The distance and dihedral angle between



**Figure 3.** Molecular structure of **3** in a ball-and-stick view (OMe units are shown as thin sticks, and H atoms are removed for clarity).

CA and the phenylene unit are 4.4 Å (centroid···centroid) and  $31.5^{\circ}$ , respectively. The size of the cycle, as measured from the Re and methylene C atoms, is ~8 × 4.7 Å. tpbO in 3 adopts an anti,syn,anti,syn-conformation mode. Similar to 1, the  $\pi$  electrons are delocalized in the upper and lower halves of the CA<sup>2-</sup> unit in 3. On the basis of the analytical and SC-XRD results, the assembly of SCCs 1–3 can be best regarded as [1 + 1], [1 + 2], and [2 + 1], respectively.

Complexes 1 and 3 show strong visible-light absorption in the range of 360–700 nm ( $\lambda_{max} = 500$  nm and  $\varepsilon = 9824$  M<sup>-1</sup> cm<sup>-1</sup> for 1;  $\lambda_{max} = 503$  nm and  $\varepsilon = 14768$  M<sup>-1</sup> cm<sup>-1</sup> for 3). Compared to free H<sub>2</sub>-CA ( $\lambda_{max}$  = 442 nm and  $\varepsilon$  = 264 M<sup>-1</sup> cm<sup>-1</sup>), the absorptions of 1 and 3 red-shifted by 58/61 nm with 37/56-fold higher molar absorption coefficients, respectively (Figure S7 in the SI). On the basis of time-dependent density functional theory (TDDFT) calculations, the broad absorptions in 1 and 3 are mainly attributed to metal-to-ligand charge-transfer transitions (MLCT; Re  $\rightarrow$  CA<sup>2-</sup>; Figure S8 and Tables S1 and S3 in the SI). The molar absorption coefficients of 1 and 3 are lower than those of the other rhenium(I)-based complexes<sup>11</sup> but significantly higher than those of the existing rhenium(I)-based SCCs.<sup>2c</sup> Complex 2 exhibits absorption (for range 385–630 nm,  $\lambda_{max}$  = 484 nm and  $\varepsilon = 3242 \text{ M}^{-1} \text{ cm}^{-1}$ ) with a smaller molar absorption coefficient than those of 1 and 3 (Figure S9 and Table S2 in the SI).

These results indicate that coordination of the neutral O donors can influence the energy levels of the highest occupied and lowest unoccupied molecular orbitals of the complexes, thus shifting the absorption to the visible region (Figure S10 in the SI). Although TDDFT calculations cannot explain the effect of the absorption shift to the red region with a significant increase in the molar absorption coefficient, the results provide the groundwork for designing optically useful rhenium-based supramolecules.

In conclusion, a new class of SCCs, containing neutral hard Odonor-bridged ligands, was constructed by spontaneously transforming the soft phosphine P donor to a hard phosphine oxide O donor in the presence of an anionic chelating O donor and  $\text{Re}_2(\text{CO})_{10}$  using a one-step multicomponent assembly. These results indicate that a change to the neutral O donor from a neutral N-donor building unit enhances the absorbance of SCCs significantly. These synthetic methodologies can be extended to synthesize stable and soluble supramolecular assemblies with various sizes/shapes and interesting photophysical properties by using partially protected metal ions.

#### ASSOCIATED CONTENT

## **Supporting Information**

Experimental section, spectra, tables, and CIF data for 1–3. This material is available free of charge via the Internet at http://pubs. acs.org.

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The authors declare no competing financial interest.

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#### DEDICATION

We dedicate this paper to Prof. Ramaswamy Murugavel (Department of Chemistry, Indian Institute of Technology— Bombay, Bombay, India).

## REFERENCES

(1) (a) Lehn, J. M. Angew. Chem., Int. Ed. 2013, 52, 2836. (b) Cook, T. R.; Zheng, Y. R.; Stang, P. J. Chem. Rev. 2013, 113, 734. (c) Inokuma, Y.; Kawano, M.; Fujita, M. Nat. Chem. 2011, 3, 349. (d) Wiester, M. J.; Ulmann, P. A.; Mirkin, C. A. Angew. Chem., Int. Ed. 2011, 50, 114. (e) Wang, Z. J.; Clary, K. N.; Bergman, R. G.; Raymond, K. N.; Dean Toste, F. Nat. Chem. 2013, 5, 100. (f) Smulders, M. M. J.; Riddell, I. A.; Browne, C.; Nitschke, J. R. Chem. Soc. Rev. 2013, 42, 1728. (g) Saalfrank, R. W.; Maid, H.; Scheurer, A. Angew. Chem., Int. Ed. 2008, 47, 8794. (h) Hiratani, K.; Albrecht, M. Chem. Soc. Rev. 2008, 37, 2413. (i) Ward, M. D. Chem. Commun. 2009, 4487. (j) Han, Y. F.; Li, H.; Jin, G. X. Chem. Commun. 2010, 46, 6879. (k) Saha, M. L.; De, S.; Pramanik, S.; Schmittel, M. Chem. Soc. Rev. 2013, 42, 6860. (1) Frischmann, P. D.; MacLachlan, M. J. Chem. Soc. Rev. 2013, 42, 871. (m) Lippert, B.; Miguel, P. J. S. Chem. Soc. Rev. 2011, 40, 4475. (n) Sauvage, J. P.; Amabilino, D. B. Top. Curr. Chem. 2012, 323, 107. (o) Therrien, B. Top. Curr. Chem. 2012, 319, 35. (p) Zangrando, E.; Casanova, M.; Alessio, E. Chem. Rev. 2008, 108, 4979. (q) Chifotides, H. T.; Dunbar, K. R. Acc. Chem. Res. 2013, 46, 894. (r) Yam, V. W. W.; Wong, K. M. C. Chem. Commun. 2011, 47, 11579. (s) Safont-Sempere, M. M.; Fernandez, G.; Wurthner, F. Chem. Rev. 2011, 111, 5784. (t) Lim, S. H.; Su, Y.; Cohen, S. M. Angew. Chem., Int. Ed. 2012, 51, 5106. (u) Cook, T. R.; Vajpayee,

V.; Lee, M. H.; Stang, P. S.; Chi, K. W. Acc. Chem. Res. 2013, DOI: 10.1021/ar400010v.

(2) (a) Dinolfo, P. H.; Hupp, J. T. Chem. Mater. 2001, 13, 3113.
(b) Kumar, A.; Sun, S. S.; Lees, A. J. Coord. Chem. Rev. 2008, 252, 922.
(c) Thanasekaran, P.; Lee, C. C.; Lu, K. L. Acc. Chem. Res. 2012, 45, 1403. (d) Thorp-Greenwood, F. L.; Balasingham, R. G.; Coogan, M. P. J. Organomet. Chem. 2012, 714, 12. (e) Rajakannu, P.; Elumalai, P.; Shankar, B.; Hussain, F.; Sathiyendiran, M. Dalton Trans. 2013, 42, 11359 and ref 5 cited therein.

(3) (a) Jeon, S. O.; Lee, J. Y. *J. Mater. Chem.* **2012**, *22*, 4233. (b) Han, C.; Zhang, Z.; Xu, H.; Yue, S.; Li, J.; Yan, P.; Deng, Z.; Zhao, Y.; Yan, P.; Liu, S. *J. Am. Chem. Soc.* **2012**, *134*, 19179.

(4) (a) Rosario-Amorin, D.; Duesler, E. N.; Paine, R. T.; Hay, B. P.; Delmau, L. H.; Reilly, S. D.; Gaunt, A. J.; Scott, B. L. *Inorg. Chem.* 2012, *51*, 6667. (b) Redmond, M. P.; Cornet, S. M.; Woodall, S. D.; Whittaker, D.; Collison, D.; Helliwell, M.; Natrajan, L. S. *Dalton Trans.* 2011, *40*, 3914. (c) Guseva, E. V.; Naumova, A. A.; Karimova, D. T.; Sokolova, A. V.; Gavrilova, E. L.; Busygina, T. E. *Russ. J. Gen. Chem.* 2012, *82*, 1. (d) Cheng, F.; Codgbrook, H. L.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Polyhedron* 2007, *26*, 4147. (e) Lees, A. M. J.; Platt, A. W. G. *Inorg. Chem.* 2003, *42*, 4673. (f) Peveling, K.; Dannappel, K.; Schurmann, M.; Costisella, B.; Jurkschat, K. *Organometallics* 2006, *25*, 368.

(5) (a) Atefi, F.; McMurtrie, J. C.; Turner, P.; Duriska, M.; Arnold, D. P. *Inorg. Chem.* **2006**, 45, 6479. (b) Atefi, F.; McMurtrie, J. C.; Arnold, D. P. *Dalton Trans.* **2007**, 2163. (c) Sinelshchikova, A. A.; Nefedov, S. E.; Enakieva, Y. Y.; Gorbunova, Y. G.; Tsivadze, A. Yu.; Kadish, K. M.; Chen, P.; Bessmertnykh-Lemeune, A.; Stern, C.; Guilard, R. *Inorg. Chem.* **2013**, *52*, 999. (d) Beletskaya, I.; Tyurin, V. S.; Tsivadze, A. Y.; Guilard, R.; Stern, C. *Chem. Rev.* **2009**, *109*, 1659. (e) Xiangdong, Z.; Chunhua, G.; Jing, Y.; Yang, Z.; Cui, H. *Chin. J. Chem.* **2009**, *27*, 1195. (f) Marchetti, F.; Pettinari, C.; Pizzabiocca, A.; Drozdov, A. A.; Tryanov, S. I.; Zhuravlev, C. O.; Semenov, S. N.; Belousov, Y. A.; Timokhin, I. G. *Inorg. Chim. Acta* **2010**, *363*, 4038. (g) Liu, X.; Guo, G. C.; Liu, B.; Chen, W. T.; Huang, J. S. *Cryst. Growth Des.* **2005**, *5*, 841. (h) Spichal, Z.; Jancarik, A.; Mazal, C.; Pinkas, J.; Pekarkova, P.; Necas, M. Polyhedron **2013**, *62*, 83 and references cited therein. (i) Pekarkova, P.; Spichal, Z.; Taborsky, P.; Necas, M. Luminescence **2011**, *26*, 650.

(6) (a) Maxim, C.; Matni, A.; Geoffroy, M.; Andruh, M.; Hearns, N. G. R.; Clerac, R.; Avarvari, N. *New J. Chem.* **2010**, *34*, 2319. (b) Sues, P. E.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **2012**, *51*, 9322. (c) Kaempfe, P.; Stock, N. *Z. Anorg. Allg. Chem.* **2008**, *634*, 714.

(7) (a) Rodriguez-Palacios, R.; Reyes-Lezama, M.; Marquez-Pallares, L.; Lemus-Santana, A. A.; Sanchez-Guadarrama, O.; Hopfl, H.; Zuniga-Villarreal, N. *Polyhedron* **2010**, *29*, 3103. (b) Lemus-Santana, A. A.; Reyes-Lezama, M.; Zuniga-Villarreal, N.; Toscano, R. A.; Espinosa-Perez, G. E. *Organometallics* **2006**, *25*, 1857.

(8) Calcagno, P.; Kariuki, B. M.; Kitchin, S. J.; Robinson, J. M. A.; Philp, D.; Harris, K. D. M. *Chem.—Eur. J.* **2000**, *6*, 2338.

(9) (a) Barder, T. E.; Buchwald, S. L. J. Am. Chem. Soc. **2007**, *129*, 5096. (b) To confirm the formation of O=P-P=O, the free P-P ligand was subjected to reaction conditions similar to those of **1**; crystalline products A containing a mixture of O=P-P=O and P-P were obtained; <sup>1</sup>H NMR study indicates that 75% of P-P was converted into O=P-P=O (Figure S4 in the SI).

(10) Chuang, C. H.; Sathiyendiran, M.; Tseng, Y. H.; Wu, J. Y.; Hsu, K. C.; Hung, C. H.; Wen, Y. S.; Lu, K. L. Organometallics **2010**, *29*, 283.

(11) Yi, X.; Zhao, J.; Sun, J.; Guo, S.; Zhang, H. Dalton Trans. 2013, 42, 2062 and references cited therein.