

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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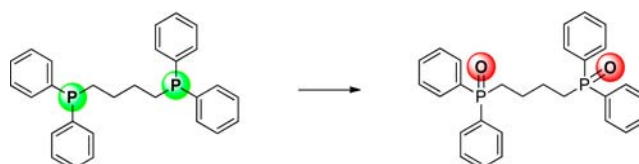
Supporting Information

ABSTRACT: A one-pot, multicomponent, coordination-driven self-assembly approach was used to synthesize the first examples of neutral bridging phosphine oxide donor-based supramolecular coordination complexes. The complexes were self-assembled from a *fac*- $\text{Re}(\text{CO})_3$ acceptor, an anionic bridging O donor, and a neutral soft phosphine or hard phosphine oxide donor.

Over 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.^{1,2} The synthesis of SCCs by coordination-driven self-assembly, using predesigned transition-metal-based acceptors and organic donor precursors, is well-established. 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,² which exhibit rich photophysical properties and potential applications in many fields,^{1b,j-1,2} 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.³ 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.⁷ 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*- $\text{Re}(\text{CO})_3$ acceptor, anionic O donors, and a neutral ditopic phosphine donor ligand, whereas **3** was assembled from *fac*- $\text{Re}(\text{CO})_3$, 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_2 -CA), and tetrahydroxy-1,4-quinone hydrate (H_4 -

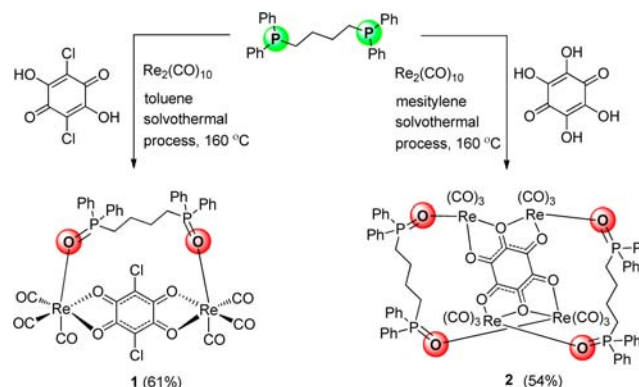
Scheme 1. Neutral Ditopic Donors



$\text{thq} \cdot x\text{H}_2\text{O}$) 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*- $\text{Re}(\text{CO})_3$ -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_2 -CA for **1** and H_4 - $\text{thq} \cdot x\text{H}_2\text{O}$ for **2**) in a one-pot procedure (Scheme 2). The products are air- and

Scheme 2. Synthesis of **1** and **2**



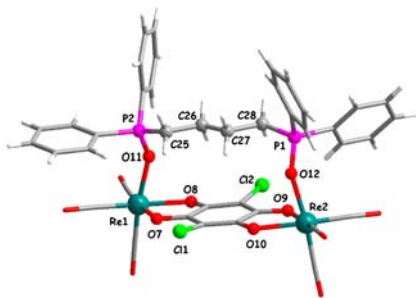
moisture-stable. Complex **1** is soluble in polar organic solvents, whereas **2** is sparingly soluble. The Fourier transform infrared (FT-IR) spectrum of **1** exhibits strong bands at 2014, 1919, and 1878 cm^{-1} , characteristic of *fac*- $\text{Re}(\text{CO})_3$.^{2a} The band at 1522 cm^{-1} indicates the presence of a bis-chelating CA^{2-} unit in **1**. A strong band at 1149 cm^{-1} was assigned to the $\nu(\text{P}=\text{O})$

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stretching of the coordinated bis(P=O) unit.^{5f} The ¹H NMR spectrum of **1** shows signals for protons of the CH₂ and phenylene units, corresponding to 1,4-bis(diphenylphosphino)butane dioxide (O=P–P=O).⁸ Further, the ³¹P{¹H} NMR spectrum of **1** confirms the presence of the O=P–P=O unit (δ 30.65).⁸ It is well-known that the highly oxophilic phosphine ligand can transform into P=O under thermal conditions.⁹ Similar FT-IR and ³¹P 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 M₂LL'-type pseudorectangular structure (Figure 1). The



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 O-donor-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 photo-physical 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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■ Notes

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).

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