Rhenium(I)-Based Monocyclic and Bicyclic Phosphine Oxide-Coordinated Supramolecular Complexes

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Supporting Information

ABSTRACT: Neutral, flexible ditopic phosphine (P−P) or phosphine oxide (O=P−P=O) donors, rigid anionic bis-chelating oxygen donors, and Re₂(CO)₁₀ were used to assemble ten phosphine oxide (P=O)-donor-based neutral monocyclic M₂LLL′₂⁻, bicyclic M₄L₂L₂⁻, and bicyclic M₄LL'L'-type supramolecular coordination complexes (SCCs). A soft ditopic phosphine donor was transformed into a hard ditopic phosphine oxide donor, during the formation of the cyclic complexes 1−3, 5−6, and 9−10. Complexes 4, 7, and 8 were obtained using a hard P=O donor ligand. These SCCs were characterized using elemental analysis, FTIR, NMR, and single-crystal X-ray diffraction analysis. The absorption properties of 1−8 were studied using absorption UV−vis spectroscopic methods, and the results were analyzed using theoretical calculations. The results revealed that the neutral P=O donor significantly influenced the photophysical properties by enhancing the absorption coefficient in the visible region.

INTRODUCTION

Designing supramolecular coordination complexes (SCCs), using various preprogrammed metal-based acceptors and organic-donor frameworks, has gained considerable research interest in the past two decades because of their potential applications in various fields including host−guest encapsulation, catalysis, and medicine. 1−8 Among the available metal-directed approaches, the fac-Re(CO)₃-core-based method is one of the well-known processes for synthesizing heteroleptic SCCs with various sizes, shapes, and functionalities. 2−5 Owing to their high significance in several important areas, research is being channeled toward synthesizing new SCCs with improved properties and designing a one-step synthetic approach for multicomponent assembly. In this direction, ditopic phosphine oxide donors have been recently introduced in place of neutral ditopic nitrogen donors, which are one of the few organic-framework-building units in heteroleptic rhenium(I)-based SCCs. 6a It is noteworthy that phosphine oxide donor ligands have been used as bridging ligands between the metal centers in metal−organic polymers and discrete lanthanide-based complexes. 7−11 However, the use of the P=O-donor-based ligands as framework-building units for a discrete rhenium(I)-based SCCs is limited. 6a In addition, the idea of using hydroxyl/carboxyl groups as the sources of neutral and anionic oxygen donors is quite popular now for synthesizing the SCCs. 1−8 However, the use of oxygen donors from the P=O unit for synthesizing the SCCs is rare. 6a−8 Although the P=O donor can coordinate like the nitrogen donor, the electronic differences between these two donors result in SCCs with different photophysical properties. Initial results revealed that moving from the N-donor- to the P=O-donor-based building units significantly increases the absorbance of rhenium(I)-based cyclic complexes. 6a As a continuation of our previous approach, that is, mixing Re₂(CO)₁₀ rigid bis-chelating HO−O−O=OH donor (H₂-L = H₂-CA = chloranilic acid), and flexible phosphine (P−P)/phosphine oxide (O=O−P=O) donor for the development of the P=O-donor-based strong visible-light-absorbing SCCs (Scheme 1) 6a we plan to modulate a spacer and an organic group attached to phosphorous of flexible organic ligands and the substitution on bis-chelating O donor that would expectedly result in similar SCCs with different photophysical properties.

Herein, we report the preparation and characterization of seven neutral monocyclic SCCs 1−7 and three bicyclic SCCs

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The complexes 1–3, 5–6, and 9–10 were obtained by treating the neutral ditopic phosphine donors [1,4-bis(diphenylphosphino)butane, L1; 1,3-bis(diphenylphosphino)propane, L2; 1,3-bis(diphenylphosphinomethyl)benzene, L3], bis-chelating HO–O–OH donor (chloranilic acid, H2-CA; 2,5-dihydroxy-1,4-benzoquinone, H2-DHBQ; tetrahydroxy-1,4-benzoquinone, H2-thq), and Re2(CO)10 in a one-pot approach.6a In this method, the soft phosphine donor was used as an indirect starting material for the oxygen donor ligand, which in turn got transformed to a hard phosphine oxide donor during the reaction (Scheme 1). Complexes 4, 7, and 8 were obtained using 1,4-bis(dimethylphosphoryl)-2,3,5,6-tetramethylbenzene (L4) or 1,2,4,5-tetakis(dimethylphosphoryl)benzene (L5) as a neutral hard phosphine oxide donor, H2-CA/H2-DHBQ and Re2(CO)10. The complexes were characterized using elemental analysis and 1H- and 31P-NMR spectroscopy.
31P-NMR spectroscopic methods. The molecular structures of the SCCs were further analyzed using single-crystal X-ray diffraction analysis. The absorption properties of 1−8 were examined using UV−vis spectroscopic methods and were analyzed using time-dependent density functional theory (TDDFT) calculations.

RESULTS AND DISCUSSION

Complexes 1−10 were prepared by treating Re2(CO)10, a phosphine donor (L1/L2/L3)/phosphine oxide donor (L4/L5), H2-CA/H2-DHBQ/H4-thq-xH2O, and mesitylene/toluene using a solvothermal method (Schemes 2 and 3). The complexes were stable in air and moisture. Complexes 1−8 were soluble in polar organic solvents, whereas complexes 1 and 10 were sparingly soluble. The 31P{1H} NMR spectra of 1−10 displayed a single sharp chemical resonance peak in the range of δ 27−30 in DMSO-d6 (Figures S1−S7), indicating the presence of single symmetrical complexes. The disappearance of the peak at δ −11, which corresponds to the phosphine P of L1, and the appearance of the new peak at −δ 27 for 3, 6, and 10 indicated the presence of O=Re−CH2−C6H4−CH2−Re=O building units in these complexes. This observation indicated that the highly exophilic phosphine ligand could be transformed into phosphine oxide, in the presence of air under solvothermal conditions.12 The free ligand also exhibited a peak at δ 28, corresponding to the P=O donor unit. This clearly confirmed that the starting phosphine donor was transformed into phosphine oxide.

Compared with those of the free ligand, the 1H NMR spectra of 1−10 showed very clear chemical resonance peaks both in the aromatic and in the aliphatic regions (Figures S8−S14). In particular, the protons of the methylene −CH2− group showed a doublet (∼δ 3.8), with a coupling constant of 13.8 (JHH), consistent with the presence of the phosphine oxide donor unit in the complexes 3−4, 6−8, and 10.13 A similar chemical resonance peak of CH2 was also observed in the case of free 1,4-bis(diphenylphosphinomethyl)benzene dioxide and its coordination complex.13

Crystal Structures of Metallacycles 1−5 and 7−10. The molecular structures of 1−5 and 7−10 were proved using single-crystal X-ray diffraction analysis (Figures 1−3 and S15−S17, and Tables S1−S3). Both solvothermal and recrystallization methods did not yield good-quality crystals of complex 6. Complexes 1−5 and 7 would be represented as a [1 + 1] assembly, that is, a single molecular clip [(Re(CO)3)(μ-L)(Re(CO)3)] capped by a ditopic O=Re=O ligand. Complex 1 adopted a pseudorhombic structure (Figure S15), which was similar to complex 1.69 The neutral O=Re=O donor unit coordinated the molecular clip using its two oxygen atoms and took a syn conformation mode with anti-cofaciality. The rhenium atom adopted distorted octahedral geometry and was coordinated with three carbon atoms and three oxygen atoms.

Complexes 2 and 5 were isostructural (Figure 1A,B). Because of the boatlike conformation of the [((Re(CO)3)(μ-L)(Re(CO)3))] motif in 2 and 5, the structures of these complexes differed slightly from the dinuclear complexes 1 and 1. Although the CA2+/DHBQ2− moiety was planar in the complex, this unit was below the plane of Re−Re atoms. The two O=Re groups (O11≡P2=P1≡O12 for 2 and O5≡P1≡P2≡O6 for 5) pushed the CA2+/DHBQ2− moiety from the plane of Re−Re atoms in 2 and 5. The distance between the two rhenium atoms in the [Re(μ-L)Re] unit was 7.84/7.87 Å, which was significantly shorter than that for complexes 1 and 1 (dRe−Re = 8.08/8.08 Å for 1/1). In both the complexes, the O≡
P−P−O donor unit acted as a molecular clip and adopted a syn-conformation. The conformation of O=P−(CH2)3−P−O in this complex was comparable with that of the uncoordinated ligand, except for the parallel arrangement of the two phenylene units.13 Because of the metal coordination, the bond distances of P−O in these complexes were marginally longer than that in the free phosphine ligand.

In complex 3 (Figure S16), the bis-chelating CA2− unit was slightly twisted, that is, deviated from the planarity. However, the coordination mode and the bonding nature of the CA2− unit were similar to those of the same moiety in complexes 1 and 2. The O=P−CH2−C6H4−CH2−P=P−O unit acted as a molecular clip and adopted an anti-conformation with respect to the plane of the central benzene core. The free ligand O=P−CH2−C6H4−CH2−P=P−O also took a similar arrangement.13

The bond distances of P=O (1.508 and 1.512 Å) were slightly longer than the bond distances found in the free ligand (1.482 and 1.488 Å),13 which indicated that the coordination of P=O with rhenium was responsible for the bond elongation. The central benzene plane was vertical to the plane of the CA2− unit (dihedral angle = 90°), and its arene CH group (C13−H) was directed toward the center of the CA 2− unit (dH···centroid = 2.8350 Å). The distances between P···P, P−O···O−P, and Re···Re were 7.690, 6.707, and 8.148 Å, respectively, which suggested that the ditopic O=P−CH2−C6H4−CH2−P=P−O donor was an ideal molecular-coordinating clip to the [(CO)3Re)(μ-CA)(Re(CO)3)] unit. It is known that a ditopic phosphine oxide unit acted as an eight-membered chelating ligand in Er-L3-based complexes.13

In complexes 4 and 7, the planar CA2−/DHBQ2− unit coordinated two rhenium atoms symmetrically (Figure S17). The coordination mode and bonding nature of the CA2−/DHBQ2− unit were similar to those of the same moiety in complexes 1 and 1. The phosphine oxide unit adopted a syn...
conformation with respect to the plane of the central benzene core and coordinated as a molecular clip. The central tetramethylphenylene core was closely parallel (dihedral angle = 29°/36°) to the plane of the CA2−/DHBQ2− unit.

Complex 8 adopted a M4L2L′-type bicyclic structure and was composed of four fac-Re(CO)3 moieties, two DHBQ2− units, and a neutral tetratopic O=P donor unit (Figure 2). The complex was regarded as the [2 + 1] assembly product of two molecular clips, [{(Re(CO)3)(μ-L)(Re(CO)3)}], bridged by a bis-ditopic P=O donor ligand. The three six-membered rings (DHBQ2−···benzene···DHBQ2−) are arranged like a ladder (distance (centroid) = 4.26 Å; dihedral angle = 37°). The bonding nature of both DHBQ2− and L5 in the complex 8 was normal and was similar to the bicyclic complex II.6a

Complexes 9 and 10 adopted a M4LL′2-type bicyclic structure and thus could be regarded as [1 + 2] assembly products with one [{(Re(CO)3)(μ-thq)(Re(CO)3)}] and two O=P=P=O units (Figure 3).6a The rhenium atom in the complexes adopted distorted octahedral geometry, with a C4O4 donor environment. The hexadentate 12-electron donor thq4− unit used all its oxygen atoms to coordinate with four rhenium atoms and adopted two μ2:η1:η2:η1 modes. The delocalization of π-electrons in the C6O6 ring was separated into two parts, [complex 9, part 1: (−O5−Re2−O6−C35−C36(O5)−C37−O4−Re1−O5) and part 2: (−O2−Re3−O1−C32−C33(O2)−C34−O3−Re5−]

Figure 4. Absorption spectra of I–II and 1–8 in THF.
Table 1. UV–Vis Data for I–II and 1–10 in (THF/DMSO)

| compound | anionic unit in complex | P=O unit of L* | visible-light absorption region (nm) | \( \lambda_{\text{max}} \) (nm) | \( \epsilon \) (M⁻¹ cm⁻¹) |
|----------|------------------------|---------------|--------------------------------------|------------------|------------------|
| 1        | CA                     | R′R′PO of L₁  | 360–700                              | 500              | 9824             |
| 1        | DHBQ                   | R′R′PO of L₁  | 350–700                              | 488              | 10 387           |
| 2        | CA                     | R′R′PO of L₂  | 350–700                              | 496              | 11 620           |
| 5        | DHBQ                   | R′R′PO of L₂  | 350–700                              | 482              | 5610             |
| 3        | CA                     | R′R′PO of L₂  | 365–710                              | 497              | 4130             |
| 6        | DHBQ                   | R′R′PO of L₂  | 350–700                              | 480              | 4146             |
| 4        | CA                     | (R′O)₉R′PO of L₉ | 350–700                              | 495              | 11 170           |
| 7        | DHBQ                   | (R′O)₉R′PO of L₉ | 350–680                              | 472              | 18 324           |
| II       | CA                     | (R′O)₉R′PO of L₉ | 360–700                              | 500              | 14 768           |
| 8        | DHBQ                   | (R′O)₉R′PO of L₉ | 340–700                              | 472              | 26 796           |
| 9        | thq                    | R′R′PO of L₂  | 400–600                              | 450              | 6788             |
| 10       | thq                    | R′R′PO of L₂  | 370–600                              | 391              | 7972             |

*\( R = \text{phenyl, } R' = \text{CH}_2\text{, and } R'' = \text{CH}_3.\)*

O2))], and confined to two chelating motifs, which were again separated by two C=C single bonds (complex 9: C29–C34/ C31–C32 = 1.493/1.474 Å; and complex 10: C35–C34/C37– C32 = 1.503/1.500 Å). The average (av) of the C=C and C=O bond distances of the thq⁻⁺ unit (av C=C = 1.417 Å, av C=O = 1.306 Å) in these complexes and that of the free H₄-thq unit (av C=C = 1.438 Å, av C=O = 1.317 Å) and complex II (Scheme 2) were similar, which confirmed that the C₆O₆ ring was a tetra-anionic motif.14,6a

Each O=PO=PO donor unit adopted a syn-conformation and bound two rhenium cores in these complexes. However, the choice of the two metal cores by the O=PO=PO donor among the four metal centers in the \([\{(CO)₃Re\}₄(\mu-thq)\] core was different from complex to complex. The spacer, –(CH₂)₉– and –CH₆–(C₆H₆)–CH₆–, present in the P=O donor unit played an important role in the selection of the two metal ions in the \([\{(CO)₃Re\}₄(\mu-thq)\] motif.

In complex 9, the molecular clip of O=PO=PO donor units coordinated two rhenium atoms, which were separated by four atoms [part I (black color): Re4–O18–C–C–O17–Re5 and part II (blue color): Re1–O20–C31–C32–O21–Re3 in Figure 3A]. These two rhenium cores were not located in the fused bis-chelating motif, and this led to the formation of the 13-membered cyclic core in the complex. Two such cyclic systems, one above and the other below the plane of the \([\{(CO)₃Re\}₄(\mu-thq)\] motif, were present in complex 9. In complex 10, O=PO=PO donor units coordinated two rhenium atoms that were separated by only one oxygen atom [part I (black color): Re2–O5–Re1 and part II (blue color): Re3–O22–Re5] and were part of the fused bis-chelating motif. Each cycle in complex 10 gave rise to a 12-membered monocyclic ring. It is worth mentioning that the bridging nature of the two O=PO=PO donor units of the \([\{(CO)₃Re\}_₄(thq)\] motif in M₄L₄L′₂-complex III was different from the bridging nature of PO=PO donor units in complexes 9 and 10 (Scheme S1). The central benzene core was vertical to the plane of the thq⁻⁺ unit in complex 10, and its arene CH group (C₅-H) was projected toward one of the edges of the thq⁻⁺ unit (\( d_{\text{centroid}} = 2.8350 \) Å). In addition to that, the intramolecular edge-to-face C–H···π interactions were found between the two oppositely arranged phenylene units of the O=PO=PO motif (\( d_{\text{centroid}} = 4.89 \) Å and dihedral angle = 84°; Figure 3).

**Photophysical Studies of Complexes.** The dinuclear complexes 1–7 and the tetranuclear complex 8 showed a broad and structureless visible-light absorption band covering the entire visible spectrum (350–710 nm) in THF (Figure 4, Table 1). The complexes also displayed an UV absorption band centered at ~300 nm. The spectral patterns of these complexes (1–8) were similar to those of complexes I and II, with minor shifts in the absorption maxima in the visible region. On the basis of previous studies, the broad low-energy absorptions in these complexes were assigned to a mixture of metal-to-ligand charge-transfer transitions (MLCT, Re → CA²⁻/DHBQ⁻²) and ligand-centered (intraligand charge-transfer, ILCT and/or ligand-to-ligand charge-transfer, LLCT) electronic transitions. The high-energy bands can be assigned to the ILCT and LLCT transitions.

Assignment of spectral bands was further confirmed by TDDFT calculations using a THF solvation model (Figures S18 and S19; Tables S4–S11). The visible-light absorptions of 1–7 were largely ascribed to the transition from the highest occupied molecular orbitals (HOMOs) to the lowest unoccupied molecular orbital (LUMO). In the HOMOs, the electron density was predominantly localized on the Re atoms, with a significant electron distribution on the three CO groups and the CA²⁻/DHBQ⁻² units; the contribution from the phosphate group is negligible. The electron density of the LUMO was localized over the CA²⁻/DHBQ⁻² units (91%). This observation clearly indicated that MLCT (Re → CA²⁻/ DHBQ⁻²), LLCT (CO → CA²⁻/DHBQ⁻²), and ILCT (CA²⁻/ DHBQ⁻² → CA²⁻/DHBQ⁻²) transitions were responsible for the absorption at longer wavelengths. The higher-energy transitions at ~306–338 nm occurred mainly because of the ligand transitions with minor contribution from the MLCT transitions (Re → CA²⁻/DHBQ⁻²). A close inspection of the relevant molecular orbitals revealed that the electron density of the HOMOs was predominantly localized over the O=PO=PO and/or the DHBQ⁻²/CA²⁻ units. The electron density of the LUMO was localized over the CA²⁻/DHBQ⁻² units. These studies clearly indicated that the higher-energy transitions for complexes 1–3, 5, and 6 occurred because of a combination of ILCT (DHBQ⁻²/CA²⁻ → CA²⁻/DHBQ⁻²) and LLCT (phenylene of O=PO=PO → CA²⁻/DHBQ⁻²). Complexes 4, 7, and 8 displayed higher-energy LLCT (phenylene of O=PO=PO → CA²⁻/DHBQ⁻²) transitions.

Complexes 9 and 10 showed a broad absorption between 400 and 600 nm. A similar absorption was found in complex II possessing O=PO=PO and thq⁻⁺ units. The visible absorption range of 9 and 10 was smaller than those of the other complexes.
Compared with free H₃-CA ($\lambda_{max} = 442$ nm, $\epsilon = 264$ M⁻¹ cm⁻¹) and H₂-DHBQ, these complexes exhibited red-shifted absorptions with several-times-higher molar absorption coefficients. All complexes displayed strong absorptions ($\epsilon > 10000$ M⁻¹ cm⁻¹) in the visible region, except for complexes 3, 5, and 6 ($\epsilon < 6000$ M⁻¹ cm⁻¹). These results further indicated that the absorption maxima ($\lambda_{max}$) in the visible region were blue-shifted by 12–18 nm on replacing the CA²⁻ unit by a DHBQ²⁻ unit in complexes 1–8; no influence was observed while changing the phosphine oxide donor unit. Furthermore, the molar absorption coefficients ($\epsilon$) of the complexes at $\lambda_{max} \approx 500$ nm were significantly enhanced/reduced either by replacing the CA²⁻ unit by a DHBQ²⁻ unit or by tuning the methylene spacer of the O=P-(CH₂)m-P=O (m = 4 or 3) donors in complexes I, I, 2, and 5; no smooth trend in the molar absorption coefficient of the complexes was observed by either of the two changes. However, replacing O=P-(CH₂)m-P=O (L¹ or L²) by O=P-CH₂-mCH₂-H₂=CH₂-P=O (L³), possessing an aren spacer, dramatically reduces the $\epsilon$ values in the visible region. Replacing CA²⁻ with DHBQ²⁻ did not affect the molar absorption coefficient in complexes 3 and 6. This result indicates that the aren spacer in the complexes plays a significant role in decreasing the $\epsilon$ value, probably because of the noncovalent interactions between the aren spacer and the bis-chelating unit in complex 6. Close inspection of the molecular structure of 6 clearly indicates the CH−π interactions between the aren and the CA²⁻/DHBQ²⁻ moiety.

For the phosphate ester-donor-based complexes 4, 7, 8, and 8, replacing CA²⁻ by DHBQ²⁻ enhances the molar absorption coefficient remarkably. These results further imply that both the phosphate ester group and the anionic unit influence the photophysical properties of complexes 4, 7, 8, and 8. Complexes II and 8 displayed higher $\epsilon$ values than complexes 4 and 7, probably because of the presence of nearly two units of 4 and 7 in complexes II and 8, respectively.

**CONCLUSIONS**

The P=O-donor-based SCCs, containing rhenium(l)carbonyl cores, bis-chelating O=O−O=O donors, and ditopic phosphate oxide donors, linked to butyl, propyl, xylene, or substituted xylene, were reported. Using a one-pot multicomponent solvothermal approach, these SCCs were synthesized by a spontaneous transformation of the soft phosphate into a hard phosphate oxide, in the presence of a bis-chelating oxygen donor ligand and Re₂(CO)₁₀. Direct combination of O=P−P=O, bis-chelating oxygen donor ligand, and Re₂(CO)₁₀ resulted in the formation of phosphate oxide-donor-based SCCs. The formation of the reported SCCs 1–8 experimentally supported the fact that the proposed synthetic approach was feasible. The results confirmed that a change to a neutral oxygen donor of phosphate oxide from a neutral nitrogen building unit significantly improves the absorbance of the SCCs in the visible region. In addition, the results predicted that the P=O donor of the ester ligand is a suitable building unit to make strong visible-light-absorbing rhenium-based SCCs. The construction of SCCs using ditopic/tritopic/multitopic P=O donors with conjugated spacer and acyclic complexes with different organic groups on P are under way.

**EXPERIMENTAL SECTION**

**General Data.** Re₂(CO)₁₀ H₂-C₆, H₂-DHBQ, H₂-thq: xH₂O, (HCHO)₉, HBr, P(OMe)₉, 1,2,4,5-tetramethylbenzene, toluene, mesitylene, L¹ (97%, Spectrochem, India), L² (97%, Spectrochem, India), and L₃ were used as received. Ligands L₄ and L₅ were prepared.¹⁵,¹⁶ Solvents hexane and toluene were purified using conventional procedures. NMR spectra were recorded on Bruker Avance III 400 and 500 MHz instruments. FTIR spectra were recorded on a JASCO 5300 FTIR spectrometer. Elemental analyses were performed on a Flash EA series 1112 CHNS analyzer. ESL-TOF mass spectra were recorded on a Bruker maXis mass spectrometer. Spectroscopic-grade solvents, tetrahydrofuran (THF, Finar) and dimethyl sulfoxide (DMSO, Spectrochem), were used as received. Absorption spectra were recorded on a UV-3600 Shimadzu UV−vis−NIR spectrophotometer.

**General Synthetic Approach for 1−10.** Re₂(CO)₁₀ H₂-C₆ (or) H₂-DHBQ (or) H₂-thq-xH₂O, mesitylene (or) toluene (~10 mL), and hexane (~6 mL) were kept in a Teflon vessel. The vessel was kept in the stainless steel solvothermal bomb for 48 h and cooled to room temperature. Crystals or powder found in the bomb were filtered, washed with hexane, and air-dried. In a few cases, crystals were obtained by adding hexane to the clear solution obtained in the bomb and keeping as such at room temperature.

**Synthesis of [[(Re(CO)₅)(μ-DHBQ)(Re(CO)₅)]L¹] (1).** Dark crystals of 1 were obtained using Re₂(CO)₁₀ (100.1 mg, 0.1534 mmol), H₂-DHBQ (21.7 mg, 0.1540 mmol), L¹ (65.9 mg, 0.1545 mmol), and mesitylene (20 mL). Yield: 47% (81.2 mg, weight of crystals).¹¹ H NMR (500 MHz, DMSO-d₆): 7.76−7.47 (m, 20H, ArH), 2.39 (m, 4H, PCH₂), 1.53 (m, 2H, PCH₂CH₂). ³¹P{¹H} NMR (500 MHz, DMSO-d₆): 30.1 (s). Anal. Calcd for C₄₄H₂₈Cl₂O₁₂P₂Re₂: C, 42.25; H, 2.66. Found: C, 42.36; H, 2.61. IR (KBr, cm⁻¹): 2106 (s), 1896 (s), 1518 (s), 1145 (s).

**Synthesis of [[(Re(CO)₅)(μ-CA)(Re(CO)₅)]L²] (2).** Dark crystals of 2 were obtained using Re₂(CO)₁₀ (100 mg, 0.1532 mmol), H₂-C₆ (32 mg, 0.1532 mmol), L² (65 mg, 0.1532 mmol), and mesitylene (10 mL). Yield: 45% (82.1 mg, weight of crystals).¹¹ H NMR (500 MHz, DMSO-d₆): 7.72−7.47 (m, 20H, ArH), 2.58−2.54 (m, 4H, PCH₂), 1.68−1.55 (m, 2H, PCH₂CH₂). ³¹P{¹H} NMR (500 MHz, DMSO-d₆): 29.95 (s). Anal. Calcd for C₄₆H₃₀Cl₂O₁₆P₂Re₂: C, 39.30; H, 2.20. Found: C, 39.15; H, 2.41. IR (KBr, cm⁻¹): 2010 (s), 1884 (s), 1528 (s), 1144 (s).

**Synthesis of [[(Re(CO)₅)(μ-CA)(Re(CO)₅)]L³]·3C₆H₆ (3).** Dark crystals of 3 were obtained using Re₂(CO)₁₀ (101.4 mg, 0.1551 mmol), H₂-C₆ (32.9 mg, 0.1583 mmol), L³ (73.9 mg, 0.1546 mmol), and toluene (10 mL). Yield: 44% (106.5 mg, weight of crystals).¹¹ H NMR (500 MHz, DMSO-d₆): δ 7.78−7.45 (m, 20H, ArH), 7.13 (s, 1H, ArH), 6.95−6.91 (m, 3H, ArH), 3.75 (d, JHP = 14 Hz, 4H, CH₂). ³¹P{¹H} NMR (500 MHz, DMSO-d₆): δ 27.49 (s). Anal. Calcd for C₄₆H₃₀Cl₂O₁₆P₂Re₂: C, 42.14; H, 2.25. Found: C, 42.25; H, 2.21. IR (KBr, cm⁻¹): 2022 (s), 1912 (s), 1512 (s), 1151 (s).

**Synthesis of [[(Re(CO)₅)(μ-CA)(Re(CO)₅)]L⁴] (4).** Dark crystals of 4 were obtained using Re₂(CO)₁₀ (100 mg, 0.1532 mmol), H₂-C₆ (32.0 mg, 0.1532 mmol), L⁴ (75.96 mg, 0.1532 mmol), and mesitylene (8 mL). Yield: 42% (73.4 mg, weight of crystals).¹¹ H NMR (400 MHz, DMSO-d₆): δ 3.55 (d, JHP = 10.64 Hz, 4H, CH₂), 3.38−3.29 (m, 12H, OCH₂), 2.22 (s, 12H, CH₂). ³¹P{¹H} NMR (400 MHz, DMSO-d₆): δ 29.61 (s). ESI-TOF-MS. Calcd for C₂₈H₂₈Cl₂O₁₆P₂Re₂ ([M + H]+): m/z 1126.9411; found: m/z 1126.9146. Anal. Calcd for
C₂H₄Cl₂O₄P₂Re₂: C, 29.87; H, 2.51. Found: C, 29.72; H, 2.62. IR (KBr, cm⁻¹): 2022 (s), 1907 (s), 1501 (s), 1184 (s).

Synthesis of [(Re(CO)]₃(μ-DHBQ)(Re(CO)]₃(L²)] (5). Pale brown crystals of 5 were obtained using Re₃(CO)₁₀ (101.1 mg, 0.1532 mmol), H₂-DHBQ (21.8 mg, 0.1532 mmol), L₁ (63.4 mg, 0.1532 mmol), and mesitylene (10 mL). Yield: 25% (43.3 mg, weight of crystals). ¹H NMR (400 MHz, DMSO-d₆): δ 7.73–7.47 (m, 20H, ArH), 5.78 (s, 1H, ArH), 2.58–2.54 (m, 4H, PCH₂), 1.65–1.57 (m, 2H, PCH₂CH₂). ³¹P{¹H} NMR (400 MHz, DMSO-d₆): δ 29.93 (s). Anal. Calcd for C₃₉H₂₈O₁₂P₂Re₂: C, 41.71; H, 2.51. Found: C, 41.62; H, 2.58. IR (KBr, cm⁻¹): 2016 (s), 1896 (s), 1528 (s), 1167 (s).

Synthesis of [(Re(CO)]₃(μ-DHBQ)(Re(CO)]₃(L²)] (6). Brown powder of 6 was obtained using Re₃(CO)₁₀ (100.6 mg, 0.1551 mmol), H₂-DHBQ (22.2 mg, 0.1532 mmol), L₁ (73.2 mg, 0.1532 mmol), and toluene (10 mL). Yield: 14% (25.5 mg, weight of crystals). ¹H NMR (400 MHz, DMSO-d₆): δ 7.12 (s, 1H, ArH), 6.92 (m, 3H, ArH), 5.79 (s, 1H, ArH), 3.75 (d, 2H, CH₂). ³¹P{¹H} NMR (500 MHz, DMSO-d₆): δ 7.48 (m, 20H, ArH), 2.58 (s, 1H, ArH), 3.59 (d, 2H, CH₂). ³¹P{¹H} NMR (400 MHz, DMSO-d₆): δ 29.88 (s). Anal. Calcd for C₇₂H₅₂O₂₂P₄Re₄: C, 40.45; H, 2.45. Found: C, 40.36; H, 2.51. IR (KBr, cm⁻¹): 2016 (s), 1896 (s), 1523 (s), 1151 (s).

Synthesis of [(Re(CO)]₃(μ-DHBQ)(Re(CO)]₃(L²)] (7). Dark crystals of 7 were obtained using Re₃(CO)₁₀ (100 mg, 0.1532 mmol), H₂-DHBQ (21.9 mg, 0.1532 mmol), L₂ (58.4 mg, 0.1532 mmol), and mesitylene (8 mL). Yield: 49% (79.1 mg, weight of crystals). ¹H NMR (400 MHz, DMSO-d₆): δ 7.69 (s, 1H, ArH), 3.55 (d, 2H, CH₂), 3.34–3.29 (m, 12H, OCH₃). ³¹P{¹H} NMR (400 MHz, DMSO-d₆): δ 29.62 (s). ESI-TOF-MS. Calcd for C₄₂H₃₈O₃₂P₄Re₄: (M + H⁺): m/z 1057.0170; found: m/z 1056.9374. Anal. Calcd for C₃₂H₂₆O₂₁P₄Re₂: C, 44.59; H, 2.55. Found: C, 44.65; H, 2.51. IR (KBr, cm⁻¹): 2011 (s), 1890 (s), 1512 (s), 1167 (s). ³¹P{¹H} NMR (400 MHz, DMSO-d₆): δ 29.93 (s). Anal. Calcd for C₈₂H₅₆O₂₂P₄Re₄: C, 43.54; H, 2.50. Found: C, 43.41; H, 2.56. IR (KBr, cm⁻¹): ν = 2027 (s), 1890 (s), 1145 (s).

X-ray Crystallography. Intensity data of crystals of 1–3, 5–8, and 10 were collected on a Bruker D8 Quest diffractometer [λ(Mo Kα) = 0.71073 Å]. Intensity data of 4 were collected on an Oxford Xcalibur S diffractometer. Intensity data of 9 were collected on a Rigaku Saturn 724 CCD diffractometer. The structures were solved by direct methods using SHELXS-97 and refined using the SHELXL-2014/7 program (within the WinGX program package). Non-H atoms were refined anisotropically. Some of the lattice solvent molecules could not be modeled, and hence their contribution to the intensities was excluded using the SQUEEZE option in PLATON. The crystallographic data of 1–5 and 7–10 are provided in Tables S1–S2.

Computational Section. The atomic coordinates were obtained from the X-ray crystal structures of 1–5 and 7–8. The ground-state geometry optimizations of 1–8 were performed in the gas phase using the B3LYP method. A Stuttgart–Dresden (SDD) basis set for the rhenium atom and the 6-311G model) solvent model with THF. The TDDFT analysis was carried out, and the B3LYP functional and SDD/6-311G basis set for 1–8 were used in the optimization step. A total of the lowest 100 singlet excited states and their corresponding oscillator strengths were determined using a TDDFT calculation for 1–8. The GaussSum programs were used to calculate the percentage contribution of various groups and the electronic spectral simulation.
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DEDICATION

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