# **Inorganic Chemistry**

# Homoleptic Tris-Diphosphine Re(I) and Re(II) Complexes and Re(II) **Photophysics and Photochemistry**

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S Supporting Information

ABSTRACT: The ligand-to-metal charge transfer state (LMCT) of [(dmpe)<sub>3</sub>Re]<sup>2+</sup> (dmpe = 1,2-bis(dimethylphosphino)ethane) has been demonstrated to be a potent oxidant  $(E^0(\text{Re}^{2+*}/\text{Re}^+) = 2.61 \text{ V}$  vs standard calomel electrode). This complex has been traditionally prepared by nontrivial routes in low yields, and very little has been achieved in optimizing the ground state and emission energy properties of the general class of complexes  $[(PP)_2Re]^{2+}$  (PP = chelating diphosphine) through phosphine modification. Improved syntheses for Re(I) tris-homoleptic diphosphine complexes  $[(PP)_3Re]^+$  (PP = 1,2-bis(dimethylphosphino)ethane (dmpe), 1,2-bis(diethylphosphino)ethane (depe), bis-(dimethylphosphino)methane (dmpm), bis(diphenylphosphino)methane (dppm), Me<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, 1,3-bis(dimethylphosphino)propane (dmpp), or 1,2-bis(dimethylphosphino)benzene (dmpb)) were achieved by single-pot reactions exploiting the



reducing potential of the phosphines when reacted with Re<sup>V</sup> oxo-complexes in 1,2-dichlorobenzene at 160-180 °C. Singleelectron chemical oxidation of  $[(PP)_3Re]^+$  yields luminescent  $Re^{II}$  analogues; appropriate use of  $Ph_3C^+$ ,  $Cp_2Fe^+$ , or  $(4-BrC_6H_4)_3N^+B(C_6F_5)_4^-$  salts produced  $[(PP)_3Re]^{2+}$  complexes in good yields. Crystallographic trends for the  $Re^+/Re^{2+}$  pairs show significantly lengthened  $Re^{2+}-P$  bonds for  $[(PP)_3Re]^{2+}$  relative to the corresponding  $[(PP)_3Re]^+$  system. The redox and luminescence behavior of the complexes indicates the luminescence is from a ligand  $P(\sigma)$ -to-metal ( $Re(d\pi)$ ) charge transfer (<sup>2</sup>LMCT) state for all the complexes. Structured luminescence at 77 K is postulated to originate from relaxation of the <sup>2</sup>LMCT state into two spin-orbit coupled states: the ground state and a state  $\sim 3000$  cm<sup>-1</sup> above the ground state. The excited-state reduction potential  $(\text{Re}(II^*/I))$  for  $[(\text{depe})_3\text{Re}]^{2+}$  was determined from the free energy dependence of luminescence quenching rate constants. Yields for formation of charge separated ions were determined for three of the complexes with a variety of electron donors. Despite favorable electrostatics, no charge separated ions were observed for radical ion pairs for which the energy of back electron transfer exceeded 1.1 V.

# INTRODUCTION

In comparison to the wide variety and scope of  $d^6 Re(I)$ coordination compounds, relatively few stable low-spin d<sup>5</sup> Re<sup>II</sup> monomeric complexes are known.<sup>1-11</sup> Heteroleptic diimine and diphosphine carbonyls [(diimine)(CO)<sub>3</sub>ReX]<sup>+</sup>,<sup>12,13</sup> trans- $[(PP)_2(CO)_2Re]^{2+}$  and  $trans-[(dppe)_2(CO)ReBr]^{+,14,15}$  have been generated electrochemically and have generally limited stabilities (PP = 1,2-bis(dimethylphosphino)ethane (dmpe), 1,2-bis(diethylphosphino)ethane (depe), bis-(dimethylphosphino)methane (dmpm), bis-(diphenylphosphino)methane (dppm), Me<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, 1,3bis(dimethylphosphino)propane (dmpp), or 1,2-bis-(dimethylphosphino)benzene (dmpb); dppe = 1,2-bis-(diphenylphosphino)ethane). More recently,  $[Re(CO)_2Br_4]^{2-}$ has been reported as a useful precursor for a variety of  $[\text{Re}(\text{CO})_2\text{Br}_2(\text{L})_2]$  products.<sup>16–19</sup> Very few simple homoleptic Re<sup>II</sup> complexes are known:  $[(bpy)_3Re]^{2+}$  (bpy = 2,2'-bipyridine),  $^{20,21}$   $[(2,2'-azobipyridine)_3Re]^{2+}, ^{22}$   $[(dmpe)_3Re]^{2+,22}$  and most recently the mixed diphosphine chelate systems  $[(depe)_{3-x}(dmpe)_x \text{Re}]^{2+}$   $(x = 0-3)^{2+}$ 

 $[(dmpe)_3 Re]^{2\scriptscriptstyle +}$  and its congener  $[(dmpe)_3 Tc]^{2\scriptscriptstyle +}$  exhibit unique luminescence properties in solution, with higher quantum efficiencies  $(\Phi_{em})$  than  $[(bpy)_3Ru]^{2+,26,27}$  In addition, this class of complexes has been highlighted as potentially useful since their excited states are strongly oxidizing; they have been labeled as highly oxidizing excited states (HOES).<sup>28,29</sup> In the case of  $[(dmpe)_3 Re]^{2+}$ , excited-state guenching by a series of substituted aromatic hydrocarbons has shown that the photoexcited complex is an extremely strong oxidant  $(E^{0}(\text{Re}^{2+*}/\text{Re}^{+}) = +2.58 \text{ V vs standard calomel electrode}$ (SCE)).<sup>28,29</sup> [(dmpe)<sub>3</sub>Re]<sup>2+</sup> is unique in having a doublet– doublet absorption transition that is essentially ligand-to-metal charge transfer (LMCT) in nature, with the excited-state electron hole essentially residing in the phosphorus  $\sigma$ -bonding lone-pair molecular orbital set. In contrast, the majority of strong photooxidant complexes reported to date are based on metal-to-ligand charge transfer (MLCT) transitions with bipyridine-type ligands, such as  $[(TAP)_3Ru]^{2+}$  (TAP =

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Scheme 1



1,4,5,8-tetraazaphenanthrene),<sup>30,31</sup> [(bpy)Re(CO)<sub>4</sub>]<sup>+</sup>,<sup>32</sup> [(bpz)<sub>3</sub>Ru]<sup>2+,33,34</sup> (bpz = 2,2'-bipyrazine), and [Pt(dppe)(5,6-Me<sub>2</sub>phen)]<sup>2+,35</sup> Some of these complexes have found applications in selective DNA cleavage by single-electron oxidation<sup>30</sup> and as "phototriggers" to generate radicals to study their initiation and propagation in biology.<sup>36,37</sup> LMCT systems are less common and are typically metal oxides, such as the uranyl ion  $UO_2^{2+,38,39}$  and molybdenum or tungsten polyoxometalate (POM) complexes;<sup>40,41</sup> these systems typically involve higher energy excitation thresholds ( $\leq$ 420 nm) and have been demonstrated to oxidize a variety of organic substrates including common environmental pollutants.<sup>42,43</sup> Several organic-based HOES systems are known, recent examples being pyrylogens<sup>44</sup> and chloride oxidation by guanine in DNA.<sup>45</sup>

We have been interested in expanding this unique class of  $[(PP)_3Re]^{2+}$  photooxidants in an effort to systematically optimize ESP<sub>ox</sub> and photophysical properties. Besides  $[(dmpe)_3Re]^{2+}$ , the only modest extension of this class has been to the series  $[(dmpe)_{3-x}(depe)_xRe]^{2+.25}$  Diphosphines have good flexibility in terms of pendant group and phosphine-linker modifications and have a considerable potential for tuning ground state and emission properties. Here we report the extension of  $[(PP)_3Re]^+$  systems to a broader range of trischelate compounds and their associated  $Re^{II}$  analogues,  $[(PP)_3Re]^{2+}$ . An assessment of HOES potentials based on ground-state and luminescence studies provide invaluable insights on how to further optimize and more fully develop this distinctive class of compounds.

# RESULTS AND DISCUSSION

Synthesis and Characterization of  $[(PP)_3Re]^+$  Complexes. Broader access to  $[(PP)_3Re]^+$  complexes requires a more generally applicable synthetic approach. The initial synthesis of  $[(dmpe)_3Re]^+$  involved the reduction of  $[ReO_4]^-$  to Re(III) with 10 equiv of dmpe and HCl under pressure at 155 °C to produce  $[(dmpe)_2ReCl_2]^+$  in good yield.<sup>46</sup> Further reduction of  $[(dmpe)_2ReCl_2]^+$  to  $[(dmpe)_3Re]^+$  was performed

using an additional 5 equiv of dmpe in a methanolic KOH solution at 155 °C for 12 h (70% yield).<sup>24</sup> A subsequent improvement was reported using the Re(V) precursors  $[(py)_4 ReO_2]^+$  or  $[(PPh_3)_2 ReCl_2(O)OEt]$  with 4 equiv of dmpe in the presence of thiophenol as a catalyst to give  $[(dmpe)_3Re]^+$  in ~50% yield.<sup>47</sup> Most recently  $[(dmpe)_3Re]^+$ has been prepared in moderate yield from [(benzil) (PPh<sub>3</sub>)<sub>2</sub>ReCl<sub>3</sub>] using excess dmpe (11 equiv) as both reductant and trapping ligand and excess TlPF<sub>6</sub> as a chloride acceptor.<sup>25</sup> Extending this procedure to the ethyl-substituted chelate depe with the addition of zinc amalgam as a reducing agent afforded  $[(depe)_3 Re]^+$  in only 4.7% yield. The mixed phosphine chelate complexes [(dmpe)<sub>2</sub>(depe)Re]<sup>+</sup> and [(depe)<sub>2</sub>(dmpe)Re]<sup>2+</sup> were prepared from the reactions of  $[(dmpe)_2 ReCl_2]^+$  and  $[(depe)_2 ReCl_2]^+$  with excess depe and dmpe, respectively. A complete reduction of  $[(PPh_3)_2ReI(O)_2]$  with excess dppm in refluxing methanol gives  $[(dppm)_3Re]^+$  in 30% yield.<sup>4</sup>

Building upon these prior syntheses, we successfully converted Re(V) oxo complexes [(PPh<sub>3</sub>)<sub>2</sub>ReI(O)<sub>2</sub>],  $[(PPh_3)_2ReI_2(O)OEt]$ , or  $[(py)_4Re(O)_2]^+OTf^-$ , directly to  $[(PP)_{3}Re]^{+}$  products in moderate to excellent yields (49–93%) in a one-pot reaction using 5-6 equiv of the appropriate diphosphine (dmpe, dmpm, depe, Me<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, dmpb (ophenylenebis(dimethylphosphine)) in 1,2-dichlorobenzene at 170-180 °C. The propyl-bridged dimethylphosphine chelate dmpp was found to react only with  $[(py)_4 \text{Re}(O)_2]^+$  under similar conditions to give the desired product  $[(dmpp)_3Re]^+$ . An improved synthesis of previously reported<sup>48</sup>  $[(dppm)_3 Re]^+$ from  $[(PPh_3)_2ReI(O)_2]$  was achieved by extending the reflux time in methanol from 3 to 24 h (Scheme 1).  $[(PP)_3Re]^{+/2+}$ complexes often suffer from poor solubility, which hampers full characterization. Accordingly, all initially formed [(PP)<sub>3</sub>Re]<sup>+</sup> complexes were treated with  $K[B(C_6F_5)_4]$  in CH<sub>2</sub>Cl<sub>2</sub> to give the highly soluble corresponding borate anion products,  $[(PP)_{3}Re]B(C_{6}F_{5})_{4}.$ 

[(PP)<sub>3</sub>Re]<sup>+</sup> complexes were characterized by NMR, X-ray diffraction, and elemental analysis. <sup>31</sup>P NMR resonances for all the complexes, except for that of Me<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, appear as





complex	Re–P, ave (Å)	P-Re-P (deg) ave, <i>intra</i> chelate	P-Re-P (deg) ave, interchelate	$\Delta$ (Å) <sup>a</sup>
$[(dmpp)_{3}Re]^{+}(\underline{5})$	2.420	88.3		
$[(dmpp)_{3}Re]^{2+}$ (12)				
[(dmpe) <sub>3</sub> Re] <sup>+</sup> ( <u>1</u> )	2.381	82.4	92.7	0.067
$[(dmpe)_{3}Re]^{2+}(\underline{8})$	2.448	80.8	93.3	
$[(depe)_{3}Re]^{+}(\underline{2})$	2.405	80.9	93.3	0.054
[(depe) <sub>3</sub> Re] <sup>2+</sup> ( <u>9</u> )	2.459	80.2	93.6	
$[(dmpm)_3Re]^+$ (3)	2.371	68.9	98.1	0.046
$[(dmpm)_{3}Re]^{2+}$ ( <u>10</u> )	2.417	68.5	98.2	
$fac-[(Me_2PCH_2PPh_2)_3Re]^+$ (4)	2.376 (PMe <sub>2</sub> ) 2.419 (PPh <sub>2</sub> )	68.5	98.1	0.023 (PMe <sub>2</sub> ) 0.046 (PPh <sub>2</sub> )
$fac-[(Me_2PCH_2PPh_2)_3Re]^{2+}$ (11) <sup>b</sup>	2.399 (PMe <sub>2</sub> ) 2.465 (PPh <sub>2</sub> )	68.7	105.7, 93.2	
$[(dmpb)_3Re]^+$ (7)	2.372	82.2	92.8	0.053
$[(dmpb)_{3}Re]^{2+}$ ( <u>14</u> )	2.425	81.9	92.9	
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 ${}^{a}\Delta$  is defined as  $\Delta = [(\text{Re}^{2+}-\text{P})_{\text{ave}} - (\text{Re}^{+}-\text{P})_{\text{ave}}]$ .  ${}^{b}$ The three Re-PMe<sub>2</sub> and the three Re-PPh<sub>2</sub> bonds are symmetry-related by a crystallographic  $C_3$  axis and thus are not averaged.

broad singlets:  $\delta$  –50.3 ( $\nu_{1/2}$  = 6 Hz) (dppm), 16.8 ( $\nu_{1/2}$  = 225 Hz) (depe), 2.1 ( $\nu_{1/2}$  = 790 Hz) (dmpe), 1.5 ( $\nu_{1/2}$  = 345 Hz) (dmpb), -53.8 ( $\nu_{1/2}$  = 165 Hz) (dmpp), and -66.2 ( $\nu_{1/2}$  = 50 Hz) (dmpm). The significant broadening of <sup>31</sup>P NMR signals is tentatively attributed to quadrupolar relaxation by <sup>185</sup>Re and <sup>187</sup>Re in an octahedral coordination environment.<sup>49</sup> For the unsymmetrical complex fac-[(Me<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>Re]<sup>+</sup>, <sup>31</sup>P NMR spectra showed two doublets centered at -45.9 and -63.3 ppm with  ${}^{2}J_{PP}(\text{trans}) = 94$  Hz, which show unresolved  ${}^{2}J_{PP}(\hat{\text{cis}})$ coupling. Proton methyl resonances for  $[(PP)_3Re]^+$ , where PP = dmpe, dmpm, dmpp, and dmpb, appear as two distinct broad singlets due to reduced symmetry imposed by the threechelating ligands. Previous <sup>1</sup>H NMR spectra for (dmpe)<sub>3</sub>Re<sup>+</sup> do not report CH<sub>2</sub>CH<sub>2</sub> ligand backbone resonances,<sup>47</sup> probably due to significant overlap in the lower resolution spectra (250 MHz) with the more intense methyl resonances. <sup>1</sup>H NMR spectra for  $[(depe)_3 Re]^+$  show one broad unresolved methyl resonance at  $\delta$  1.15 with the pendant diastereotopic ethyl CH<sub>2</sub> groups appearing as two separate resonances at  $\delta$  1.61 and 1.89. For the asymmetric diphosphine complex  $[(Me_2PCH_2PPh_2)_3Re]^+$  (4) a mixture of isomers may be anticipated with mutually facial or meridional sets of Me2P and Ph<sub>2</sub>P groups. Under the conditions employed in the synthesis of 4, only the facial isomer was observed and the stereochemistry was confirmed by X-ray diffraction (vide infra). Elemental analyses of the [(PP)<sub>3</sub>Re]<sup>2+</sup> complexes were satisfactory, although a few exhibited deviations of slightly more than 0.5% in analysis of one element in the complex. The

origin of this discrepancy is not clear, but the spectroscopic data all support a level of purity in excess of 95%.

 $[(\hat{PP})_3 Re]^{2+}$  Syntheses. Single-electron chemical oxidations of  $[(dmpe)_3 Re]^+$  or  $[(depe)_3 Re]^+$  have been performed using  $H_2O_2$  as the oxidant to give the corresponding Re(II) products in low yields.<sup>50,23</sup> Kirchhoff has more recently shown that  $[(dmpe) (depe)_2 Re]^{2+}$  can be prepared in situ by the reduction of the Re(III) precursor  $[(depe)_2 ReCl_2]^+$  in the presence of excess dmpe with Zn/Hg amalgam, but this approach has not been extended to other systems.<sup>25</sup>

In light of the general reversibility of  $[(PP)_3Re]^{2+/+}$  redox couples (vide infra), simple stoichiometric one-electron chemical oxidants were used to prepare the corresponding  $[(PP)_3Re]^{2+}$  complexes in good yield (66–95%, Scheme 2). For the more readily oxidized complexes  $[(PP)_3Re]^+$  (PP = dmpe, depe, dmpm, Me<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, or dmpp), the oxidants Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> (-0.11 mV vs Cp<sub>2</sub>Fe<sup>+</sup>, CH<sub>3</sub>CN) or  $[Cp_2Fe]$ -B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-1</sup> readily gave the corresponding  $[(PP)_3Re]^{2+}$  complexes. The more powerful oxidant (4-BrC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>N<sup>+</sup>B-(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-1</sup> (+0.67 V vs Cp<sub>2</sub>Fe<sup>+</sup>, CH<sub>3</sub>CN) was required for the more electron-poor complexes  $[(dmpb)_3Re]^+$  and  $[(dppm)_3Re]^+$ . Oxidation of more electron-rich  $[(PP)_3Re]^+$  systems with (4-BrC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>N<sup>+</sup> led to overoxidation and the formation of uncharacterized orange solids, which are presumed to be Re<sup>III</sup> products.

**Crystallographic Studies.** As a general class of coordination compounds, structurally characterized six-coordinate phosphine complexes  $[(R_3P)_6M]$  have been reported for Mn,<sup>52</sup> Re,<sup>25,53,54</sup> Fe,<sup>55–57</sup> Rh,<sup>58</sup> Co,<sup>59</sup> Cr,<sup>60–64</sup> Mo,<sup>60,63,65–67</sup> W,<sup>56,60,63,68,69</sup> V,<sup>63,70</sup> Nb and Ta,<sup>63</sup> Zr,<sup>71</sup> and Ru.<sup>72</sup> Structural data for tris phosphine chelate Re complexes have been reported for  $[(dppm)_3Re]^{+.54}$  and for the redox pairs  $[(dmpe)_2(depe)Re]^{2+}$  and  $[(dmpe)_2(depe)Re]^{+.25}$  Direct isostructural comparisons of metals in different oxidation states are not widely available, and to our knowledge this isostructural Re<sup>+/2+</sup> pair is the only known example for a homoleptic polyphosphine complex.

Interestingly, Re–P bond lengths for  $[(dmpe)_2(depe)Re]^{+/2+}$ indicate a lengthening of the bonds of ~0.05 Å following oxidation. The result is in agreement with earlier  $[(dmpe)_3Re]^{2+/+}$  EXAFS data.<sup>23</sup> Structural data for all obtainable  $[(PP)_3Re]^{2+/+}$  pairs in the present study (Table 1) also show significantly longer Re<sup>2+</sup>-P bonds than their Re<sup>+</sup>-P counterparts (average Re-P bond length difference defined as  $\Delta$ ):  $\Delta$ (dmpe)  $\approx 0.07$  Å, depe  $\approx 0.05$  Å, dmpm  $\approx 0.05$  Å, dmpb  $\approx 0.05$  Å, and for Me<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> the two distances are  $\sim 0.02$ for Me<sub>2</sub>P-Re and ~0.05 Å for Ph<sub>2</sub>P-Re. No standard ionic radii for Re<sup>+</sup> and Re<sup>2+</sup> have been established; nevertheless, the simplistic expectation is that Re<sup>+</sup>-P bond lengths would be longer, not shorter, than the corresponding Re<sup>2+</sup>-P bond lengths. We performed density functional theory (DFT) calculations for the  $\lceil (dmpe)_3 Re \rceil^{2+/+}$  pair to further explore this phenomenon. Optimized structures confirm the observed bond length trend: the Re-P average bond distances for  $[(dmpe)_{3}Re]^{+}$  (2.409, 2.381 Å observed) and  $[(dmpe)_{3}Re]^{2+}$ (2.475, 2.448 Å observed) are systematically lengthened by 0.027 and 0.028 Å but have a virtually identical calculated  $\Delta$ (dmpe) of 0.066 Å (0.067 Å observed). Spin-corrected Maver bond order indexes<sup>73</sup> reflect a lower effective bond order for  $\operatorname{Re}^{2+}$  relative to  $\operatorname{Re}^+$  (0.829 vs 0.896). A natural bond orbital analysis also reveals a significant increase in phosphorus lone pair p-character for  $\operatorname{Re}^{2+}-P$  (sp<sup>1.56</sup>) relative to  $\operatorname{Re}^{+}-P$  (sp<sup>1.37</sup>), which may at least partially explain the bond lengthening.<sup>74</sup> A qualitative conclusion based on "Bent's Rule" may be stated: The higher effective electronegativity of Re<sup>2+</sup> results in a shift in p-character to the phosphorus lone pair, resulting in greater atomic orbital radial extension and a longer associated Re-P bond.

The average Re–P bond length for  $[(PP)_3Re]^+$  complexes modestly increases in the following order: dmpb (2.37 Å)  $\approx$ dmpm (2.37 Å)  $\approx$  dmpe (2.38 Å)  $\approx$  Me<sub>2</sub>P–Re of Me<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (2.38 Å) < depe (2.41 Å)  $\approx$  Ph<sub>2</sub>P–Re of Me<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (2.42 Å) and qualitatively follows the increased steric demand of the PR<sub>2</sub> groups. As expected, the largest distortions from a metal octahedral environment are in the complexes containing one CH<sub>2</sub> phosphine linker. For the Re<sup>2+</sup> analogues, except for the Me<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> complexes, the bite angles become slightly more acute due to the lengthened Re–P bond lengths.

**Electronic Absorption Spectra.** While UV–vis properties for  $[(dmpe)_{3-x}(depe)_x Re]^{2+}$  complexes have been studied by absorption spectroelectrochemistry,<sup>25–27</sup> readily isolated  $[(PP)_3 Re]^{2+}$  systems in this study allow for straightforward UV–vis characterization for a wide range of phosphine chelate derivatives (Table 2). Significant changes in the  $[(PP)_3 Re]^{2+}$ absorption spectra are observed depending on the nature of the phosphine substituents, the chelate linking groups, and the chelate bite angle. A representative absorption spectrum is shown in Figure 1. Comparing alkyl phosphines with methyl substituents, an increase in the bite angle dmpm < dmpe < dmpp results in a blue shift in the absorption maximum and an

Table 2. UV-vis Absorption Maxima and Absorptivities for  $[(PP)_3Re]^{2+}$  Complexes in Deoxygenated 0.23 mM CH<sub>3</sub>CN

$[(PP)_{3}Re]^{2+}$	$nm \begin{pmatrix} \lambda_{max'} \\ cm^{-1} \end{pmatrix}$	$M^{-1}$ cm <sup>-1</sup>	P-Re-P chelate angle
dmpp, <u>12</u>	505 (19 800)	1850	
dmpe, <u>8</u>	528 (18 900)	1530	80.8
depe, <u>9</u>	531 (18 800)	1880	80.2
dmpb, <u>14</u>	541 (18 500)	550	81.9
dmpm, <u>10</u>	539 (18 550)	700	68.5
Me <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> , <u>11</u>	551 (18 150)	1400	68.7
dppm, <u>13</u>	589 (17 000)	1300	



Figure 1. Absorption spectrum of  $[Re(depe)_3]^{2+}$  in acetonitrile at room temperature.

increase in the absorptivity. For  $[(dmpe)_3Re]^{2+}$  this band has been assigned as a  $P(\sigma) \rightarrow Re(d\pi)$  LMCT transition.<sup>27</sup> The behavior, however, is also appropriate for a Re localized d-d transition. For the CH<sub>2</sub>-linked phosphine derivatives, the phenyl containing phosphines have characteristic high energy phenyl localized  $\pi \rightarrow \pi^*$  transitions in the UV; the visible transitions exhibit a shift to lower energies with increased phenyl substitution (Figure S2). The more electron-poor 1,2aryl-bridged dmpb complex <u>14</u> shows a slight shift of the lowest energy transition to lower energy relative to dmpe and depe derivatives, which, despite a significant difference in  $E^0(Re^{2+/+})$ potentials (vide infra), have very similar energies (Figure S3).

Luminescence Behavior. In earlier work, room-temperature luminescence was observed for  $[(dmpe)_3Re]^{2+}$ . The emission emanated from the  $P(\sigma) \rightarrow Re(d\pi)$  LMCT doublet excited state of the complex.<sup>27,29</sup> Some of the complexes here also have ambient temperature emission with maxima and Stokes shifts similar to the LMCT luminescence of the dmpe complex. Figure 2 illustrates two examples of room-temperature complex absorption and luminescence in acetonitrile. Spectra of all the complexes in solution at room temperature and in propionitrile/butyronitrile glasses at 77 K are shown in Supporting Information (Figures S5–S9). Steady-state and time-resolved luminescence maxima, lifetimes, and quantum yields, along with the  $E_0$  energy obtained from fits of 77 K emission, are summarized in Table 3. The luminescence in each case arises from excitation into the LMCT absorption and higher energy bands. The complexes having a methane bridge



**Figure 2.** Room-temperature absorption (solid line) and fluorescence (dashed line) for acetonitrile solutions of  $[\text{Re}(\text{dmpe})_3]^{2+}$  (upper) and  $[\text{Re}(\text{dmpp})_3]^{2+}$  (lower).

 $(PCH_2P)$  exhibit weak or no emission in solution at room temperature.

The room-temperature excited-state lifetimes for the complexes that could be measured ranged between 6 and 25 ns. Since both the ground and excited states are doublets, radiative decay rate constants could be obtained (Table 3) without consideration of intersystem crossing efficiency, as is often the case with Re(I), Ru(II), Os(II), and other luminescent transition metal complexes. For the dmpp, dmpe, and depe complexes radiative decay rate constants are on the order of  $1 \times 10^6 \text{ s}^{-1}$ , more than 20 times greater than typical MLCT radiative decay rate constants for the spin-forbidden radiative relaxation. The dmpb complex, with very weak room-temperature luminescence, appears to have a smaller radiative decay rate constant, but this will not be firmly established until an accurate luminescence quantum yield is determined.

Since room-temperature luminescence was not observed for some complexes, and the luminescence was broad and structureless for the others (except for the dmpb and dmpp complexes), spectra were obtained in glasses at 77 K for most of the complexes (Table 4). All of the 77 K spectra exhibit two clearly resolved bands. The emission maxima are nearly identical to those obtained in solution at room temperature, which is unusual for charge transfer transitions.

The energy gap between the two observed maxima is greater than 2700 cm<sup>-1</sup> for all the complexes, and, as a result, a Franck–Condon analysis to determine medium frequency modes associated with excited-state decay is not really appropriate. For nearly all Ru(II) diimine and Re(I) diimine

Table 4. Summary of Results for 77 K Emission Spectra

compound	$E_{\rm max'}~{\rm cm}^{-1}~{\rm (nm)}$	$\Delta E \ (cm^{-1})$	rel inten
$[\text{Re}(\text{dmpp})_3]^{2+}$ , 12	17 125 (583)	2725	0.44
$[\text{Re}(\text{dmpe})_3]^{2+}$ , 8	16 860 (592)	3130	0.14
$[{\rm Re(depe)}_3]^{2+}$ , 9	16 890 (592)	3160	0.14
$[\text{Re}(\text{dmpm})_3]^{2+}$ , 10	17 200 (570)	3220	0.75
$[\text{Re}(\text{dmpb})_3]^{2+}$ , 14	16 240 (614)	2970	0.14
$[\text{Re}(\text{dppm})_3]^{2+}$ , 13	16 600 (602)	2958	0.30
$[\text{Re}(\text{Ph}_2\text{PCH}_2\text{PMe}_2)_3]^{2+}$ , 11	15 730 (634)	3310	0.15



**Figure 3.** 77 K fluorescence spectra of  $[\text{Re}(\text{dmpe})_3]^{2+}$  (upper) and  $[\text{Re}(\text{dmpp})_3]^{2+}$  (lower) in 4:1 ethanol/methanol glasses.

complexes measured, the average medium frequency mode is typically  $1200-1400 \text{ cm}^{-1}$ , and the much larger frequencies obtained here are compatible only with C–H stretching modes of the molecules studied; it is unlikely that these modes contribute to excited-state relaxation.

This large separation between the luminescent components of the 77 K emission spectrum, approaching and sometimes exceeding 3000 cm<sup>-1</sup> (Table 4), may be rationalized by considering spin—orbit coupling effects of the Re(II) center. In earlier work on Re(II) tris(diphosphine) complexes, Sullivan and co-workers noted that time-dependent density functional calculations on  $[\text{Re}(\text{dmpe})_3]^{2+}$  revealed a low-energy excited state ~2400 cm<sup>-1</sup> above the ground state.<sup>29</sup> The state arises because of splitting of the <sup>2</sup>T ground state (assuming a pseudooctahedral geometry) into two states resulting from spin—orbit coupling interactions (twofold and fourfold degenerate states).

Table 3. Absorption and Room-Temperature Emission Properties for Selected  $(PP)_3Re^{2+}$  Complexes in Deoxygenated  $CH_3CN$  and in 77 K  $CH_3CH_2CN/CH_3CH_2CN$  Matrices

complex	$abs max (cm^{-1})$	$E_{\rm m}^{a} ({\rm cm}^{-1})$ 298 K	E <sub>0</sub> (cm <sup>-1</sup> ) 77 K	stokes shift $(cm^{-1})$	Ф <sub>ет</sub> 298 К	τ (ns) 298 K	$\begin{array}{c} k_{\rm r}~({ m s}^{-1})\  imes~10^6 \end{array}$	$\substack{k_{ m nr}\ (s^{-1})\  imes\ 10^7}$
$[\text{Re}(\text{dmpp})_3]^{2+}$ , 12	19 800	17 240	17 150	2560	0.069	25	2.7	3.7
$[\text{Re}(\text{dmpe})_3]^{2+}$ , 8	18 900	16 800	16 900	2100	0.066	12	5.5	5.8
$[\text{Re}(\text{depe})_3]^{2+}$ , 9	18 800	16 750	16 890	2050	0.043	19	2.3	5.0
$[\text{Re}(\text{dmpb})_3]^{2+}$ , 14	18 500	16 750	16 290	1750	< 0.001	6	<0.2	>2
$[\text{Re}(\text{dmpm})_3]^{2+}$ , 10	18 550	17 500	17 200	1050	< 0.001			
$[Re(Ph_2PCH_2PMe_2)_3]^{24}$	, 11 18 150	NE <sup>b</sup>	15 760	2390 <sup>c</sup>				
$[\text{Re}(\text{dppm})_3]^{2+}$ , 13	17 000	NE <sup>b</sup>	16 620	380 <sup>c</sup>				

<sup>a</sup>Not corrected for detector response. <sup>b</sup>NE: no emission observed. <sup>c</sup>Stokes shift calculated using 77 K emission maximum.

Given the free ion spin-orbit coupling of nearly 3000 cm<sup>-1</sup> for Re, the state splitting should result in an absorption transition in the mid-infrared. In fact, the infrared spectra of two of the chromophores,  $[(dmpe)_3Re]^{2+}$  and  $[(dmpp)_3Re]^{2+}$ , both exhibit a broad, weak absorption between 2500 and 2700 cm<sup>-1</sup>, close to the energy splitting of the <sup>2</sup>T state predicted through DFT analysis (Figure S10). The lower energy transition is not observed in the room-temperature emission spectra except for the dmpp complex. This is in part due to the larger bandwidth at room temperature that serves to obscure the weaker lower energy luminescence.

For the complex series dmpm, Me<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, dppm, the absorption energy decreases with increasing degree of phenyl substitution, while the emission energies do not vary systematically. It is also important to note that the dppm complex has a very small experimental Stokes shift when comparing the room-temperature absorption maximum and the 77 K luminescence maximum. Since, for other complexes, relatively minor changes are observed between room-temperature and 77 K luminescence maxima, the observation for the dppm complex is likely a realistic estimate of the room-temperature Stokes shift. For fluorescence, the Stokes shift is directly related to the degree of excited-state distortion; thus, the implication is that phenyl substitution in place of methyl groups leads to a significantly smaller excited-state distortion.

**Redox Behavior.**  $[(dmpe)_3Re]^+$ ,  $[(dmpe)_2(depe)Re]^+$ ,  $[(dmpe)(depe)_2Re]^+$ , and  $[(depe)_3Re]^+$  have previously been studied by cyclic voltammetry;<sup>26–29,75</sup> the complexes all have reversible single-electron  $E^0(Re^{2+/+})$  waves and partially reversible  $Re^{3+/2+}$  waves that are clearly accompanied by some decomposition.<sup>25</sup> Results for the reversible one-electron potentials in CH<sub>3</sub>CN/TBAPF<sub>6</sub> (TBAPF<sub>6</sub> = tetrabutylammonium hexafluorophosphate) for the series of complexes  $[(PP)_3Re]^+$  are given in Table 5. For the  $E^0(Re^{2+/+})$  redox couples  $i_{pc}/i_{pa}$  ratios were essentially unity, whereas for the  $Re^{3+/2+}$  couples, the ratios were less than one and varied with sweep rate.

Table 5.  $E^0(\text{Re}^{2+/+})$  and  $E^0(\text{Re}^{3+/2+})$  Potentials for the Series  $[(\text{PP})_3\text{Re}]^+$  in 1 mM CH<sub>3</sub>CN<sup>*a*</sup>

	$E^0({\rm Re}^{2+/+})$	$E^0({\rm Re}^{3+/2+})$	$E^0(\text{Re}^{2+*/+}), \text{ V}^b$
РР	$\begin{array}{c} E_{1/2},  \mathrm{V} \\ (\Delta_{\mathrm{P}},  \mathrm{mV}) \end{array}$	$\begin{array}{c} E_{1/2},  \mathrm{V} \\ (\Delta_{\mathrm{P}},  \mathrm{mV}) \end{array}$	
dmpp, 12	0.20 (86)		2.32
dmpe, 8	0.28 (89)	1.18 (104)	2.38
depe, <b>9</b>	0.19 (62)	1.09 (80)	2.21
dmpb, 14	0.46 (98)		2.48
dmpm, 10	0.13 (82)		2.06
Ph <sub>2</sub> PCH <sub>2</sub> PMe <sub>2</sub> , 11	0.36 (69)		2.31
dppm, 13	0.57 (65)		2.63
<sup>a</sup> Scan rate 100 mV,	0.01 M TBA	$PF_{6}$ , $Ag/Ag^{+}(Me)$	eCN) reference

scan rate 100 mV, 0.01 M TBAPF<sub>6</sub>, Ag/Ag (MeCIV) reference electrode. Also excited-state  $\operatorname{Re}^{2+*/+}$  potential derived using  $E_{00}$  values from Table 3.  ${}^{b}E_{1/2}(\operatorname{Re}^{2+*/+}) = E_{00} + E_{1/2}(\operatorname{Re}^{2+/+})$ .

The following overall order for the  $E^0(\text{Re}^{2+/+})$  for  $[(\text{PP})_3\text{Re}]^+$  was observed: PP = dmpm < depe < dmpp < dmpe < Me\_2\text{PCH}\_2\text{PPh}\_2 < dmpb < dppm. For the CH<sub>2</sub>-bridged phosphines, replacing methyl substituents with more electron-withdrawing phenyl groups results in a consistent increase in the  $E^0(\text{Re}^{2+/+})$  potential. The successive +0.23 and +0.21 V increases in  $E_{1/2}$  accompanying the replacing of a total of six methyl pendant groups with phenyls corresponds to a

change of 38 mV per pendant substituent. For the ethyl-linked phosphines depe (+0.19 V) and dmpe (+0.28 V), the relatively modest electronic effect of replacing a methyl by an ethyl group results in a decrease of  $E_{1/2}$  of 0.09 V, or 15 mV per Me/Et change.  $E^0(\text{Re}^{2+/+})$  for the phenylene-bridged complex [(dmpb)<sub>3</sub>Re]<sup>+</sup> (+0.46 V) corresponds to a 180 mV increase in potential from  $[(dmpe)_2Re]^+$  (30 mV/P–C(phenyl)), which is comparable to the effect of replacing pendant Me groups with Ph. For Me<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PMe<sub>2</sub> chelates varying n = 1, 2, 3, the ordering: dmpm (n = 1, +0.13 V) < dmpp (n = 3, +0.20 V) <dmpe (n = 2, + 0.28 V) does not reflect a simple chelate bite angle trend, and is likely due to a combination of inductive and ring-strain effects. Cyclic voltammograms (CVs) for the Re<sup>2+/+</sup> waves of representative complexes are shown in Figure 4 (CVs of other complexes are provided in Supporting Information, Figures S11 and S12).



**Figure 4.** Cyclic voltammetry for  $(PP)_3Re^+$  complexes (PP = dmpm (red), dmpe (magenta), depb (blue) in 1 mM CH<sub>3</sub>CN, scan rate 100 mV, 0.1 M TBAPF<sub>6</sub>, vs Ag/Ag<sup>+</sup>(MeCN).

 $E^{0}(\text{Re}^{3+/2+})$  potentials are less reversible than the  $E^{0}(\text{Re}^{2+/+})$ couples and are similar to those previously reported for  $[(dmpe)_3Re]^+$ ,  $[(dmpe)_2(depe)Re]^+$ , and [(dmpe) (de $pe)_2Re]^{+.25}$  The decrease in reversibility has been attributed by Kirchhoff to phosphine-arm dissociation followed by CH<sub>3</sub>CN coordination.<sup>26</sup> The most electron-rich complex [(depe)<sub>3</sub>Re]<sup>+</sup> exhibits the greatest chemical reversibility and an  $i_{pc}/i_{pa}$  ratio near unity (0.92) at a sweep rate of 100 mV/s. The Re<sup>3+/2+</sup> waves for complexes with more positive  $E^{0}(\operatorname{Re}^{3+2/+})$  potentials were typically irreversible or outside the potential window of the solvent. Chemical oxidation of  $[(dmpm)_3Re]^+$  with 2 equiv of  $(4-BrC_6H_4)_3N^+SbF_6^-$  in CH<sub>3</sub>CN produced an orange solid, which was shown by Xray diffraction to be a seven-coordinate Re<sup>III</sup> complex having a coordinated solvent molecule. The crystallographic data of this seven-coordinate complex,  $[(dmpm)_3Re(MeCN)]^{3+}(15)$ , is given in the Supporting Information.

Absorption and Luminescence Spectral Trends. The variation in absorption and luminescence energies in the series dmpm, dmpe, and dmpp can be rationalized by the relative degree of ligand field splitting expected for the complexes based upon the bite angle of the ligands and the energies of the phosphorus  $P(\sigma)$  orbitals. Assuming the absorption and luminescence arises from an LMCT transition, a semiquantitative picture emerges if the relative  $E^0(\text{Re}^{2+/+})$  potentials are viewed as a measure of the  $\text{Re}(d\pi)$  energies (relative ionization energies) and the emission energy reflects the relative energy of relaxing from the  $\text{Re}(d\pi)$  to the  $P(\sigma)$  SOMO formed upon creation of the excited state,  $(P(\sigma)^1\text{Re}(d\pi)^6 \rightarrow P(\sigma)^2\text{Re}(d\pi)^5)$ , as illustrated in Figure 5. The idea that the LMCT transitions are affected by a variety of subtle features is



**Figure 5.** Relative energies of the  $\text{Re}(d\pi)$  and  $P(\sigma)$  levels for complexes having methyl, ethyl, and propyl bridges between the dimethylphosphine moieties.

indicated by the fact that plots of the absorption maximum versus  $E^0(\text{Re}^{2+/+})$  vary considerably from linearity for the series studied here (see Figure S13). The energies of the  $d\pi$  levels vary by 0.25 V between the dmpm and dmpe complexes and by 0.08 V between dmpe and dmpp. With this approach the dmpm ligand, despite the obviously poorer overlap with Re orbitals because of the small bite angle ( $\sim 68^\circ$ ; Table 1), is the best electron donor of the group. Note that the Re-P bond distance is shortest for dmpm. In going from dmpm to dmpp the Re-P bond length increases and the intraligand P-Re-P bite angle increases; these changes oppose one another in the context of influencing the  $E^0(\operatorname{Re}^{2+/+})$  and may account for the differences observed. Assuming the relative energies of the  $P(\sigma)$ levels of the three ligands are directly related to the energy of the  $\operatorname{Re}(d\pi)$  and the emission energy as shown in Figure 5, the  $P(\sigma)$  levels vary by only 60 mV, suggesting the predominant factor in determining this level is the relative ionization energy of the coordinated  $P(\sigma)$  orbitals. Overall, the differences in emission energies are small ( $\sim$ 700 cm<sup>-1</sup>), and any explanation of the behavior for this series is likely to reflect subtle differences in the orbital overlap that cannot easily be inferred from bite angle and bond distance changes.

The series of complexes having an increasing number of diphenylphosphine moieties exhibit progressively more positive  $E^{0}(\operatorname{Re}^{2+/+})$  potentials as the net  $\sigma$  donation from the coordinated phosphine decreases with decreasing basicity (increasing number of diphenylphosphine moieties) and the degree of  $\pi$ -back-donation to the phosphines in the Re coordination environment increases. A plot of the  $E^0(\text{Re}^{2+/+})$ as a function of the number of diphenylphosphine substituents is linear, but the emission energy does not exhibit this same linearity. Employing the approach used for the dmpx (x = m, e, p) above, the relative orbital energies are presented in Figure 6. Here, the energies of the  $d(\pi)$  orbitals lower as a result of the combined decreased ligand  $\sigma$  donation and increased Re-to-P back bonding. The energies of the  $P(\sigma)$  orbitals reflect the nature of the phosphine donor moieties. For the dppm complex, the basicity is weaker and the ionization energy of the phosphorus is more positive than the dmpm phosphorus, and thus both the Re(d $\pi$ ) and P( $\sigma$ ) levels decrease in energy with increasing phosphine aryl substitution. The complex of  $(Me)_2 PCH_2 P(Ph)_2$ , however, exhibits a change in the  $Re(d\pi)$ levels, reflecting a net change in the electron density of the Re(II) center, but the P( $\sigma$ ) level that results from inclusion of the emission energy (as above) is nearly the same as that of



**Figure 6.** Relative energies of the  $\text{Re}(d\pi)$  and  $P(\sigma)$  levels for  $[\text{Re}(\text{R}_2\text{PCH}_2\text{PR}_2)_3]^{2+}$  complexes having zero, three, and six diphenylphosphino moieties. Absorption energies, using fixed  $\text{Re}(d\pi)$  levels, are represented by the dashed (blue) lines.

dmpm. Presumably the most easily ionized P center of the ligand,  $P(Me)_2$ , serves as the donor, and the neighboring  $P(Ph)_2$  moiety has a small impact on the relative ionization energy of the phosphorus of the  $P(Me)_2$  group. This serves to provide an explanation for the observation that the tris- $(Ph)_2PCH_2P(Me_2)$  complex exhibits luminescence at lower energy than either the tris-dmpm or tris-dppm complexes.

Another peculiar aspect of the behavior of the phenylphosphine-containing complexes is the observed Stokes shifts. Since the ground and excited states are both doublets, no spin change occurs between the absorbing and emitting states, and a systematic trend in the Stokes shifts would be expected. In considering the observed Stokes shifts (Table 3), drawn from energies for solution absorption at room-temperature and 77 K luminescence in nitrile solvent matrices, the value for  $(Me)_2PCH_2P(Ph)_2$  is by far the largest, while that for the dppm complex is very small (<400 cm<sup>-1</sup>). Examination of absorption spectra (Figure S2) clearly shows that the phenylphosphine-containing complexes have larger absorptivities (2x) than the dmpm complex and distinctly different absorption bandshapes. If it is assumed that, for the  $(Me)_2PCH_2P(Ph)_2$  complex, the lowest energy allowed absorption transition is dominated by the  $P(Ph)_2$  levels  $(P(Ph)_2(\sigma) \rightarrow Re(d\pi))$ , but that luminescence is assigned as  $\operatorname{Re}(d\pi) \to \operatorname{P}(\operatorname{Me})_2(\sigma)$ , the large Stokes shift observed can then be rationalized. A semiquantitative depiction of this difference in absorption and luminescence transition energies is shown in Figure 6. One final note on the Stokes shifts is that, for the dppm complex, the implication is that the excited-state distortion is very small, while for the  $(Me)_2PCH_2P(Ph)_2$ complex, significant displacement exists between the groundand excited-state potential surfaces. Re-P bond distance differences between the Re(II) and Re(I) complexes of  $(Me)_2PCH_2P(Ph)_2$  indicate that the change observed for the  $Re-P(Me)_2$  bond is smaller than that observed for the Re- $P(Ph)_2$  bond. While data are not available for the dppm complex, the results for the  $(Me)_2PCH_2P(Ph)_2$  complex alone suggest that, if Re-P displacement is an important contributor to excited-state distortion, the distortion should be larger for the  $Re-P(Ph)_2$  linkages.

**Excited-State Redox Potentials and Photoinduced Electron-Transfer Reactions.** One of the characteristics of these complexes that makes them extremely interesting is the potential of the <sup>2</sup>LMCT states to act as very strong oxidants. An

estimate of the excited-state potentials can be obtained from the emission energies and the ground-state redox potentials. The Re<sup>3+/2+</sup> potentials for  $[\text{Re}(\text{dmpe})_3]^{2+}$  and the depe complex are ~1.1 V versus Ag<sup>+</sup>/Ag, and the  $E_0$  energies obtained from fits of the 77 K emission spectra are 2.1 eV, yielding an  $E^0(\text{Re}^{3+/2+*})$  of ca. -1 V versus Ag<sup>+</sup>/Ag. However, the  $E^0(\text{Re}^{2+*/+})$ , approximately equal to the sum of  $E^0(\text{Re}^{2+/+})$ and  $E_0$  is in excess of 2.0 V for all the chromophores.<sup>28,29</sup> The  $E_0$  energies for the series of complexes of dmpm, depe, dmpe, and dmpp are 1.93 < 2.10 - 2.10 < 2.13, respectively. Using  $E^{0}(\operatorname{Re}^{2+/+})$  values from Table 5, the estimated  $E^{0}(\operatorname{Re}^{2+*/+})$ values for these complexes are all greater than 2.0 V versus Ag<sup>+</sup>/Ag and are included in Table 5. Thus, all these complexes are extraordinary oxidants in their emissive excited states. The phenyl-substituted derivatives, with more positive  $E^{0}(\operatorname{Re}^{2+/+})$ potentials and comparable  $E_0$  energies, are even stronger excited-state oxidants.

Earlier work on the dmpe complex illustrated that the excited state was quenched by aromatic hydrocarbons with very positive  $E^0(Ar^{+/0})$  potentials, and Rehm–Weller analysis of quenching rate constants provided a measure of the  $E^0(Re^{2+*/0})$  potential that did not differ significantly from the value estimated from the emission energy and ground-state redox potential.<sup>29</sup>

We continued this work by looking at the excited-state quenching of  $[\text{Re}(\text{depe})_3]^{2+}$  by a series of amines, alkoxybenzenes, and simple aromatics. The dependence of the rate constant on the redox potential of the quencher is shown in Figure 7 below. While this is a Rehm–Weller-type plot, the



**Figure 7.** Free energy dependence of luminescence quenching rate constants for reaction of photoexcited  $[\text{Re}(\text{depe})_3]^{2+}$  with a series of electron donors (tabulated quenching rate constants and quenchers in Table S21).

paucity of data at the point where the quenching rate constant decreases precipitously stopped us from fitting the data with typical expressions; the falloff occurs at ~2.1 V versus  $Ag^+/Ag$ , representing a best guess estimate of the excited-state potential. This is in reasonably good agreement with that estimated from luminescence and redox data (2.2 V).

Transient absorption spectra of the radical ions produced in the photoredox reactions for several of the quenchers were also obtained. Representative spectra are shown in Figure 8 for the quenching of  $[\text{Re}(\text{depe})_3]^{2+}$  with 1,4-dimethoxybenzene (14DMB) and 1,2,4-trimethoxybenzene (124TMB). The spectra represent the difference between the alkoxybenzene



**Figure 8.** Transient spectra obtained 1  $\mu$ s following pulsed laser excitation ( $\lambda_{ex} = 530$  nm) of [Re(depe)<sub>3</sub>]<sup>2+</sup> with (A) 14DMB and (B) 124TMB. Absorption spectrum of [Re(depe)<sub>3</sub>]<sup>2+</sup> included below B.

cation radical spectrum summed with the Re(I) complex absorption and the ground-state absorption ( $\Delta \varepsilon_{\lambda} = \varepsilon_{(MB)\lambda} + \varepsilon_{(Re(I))\lambda} - \varepsilon_{(Re(II))\lambda}$ ). The absence of ground-state bleaching of the Re complex in the transient spectra reflects the fact that the 14DMB and 124TMB radical cations have much larger molar absorptivities ( $\varepsilon > 10\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) than the Re(II) complexes, and thus, the bleaching of the [Re(LL)<sub>3</sub>]<sup>2+</sup> absorption is in the noise. The back electron transfer yielded the starting reactants and was diffusion-limited in all cases examined.

Transient spectra could not be obtained for all of the quenchers used, especially for quenchers having very positive  $Q^+/Q$  potentials. Despite the fact that the luminescence of the chromophore used was nearly completely quenched in each case studied, the expected radical ion spectra were not observed for quenchers such as anisole, xylene, or toluene for which the back reaction free energies are >1.5 V. Given the surprising failure to observe radical ions in some cases, we decided to determine charge separation yields for reactions of  $[\text{Re}(\text{PP})_3]^{2+}$  (PP = dmpe, depe, and dmpp) complexes with 14DMB and 124TMB. The results are summarized in Table 6, showing

Table 6. Summary of Results from Charge Separation YieldExperiments in Acetonitrile Solution, Including the FreeEnergy of the Back Electron Transfer Reaction

$\begin{array}{c} \text{chromophore } \Delta G_{\text{BET}} \\ \text{(V)}^a \end{array}$	% $\eta_{\rm CS}$ with 1,2,4-TMB (1.12 V)	% $\eta_{\rm CS}$ with 1,4-DMB (1.34 V)
$[\operatorname{Re}(\operatorname{dmpe})_3]^{2+}$	91 ± 3	$53 \pm 3$
$\Delta G_{\rm BET}$ (V)	0.84	1.06
$[\text{Re}(\text{depe})_3]^{2+}$	$68 \pm 3$	6 ± 4
$\Delta G_{\rm BET}$ (V)	1.0	1.22
$[\operatorname{Re}(\operatorname{dmpp})_3]^{2+}$	$16 \pm 2$	0
$\Delta G_{\rm BET}$ (V)	0.92	1.14

"Determined from the sum of  $E^0(Q^+/Q) - E^0(\text{Re}^{2+/+})$ ; the energy associated with separation of the ions from the geminate pair is not considered, but should be small and invariant among all the pairs studied here.

charge separation efficiencies for 124TMB and 14DMB with back reaction exergonicities ranging from 0.84 to 1.22 V. Additional charge separation experiments were performed utilizing the  $[\text{Re}(\text{PP})_3]^{2+}$  complexes with dimethylaniline  $(E^0(\text{DMA}^+/\text{DMA}) = 0.76 \text{ V})$  and *N*-methylphenothiazine  $(E^0(\text{MPT}^+/\text{MPT}) = 0.54 \text{ V})$  as quenchers. The charge separation yields were very high, in some cases on the order of 100% with these donors; back electron transfer exergonicities ranged from 0.26 to 0.64 V. With quenchers having more positive  $E^0(Q^+/Q)$  potentials (1,2-dimethoxybenzene (1.54 V) or anisole (1.76 V)), the charge separation yield was zero with all three of the chromophores studied; the exergonicities in this group ranged from 1.26 to 1.64 V. This complete absence of charge separated ions in cases where the free energy of back electron transfer is nearly activationless has been the subject of earlier work, and the postulate has been that, for such highly exergonic sytems, back electron transfer can occur outside the contact ion pair.<sup>76,77</sup>

Looking at the results for the three complexes with 124TMB and 14DMB, it is clear that, for each chromophore, as the free energy for back electron transfer  $(\Delta G_{\text{BET}})$  becomes more exergonic the charge separation efficiency decreases. The charge separation efficiency reflects the relative rates of the radical ions escaping the solvent cage and the rate of back electron transfer within the solvent cage. The rate of the back electron transfer process should follow Marcus electron transfer dynamics, since, in each case, the process is an outer-sphere electron transfer. Given this, the free energy of activationless electron transfer will depend intimately on the reorganizational energy associated with the  $[Re(LL)_3]^{+/2+}$  and the  $Q^{+/0}$ processes. The crystallographic results indicate that substantial nuclear reorganization is required for reoxidation of the Re complexes and that the dmpe complex Re-P bond length decrease for the process is somewhat larger than the depe complex. With the overall observations that (a) easily oxidized quenchers have nearly 100% charge separation efficiencies and (b) the yield of ions steadily decreases as the  $Q^{+/0}$  potential becomes more positive (back electron transfer becomes more exergonic in each case), the implication is that the free energy for activationless back electron transfer is at potentials somewhere between 1.1 and 1.2 V for the three complexes used in the charge separation measurements. For the more easily oxidized quenchers, back electron transfer is in the Marcus normal region, and cage escape rate constants compete more and more effectively with back electron transfer as  $\Delta G_{\text{BET}}$ becomes less exergonic, ultimately reaching  $\eta_{cs} \approx 1$  when  $E^0$  for the  $[\text{Re}(\text{PP})_3]^+/\text{Q}^+$  reaction is less than ~0.6–0.8 V versus Ag<sup>+</sup>/Ag. Given that the apparent activationless free energies are relatively low, the possibility exists to observe charge separated ions for back reactions that are more exergonic than any of the systems studied here.

# **SUMMARY**

This work expands on earlier reports of the photochemistry and photophysics of tris(diphosphine) Re<sup>2+</sup> complexes in solution. A range of fully characterized  $[\text{Re}(\text{R}_2\text{P}(\text{CH}_2)_x\text{PR}_2)_3]^{2+}$   $(x = 1 - 1)^{2+1}$ 3; R = Me, Ph) complexes were prepared in which changes in the photophysical behavior were examined as a function of the size of the chelate ring as well as the degree of aryl versus alkyl substitution on the chelating phosphines. Increasing the chelate ring size from four to six results in a blue shift in the luminescence and increases in the luminescence lifetime and quantum yield, attributable to changes in the ligand field splitting and stabilization of the  $P(\sigma)$  bonding orbitals upon increasing the bite angle of the diphosphine ligand. The redox behavior for the complexes shows that the  $E(\text{Re}^{2+/+})$  potential is small and positive for all the tris-dialkylphosphinoalkyl complexes, but becomes steadily more positive with increasing replacement of dialkylphosphino moieties with diphenylphosphino groups. The emission energies for these complexes vary in a way that suggests the nature of the half-occupied phosphine orbital (alkyl or aryl) is the determining factor as the total number of diphenylphosphino substituents on the complex increases from zero to three to six; here, both the  $\operatorname{Re}(d\pi)$  and  $\operatorname{P}(\sigma)$  levels exhibit large changes as the basicity of the coordinating phosphorus centers decreases.

Because the excited-state energies are  $\sim 2$  eV, the photoexcited complexes are extraordinary oxidizing agents. The free energy dependence of the quenching of  $[Re(depe)_3]^{2+}$  with a series of electron donors was evaluated, and the excited-state  $E^{0}(\operatorname{Re}^{2+*/+})$  potential was found to be in reasonable agreement with that estimated from the emission energy and ground-state potential. Transient absorption spectra of the photoredox products with arylamine and alkoxybenzene donors indicate that the back reaction is complete and diffusion-limited. Surprisingly, charge separation of geminate photoredox pairs is nearly zero for reactions involving donors with  $E^0(D^{+/0})$ potentials greater than ca. 1.5 V versus AgCl/Ag, implying that the back electron transfer reactions may have reorganizational energies on the order of 1.1 to 1.2 V, making them nearly activationless when the back electron transfer process is highly exergonic. This aspect of the photoredox behavior of these complexes will be investigated in greater detail.

#### EXPERIMENTAL SECTION

**Photophysical and Electrochemical Methods.** Absorption spectra were recorded on an Agilent 8453 diode-array spectrophotometer at room temperature in distilled and degassed  $CH_3CN$ . Luminescence spectra were recorded on a PTI-Felix Fluorometer with photomultiplier detector. Samples were prepared as acetonitrile solutions and were studied without degassing. Transient absorption spectra were acquired with a system described elsewhere.<sup>78</sup>

Luminescence quantum yields of fluorescence were measured utilizing  $[Ru(bpy)_3](PF_6)_2$  as a reference. Reference and sample were absorbance-matched at the wavelength of excitation. After obtaining the emission spectra for both sample and reference, the quantum yield of the sample was determined by

$$\Phi_{\rm S} = \Phi_{\rm R} \frac{I_{\rm R}(1 - 10^{-\rm Abs_{\rm S}})}{I_{\rm S}(1 - 10^{-\rm Abs_{\rm R}})}$$

where  $I_r$  and  $I_s$  are the integrated intensity of the emission, Abs represents the absorbance at the wavelength where the reference and sample were matched, and  $\Phi_R$  is the quantum yield for the reference.

Lifetime measurements were performed by time-correlated singlephoton counting, exciting with a 377 nm pulsed diode laser (IBH) and detecting emitted light at right angles with an IBH-cooled PMT and using a Tennelec TAC/Ortec Easy-MCA for acquisition of the independent delay times. The digitized data of the MCA was processed using PTI deconvolution software. Samples were prepared as acetonitrile solutions and investigated without degassing. Initially, the laser scatter was acquired at a wavelength near the excitation frequency. A bandpass filter ( $600 \pm 10$ ) was utilized during the acquisition of sample emission to eliminate scatter signal.

Electrochemical measurements were performed under N<sub>2</sub> in CH<sub>3</sub>CN solutions with 0.1 M Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> as the supporting electrolyte with 1 mM (PP)<sub>3</sub>Re<sup>+</sup> analyte using a model ED401 computer-controlled potentiostat (eDAQ). A three-electrode configuration with a glassy carbon working electrode with a nonaqueous Ag/Ag+ reference electrode (containing 0.01 mM Ag/AgNO<sub>3</sub> and 0.1 M TBAPF<sub>6</sub> in a CH<sub>3</sub>CN solution) and a platinum wire auxiliary electrode was used. The potential values were referenced to an internal ferrocenium/ferrocene couple, which is reported to be +0.40 V versus SCE in NBu<sub>4</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup> in CH<sub>3</sub>CN.<sup>51</sup>

General Synthetic Procedures. All manipulations were conducted under  $N_2$  or vacuum using high-vacuum line and glovebox

techniques unless otherwise noted. All ambient-pressure syntheses were performed under a pressure of ~590 Torr (elevation ~2195 m). All solvents were dried using standard procedures and stored under vacuum. Aprotic deuterated solvents used in NMR experiments were dried over activated 3 Å molecular sieves. Elemental analyses were performed by Columbia Analytical Services. NMR spectra were obtained with a Bruker DRX-400 instrument using 5 mm NMR tubes fitted with Teflon valves (Chemglass, CG-512). <sup>31</sup>P NMR spectra were referenced to an 85% H<sub>3</sub>PO<sub>4</sub> external standard. The phosphines dmpp, dppe, and all other reagents were purchased from Aldrich and were used without further purification except sulfuryl chloride, which was purchased from Acros Organics. (PPh<sub>3</sub>)<sub>2</sub>ReO<sub>2</sub>I and (PPh<sub>3</sub>)<sub>2</sub>ReI<sub>2</sub>(O)-OEt,<sup>79</sup> (dppm)<sub>3</sub>Re<sup>+</sup>I<sup>-</sup>,<sup>48</sup> [(py)<sub>4</sub>Re(O)<sub>2</sub>]<sup>+</sup>OTf<sup>-</sup>,<sup>47</sup> dmpe and depe,<sup>80</sup> dmpm,<sup>81</sup> Me<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>,<sup>81,82</sup> and dmpb<sup>83</sup> were prepared according to literature methods. For the synthesis of dmpp the dihalide  $Br(CH_2)_3Br$ was used instead of  $Cl(CH_2)_2Cl.^{84}$  Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>, Cp<sub>2</sub>Fe<sup>+</sup>B-(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>, and (4-BrC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>N<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> were prepared by modified procedures from the literature (see below).<sup>51,8</sup>

 $Cp_2Fe^+B(C_6F_5)_4^-$ . Modified from the literature procedure:<sup>51</sup> instead of using  $FeCl_3$  as the oxidant and  $NH_4^+PF_6^-$  as the metathesizing salt, SO<sub>2</sub>Cl<sub>2</sub> was used as the oxidant, and salt exchange employed  $K^+B(C_6F_5)_4^-$ .  $Cp_2Fe^+Cl^-$  was prepared by adding  $SO_2Cl_2$  (8.0 mL) 13.3 g, 99 mmol) dropwise to a solution of Cp<sub>2</sub>Fe (10.0 g, 53.8 mmol) in 60 mL of CH<sub>2</sub>Cl<sub>2</sub>. The orange reaction mixture immediately turned dark blue, and the product precipitated as a dark blue crystalline solid that was collected as a first crop (8.16 g) via filtration under ambient air and rinsed three times with 25 mL of diethyl ether. A second crop was collected from the filtrate by the addition of ca. 100 mL of diethyl ether (1.66 g, 82% overall yield). Method A. Cp<sub>2</sub>Fe<sup>+</sup>Cl<sup>-</sup> (0.500 g, 2.25 mmol) was dissolved in 20 mL of H<sub>2</sub>O giving a dark blue solution. A solution of  $K^+B(C_6F_5)_4^-$  (1.470 g, 2.05 mmol) dissolved in 15 mL of H<sub>2</sub>O and 2 mL of CH<sub>3</sub>CN was added dropwise to the blue solution producing a blue precipitate. The precipitate was collected via filtration, rinsed with twice with 20 mL of H<sub>2</sub>O, and dried under vacuum overnight (1.61 g, 91% yield). Method B. The product was obtained by stirring a suspension of  $K^+B(C_6F_5)_4^-$  (1.78 g, 2.48 mmol) and Cp<sub>2</sub>Fe<sup>+</sup>Cl<sup>-</sup> (0.500 g, 2.25 mmol) in 80 mL of CH<sub>2</sub>Cl<sub>2</sub> at ambient temperature for 5 h. The blue solution was filtered to remove KCl, and the volatiles were removed under vacuum. The blue residue was triturated with 25 mL of hexane three times, and during the last trituration the solution was cooled to -78 °C giving large blue flakes of the product, which were collected via filtration (1.80 g, 92% yield).

 $(4-BrC_6H_4)_3N^+B(C_6F_5)_4^-$ . This complex was prepared by adapting a literature procedure:<sup>85</sup> instead of using I<sub>2</sub> as the oxidant, SO<sub>2</sub>Cl<sub>2</sub> was used as the oxidant, and K<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> was used instead of Ag<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-.85</sup> SO<sub>2</sub>Cl<sub>2</sub> (1.0 mL, 1.67 g, 12.4 mmol) was added dropwise to a suspension of  $(4-BrC_6H_4)_3N$  (1.06 g, 2.21 mmol) and K<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>--</sup> (1.59 g, 2.21 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. Upon addition of SO<sub>2</sub>Cl<sub>2</sub> a dark blue solution was obtained along with KCl precipitate, and the reaction mixture was stirred overnight at ambient temperature. The precipitate was removed by filtration, volatiles were removed under vacuum, and the residue was triturated with ca. 20 mL of hexane, giving dark blue flakes, which were collected via filtration (2.40 g, 94% yield).

 $[(dmpe)_3Re](B(C_6F_5)_4)$  (1). (PPh<sub>3</sub>)<sub>2</sub>ReO<sub>2</sub>I (0.600 g, 0.690 mmol), dmpe (0.633 mL, 0.569 g, 3.79 mol), and 6 mL of *o*-dichlorobenzene were added to a 12 mL Teflon-valved medium-wall Pyrex reaction tube with a magnetic stirbar. The reaction mixture was heated with stirring for 6 h at 170 °C to give a clear solution with a small amount of gray precipitate. After it cooled, the solid was filtered off under ambient air. The product (dmpe)<sub>3</sub>ReI was precipitated and isolated as a microcrystalline solid from the filtrate by slowly adding ca. 40 mL of Et<sub>2</sub>O (0.470 g, 89% yield). The product was judged to be 95+% pure by NMR. The crude product (dmpe)<sub>3</sub>Re<sup>+</sup>I<sup>-</sup> (0.470 g, 0.969 mmol) and K<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> (0.904 g, 1.259 mmol) were dissolved in 25 mL of CH<sub>2</sub>Cl<sub>2</sub> and stirred at ambient temperature for 3 h to give a white suspension of KI and excess K<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>. The salts were filtered away, and 40 mL of MeOH was added to the filtrate. CH<sub>2</sub>Cl<sub>2</sub> was slowly removed by reducing the volume of the filtrate by ~50%, producing pure white microcrystalline  $\underline{1}$  that was collected by filtration (0.98 g, 77% yield).

Alternate Preparation of  $[(dmpe)_3Re](B(C_6F_5)_4)$  (1). (PPh<sub>3</sub>)<sub>2</sub>ReI<sub>2</sub>(O)OEt (2.000 g, 1.949 mmol) and dmpe (1.95 mL, 1.755 g, 11.70 mmol) and 12 mL of o-dichlorobenzene were combined in a 18 mL Teflon-valved medium-wall Pyrex reaction tube with a magnetic stirbar. The reaction mixture was heated with stirring at 180 °C for 24 h, during which time the reaction mixture changed from red, to yellow, and finally to colorless along with a large amount of a white crystalline precipitate. The reaction mixture was cooled to ambient temperature, the suspension was filtered, the solid was rinsed with 20 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the filtrates were combined. [(dmpe)<sub>3</sub>Re]I was precipitated by slowly adding Et<sub>2</sub>O to the combined filtrates to give a nearly quantitative yield of the product (1.480 g). This iodide complex and  $K^+B(C_6F_5)_4^-$  (1.540 g, 2.145 mmol) were suspended in 25 mL of CH<sub>2</sub>Cl<sub>2</sub> and stirred at ambient temperature for 18 h. The resulting white suspension was filtered to remove KI, and 60 mL of MeOH was added to the filtrate to precipitate the product. The volume was reduced to ca. 15 mL to induce further precipitation, and the product was collected under ambient air, giving  $\underline{1}$  as a pure white microcrystalline solid (2.340 g, 91% yield). Crystals suitable for single-crystal X-ray diffraction were grown from the diffusion of MeOH into a saturated CH2Cl2 solution of 1. Anal. Calcd for C42H48P6F20BRe: C, 38.29%; H, 3.68%. Found: C, 38.35%; H, 3.70%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400.13 MHz, 20 °C): δ 1.65 (m, 6H;  $(CD_2Cl_2, 161.97 \text{ MHz}, 20 \text{ °C}): \delta 2.1 \text{ (br. s, } \nu_{1/2} = 790 \text{ Hz}).$ 

 $[(depe)_3 Re](B(C_6 F_5)_4)$  (2). Complex 2 was prepared similarly to 1: (PPh<sub>3</sub>)<sub>2</sub>ReO<sub>2</sub>I (0.600 g, 0.690 mmol), depe (0.885 mL, 0.782 g, 3.793 mol), and 6 mL of o-dichlorobenzene were heated at 170 °C with stirring for 8 h to give a yellow solution. After filtration 10 mL of Et<sub>2</sub>O and 10 mL of hexanes were added, and the mixture was cooled to -20°C for 24 h, giving a dark greenish-yellow oily precipitate. The filtrate was collected, and the volatiles were removed under vacuum to give a brown oil, which was dissolved in 10 mL of CH2Cl2, and pure (depe)<sub>3</sub>Re<sup>+</sup>I<sup>-</sup> was precipitated as a white solid by the addition of 20 mL of Et<sub>2</sub>O followed by 60 mL of hexanes (0.480 g, 75% yield). Anal. Calcd for C30H72P6IRe: C, 38.62%; H, 7.78%. Found: C, 38.61%; H, 7.40%. (depe)<sub>3</sub>Re<sup>+</sup>I<sup>-</sup> (0.400 g, 0.429 mmol) and K<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> (0.400 g, 0.557 mmol) were stirred in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> for 3 h, giving a colorless solution and a white KI precipitate. After filtration, 20 mL of MeOH was added, and the volume of the filtrate was reduced to 10 mL, giving  $\underline{2}$  as a white crystalline solid, which was collected by filtration (0.503 g, 79% yield). Anal. Calcd for C54H72P6F20BRe: C, 43.66%; H, 4.89%. Found: C, 43.55%; H, 4.66%. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400.13 MHz, 20 °C): δ 1.89 (m, 18H; overlapping P(CH<sub>a</sub>H<sub>b</sub>)<sub>2</sub>P and  $P(CH_aH_bCH_3)_2)$ , 1.61 (ddq,  ${}^2J_{HP}$  = 22.4 Hz,  ${}^2J_{HH}$  = 14.9 Hz,  ${}^3J_{HH}$  = 7.5 Hz, 12H; P(CH<sub>a</sub>H<sub>b</sub>CH<sub>a</sub>)<sub>2</sub>), 1.34 (m, 6H; P(CH<sub>a</sub>H<sub>b</sub>)<sub>2</sub>P), 1.15 (br. m, 36H; P(CH<sub>a</sub>H<sub>b</sub>CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 161.97 MHz, 20 °C):  $\delta$  16.8 (br. s,  $\nu_{1/2}$  = 225 Hz). Crystals suitable for single-crystal Xray diffraction were grown from the diffusion of MeOH into a saturated CH<sub>2</sub>Cl<sub>2</sub> solution of 2.

Alternate Preparation of  $[(depe)_3Re](B(C_6F_5)_4)$  (2). (PPh<sub>3</sub>)<sub>2</sub>ReI<sub>2</sub>(O)OEt (0.900 g, 0.877 mmol), depe (1.13 mL, 0.995 g, 4.84 mmol), and 6 mL of o-dichlorobenzene were combined in a 12 mL Teflon-valved medium-wall Pyrex reaction tube with a magnetic stirbar. The reaction mixture was heated at 170 °C for 24 h, during which time the reaction mixture changed from red to pale yellow with an accompanying yellow precipitate, which decreased during the course of the reaction. The reaction mixture was cooled to ambient temperature, the solution was transferred to a round-bottom flask, and the volatiles were removed under vacuum to give an oily yellow suspension. Addition of 30 mL of diethyl ether to the suspension and stirring overnight gave a yellow solution with a yellow solid, which was isolated. Addition of  $K^+B(C_6F_5)_4^-$  (0.693 g, 0.965 mmol) to this solid suspended in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> and stirring at ambient temperature for 3 h gave a precipitate of KI, which was removed. Addition of 30 mL of MeOH to the filtrate and reduction of the volume to ca. 15 mL gave 2 as a pure white microcrystalline solid (0.652 g, 50% yield).

 $[(dmpm)_3 Re](B(C_6 F_5)_4)$  (3). Complex 3 was prepared according to the alternate preparation of 2: (PPh<sub>3</sub>)<sub>2</sub>ReI<sub>2</sub>(O)OEt (1.200 g, 1.17 mmol), dmpm (1.02 mL, 0.877 g, 6.44 mmol), and 10 mL of odichlorobenzene were combined in a 20 mL storage tube. The reaction mixture was heated at 170 °C and the work up procedure followed the alternate preparation for  $\underline{2}$ . After it stirred in Et<sub>2</sub>O and was filtered, giving the crude product as a pale brown solid (80-90% pure by NMR), it was then combined with  $K^+B(C_6F_5)_4^-$  (0.923 g, 1.28 mmol), and the product was isolated (0.725 g, 49% yield). Crystals suitable for single-crystal X-ray diffraction were grown from the diffusion of MeOH into a saturated CH<sub>2</sub>Cl<sub>2</sub> solution. Anal. Calcd for C<sub>39</sub>H<sub>42</sub>P<sub>6</sub>F<sub>20</sub>BRe: C, 36.73%; H, 3.32%. Found: C, 36.58%; H, 2.96%. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 400.13 MHz, 20 °C): δ 4.15 (m, 6H; (CH<sub>3</sub>)<sub>2</sub>PC<u>H<sub>2</sub></u>P(CH<sub>3</sub>)<sub>2</sub>), 1.77 (br. s, 18H; (C<u>H<sub>3</sub></u>)<sub>a</sub>(CH<sub>3</sub>)<sub>b</sub>P), 1.76 (br. s, 18H;  $(CH_3)_a(CH_3)_bP$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone- $d_6$ , 161.97 MHz, 20 °C):  $\delta$  -66.2 (br. s,  $\nu_{1/2}$  = 50 Hz).

 $[fac-(Me_2PCH_2PPh_2)_3Re](B(C_6F_5)_4)$  (<u>4</u>). (PPh\_3)\_2ReI<sub>2</sub>(O)OEt (0.600 g, 0.585 mmol), Me<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (0.700 g, 2.69 mmol), and 6 mL of odichlorobenzene were combined in a 12 mL Teflon-valved mediumwall Pyrex reaction tube with a magnetic stirbar. The reaction mixture was heated with stirring at 170 °C for 3 d, giving (Me<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>Re<sup>+</sup>I<sup>-</sup> as a pure crystalline solid, which was rinsed with 20 mL of MeOH and 20 mL of Et<sub>2</sub>O (0.532 g, 83% yield). Anal. Calcd for C45H54P6IRe: C, 49.35%; H, 4.97%. Found: C, 49.13%; H, 4.60%. fac-(Me2PCH2PPh2)3Re<sup>+</sup>I<sup>-</sup> (0.500 g, 0.457 mmol) and  $K^+B(C_6F_5)_4^-$  (0.328 g, 0.457 mmol) were suspended in 25 mL of CH<sub>2</sub>Cl<sub>2</sub> and stirred for 3 h at ambient temperature. The yellow solution was filtered away from KI, and 50 mL of MeOH was added to the filtrate. The volume of the filtrate was reduced to ca. 15 mL giving a yellow precipitate that was collected by filtration under ambient air (0.702 g, 93% yield). Crystals suitable for single-crystal X-ray diffraction were grown by the slow evaporation from a saturated 1:1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH solution. Anal. Calcd for C<sub>69</sub>H<sub>54</sub>BF<sub>20</sub>P<sub>6</sub>Re: C, 50.35%; H, 3.31%. Found: C, 50.20%; H, 3.93%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400.13 1.87 (d,  ${}^{2}J_{HP} = 5$  Hz, 9H; P(C<u>H</u><sub>3</sub>)<sub>a</sub>(CH<sub>3</sub>)<sub>b</sub>), 1.04 (d,  ${}^{2}J_{HP} = 6$  Hz, 9H;  $P(CH_3)_a(CH_3)_b)$ . <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 161.97 MHz, 20 °C):  $\delta$  $-45.9 (d, {}^{2}J_{PPtrans} = 94 Hz; (C_{6}H_{5})_{2}PCH_{2}P(CH_{3})_{2}), -63.3 (d, {}^{2}J_{PPtrans} = 94 Hz; (C_{6}H_{5})_{2}PCH_{2}P(CH_{3})_{2}).$ 

 $[(dmpp)_{3}Re](B(C_{6}F_{5})_{4})$  (5).  $[(py)_{4}Re(O)_{2}]^{+}OTf^{-}$  (0.500 g, 0.732 mmol), dmpp (0.625 g, 3.81 mmol), and 6 mL of o-dichlorobenzene were combined in a 12 mL Teflon-valved medium-wall Pyrex reaction tube with a magnetic stirbar. The reaction mixture was heated at 170 °C for 2 h, and (dmpp)<sub>3</sub>Re<sup>+</sup>OTf<sup>-</sup> was precipitated as an off-white solid by the slow addition of ca. 50 mL of Et<sub>2</sub>O and collected via filtration (0.398 g, 66% yield). (dmpp)<sub>3</sub>Re<sup>+</sup>OTf<sup>-</sup> (0.526 g, 0.481 mmol) and  $K^+B(C_6F_5)_4^-$  (0.382 g, 0.532 mmol) were suspended in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> and stirred at ambient temperature for 3 h, the resulting  $\rm K^+OTf^-$  was removed by filtration, 40 mL of MeOH was added to the filtrate, and the volume reduced to ca. 10 mL. The product precipitated as a white solid and was collected via filtration (0.460 g, 70% yield). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation from a saturated 1:1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH solution. Anal. Calcd for C45H54BF20P6Re: C, 39.81%; H, 4.01%. Found: C, 39.73%; H, 4.30%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400.13 MHz, 20 °C): δ 2.07 (br. m, 6H; PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P), 1.90 (br. m, 12H;  $PCH_2CH_2CH_2P$ ), 1.67 (br. s, 18H;  $P(CH_3)_a(CH_3)_b$ ), 1.60 (br. s, 18H;  $P(CH_3)_a(CH_3)_b)$ . <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 161.97 MHz, 20 °C):  $\delta$ -53.8 (br. s,  $\nu_{1/2} = 165$  Hz).

 $[(dppm)_3Re](B(C_6F_5)_4)$  (**b**). The yellow solid  $(dppm)_3Re^+I^-$  was prepared from  $(PPh_3)_2ReO_2I$  according to literature methods,<sup>54</sup> except that the reflux time in methanol was extended from 3 to 24 h (0.350 g, 69%). The  $(dppm)_3Re^+I^-$  and  $K^+B(C_6F_5)_4^-$  (0.206 g, 0.287 mmol) were suspended in 15 mL of  $CH_2Cl_2$  at ambient temperature and stirred for 2 h. The resulting KI was filtered away, 30 mL of MeOH was added to the filtrate, and the volume was reduced under vacuum

to ca. 10 mL, giving a pale yellow precipitate (0.303 g, 63% yield). The <sup>1</sup>H and <sup>31</sup>P NMR spectra were consistent with reported values. Anal. Calcd for  $C_{99}H_{66}BF_{20}P_6Re$ : C, 58.91%; H, 3.30%. Found: C, 58.79%; H, 3.21%.

 $[(dmpb)_{3}Re](B(C_{6}F_{5})_{4})$  (<u>7</u>). (PPh<sub>3</sub>)<sub>2</sub>Re(O) (OEt)I<sub>2</sub> (1.00 g, 0.975) mmol), dmpb (1.215 g, 6.10 mmol), and 10 mL of o-dichlorobenzene were combined in an 18 mL Teflon-valved medium-wall Pyrex reaction tube with a magnetic stirbar. The reaction mixture was heated at 180 °C for 24 h giving a clear solution with a white precipitate. The solid was filtered away, and the volatiles were removed under vacuum to give a white residue.  $Et_2O(30 \text{ mL})$  was added to the residue, and it was triturated at ambient temperature overnight giving crude (dmpb)<sub>3</sub>Re<sup>+</sup>I<sup>-</sup> as a white solid, which was collected via filtration and rinsed three times with 20 mL of Et<sub>2</sub>O (0.656 g). (dmpb)<sub>3</sub>Re<sup>+</sup>I<sup>-</sup> (0.656 g, 0.721 mmol) and  $K^+B(C_6F_5)_4^-$  (0.545 g, 0.759 mmol) were suspended in 15 mL of CH2Cl2 and stirred for 18 h at ambient temperature. The solution was filtered away from KI, and 50 mL of MeOH was added to the filtrate. The volume of the filtrate was reduced to ca. 8 mL giving a white precipitate that was collected by filtration under ambient air (0.459 g). A second fraction of (dmpb)<sub>3</sub>Re<sup>+</sup>I<sup>-</sup> was extracted from the initial filtered solids with 10 mL of CH2Cl2, the volatiles were removed, and the solid triturated with 25 mL of Et<sub>2</sub>O.  $(dmpb)_3Re^+I^-$  (0.400 g, 0.441 mmol) and  $K^+B(C_6F_5)_4^-$  (0.348 g, 0.485 mmol) were suspended in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> and stirred for 18 h at ambient temperature, and the product was worked up as described above (0.550 g, 71%). Crystals suitable for single-crystal X-ray diffraction were grown by the slow diffusion of MeOH (1.5 mL) layered above a solution of  $\underline{7}$  in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL). The elevated hydrogen analysis may indicate that iodide metathesis was incomplete. Anal. Calcd for C54H48P6BF20Re: C, 44.43%; H, 3.31%. Found: C, 44.93%; H, 4.26%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400.13 MHz, 20 °C):  $\delta$  7.81 (br. m, 6H; meta-C<sub>6</sub><u>H</u><sub>4</sub>(P(CH<sub>3</sub>))<sub>2</sub>), 7.58 (dd, <sup>3</sup>J = 5 Hz,  ${}^{3}J = 3$  Hz, 6H; ortho-C<sub>6</sub>H<sub>4</sub>(P(CH<sub>3</sub>))<sub>2</sub>), 2.01 (s, 18H; C<sub>6</sub>H<sub>4</sub>(P- $(CH_3)_2$ , 1.52 (s, 18H;  $C_6H_4(P(CH_3))_2$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 161.97 MHz, 20 °C):  $\delta$  1.5 (br. s,  $\nu_{1/2}$  = 345 Hz, 6P; C<sub>6</sub>H<sub>4</sub>(<u>P</u>(CH<sub>3</sub>))<sub>2</sub>).

 $[(dmpe)_3Re](B(C_6F_5)_4)_2$  (**B**). Complex **1** (0.900 g, 0.684 mmol) and Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> (0.694 g, 0.752 mmol) were dissolved in 25 mL of CH<sub>3</sub>CN. When mixed, the solution immediately turned red. The reaction mixture was stirred for 5 h at ambient temperature, and the volatiles were removed under vacuum. The residue was taken up in 50 mL of Et<sub>2</sub>O and stirred at ambient temperature for 24 h to give a suspension of the red product, which was collected via filtration (1.00 g, 73% yield). Anal. Calcd for C<sub>66</sub>H<sub>48</sub>P<sub>6</sub>B<sub>2</sub>F<sub>40</sub>Re: C, 39.70%; H, 2.42%. Found: C, 39.62%; H, 2.34%. Crystals suitable for X-ray diffraction were grown from a saturated solution of CH<sub>3</sub>CN.

 $[(depe)_3Re](B(C_6F_5)_4)_2$  (**9**). Oxidation of complex **2** to give **9** was performed analogously to **8** except that the reaction mixture was stirred for 3.5 h, and a second crop was isolated from the filtrate by removing the volatiles and triturating the residue with Et<sub>2</sub>O: **2** (0.503 g, 0.339 mmol), Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> (0.343 g, 0.373 mmol), (first crop 0.455 g, second crop 0.240 g, 95% total yield). Anal. Calcd for C<sub>78</sub>H<sub>72</sub>P<sub>6</sub>B<sub>2</sub>F<sub>40</sub>Re: C, 43.31%; H, 3.36%. Found: C, 44.02%; H, 3.13%. Crystals suitable for single-crystal X-ray diffraction were grown from a 1:2 CH<sub>2</sub>Cl<sub>2</sub>/MeOH solution.

 $[(dmpm)_3Re](B(C_6F_5)_4)_2$  (10). Complex 3 (0.150 g, 0.118 mmol) and Cp<sub>2</sub>Fe<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> (0.102 g, 0.118 mmol) were dissolved in 20 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the reaction mixture was stirred for 18 h. The product precipitated as a microcrystalline red solid, which was collected by filtration and rinsed once with 10 mL of CH<sub>2</sub>Cl<sub>2</sub> (0.178 g, 77% yield). The product was recrystallized by evaporation from a 1:2 mixture of CH<sub>3</sub>CN/chlorobenzene. Anal. Calcd for C<sub>63</sub>H<sub>42</sub>P<sub>6</sub>B<sub>2</sub>F<sub>40</sub>Re: C, 38.71%; H, 2.17%. Found: C, 38.22%; H, 2.42%. Crystals of the PF<sub>6</sub><sup>-</sup> salt of <u>10</u> suitable for single-crystal X-ray diffraction, prepared analogously using Cp<sub>2</sub>Fe<sup>+</sup>PF<sub>6</sub><sup>-</sup>, were grown by slow evaporation from a saturated CH<sub>3</sub>Cl<sub>2</sub> solution.

 $[fac^{-}(Me_2PCH_2PPh_2)_3Re](B(C_6F_5)_4)_2$  (<u>11</u>). Complex <u>4</u> (0.300 g, 0.182 mmol) and Cp<sub>2</sub>Fe<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> (0.158 g, 0.183 mmol) were dissolved in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> and stirred at ambient temperature for 3 h. The volatiles were removed from the resulting purple solution, and the residue was triturated with 25 mL of Et<sub>2</sub>O. The residue was

reprecipitated twice from CH<sub>2</sub>Cl<sub>2</sub>/hexane, and the purple product was collected via filtration (0.274 g, 66% yield). Anal. Calcd for  $C_{93}H_{54}P_6B_2F_{40}Re: C$ , 48.04%; H, 2.34%. Found: C, 47.89%; H, 3.20%. Crystals of the  $PF_6^-$  salt of <u>11</u> suitable for single-crystal X-ray diffraction were prepared by the oxidation of <u>4</u> with  $Cp_2Fe^+PF_6^-$  in CH<sub>3</sub>CN followed by slow evaporation.

 $[(dmpp)_3Re](B(C_6F_5)_4)_2$  (12). Complex <u>5</u> (0.350 g, 0.258 mmol) and  $Cp_2Fe^+B(C_6F_5)_4^-$  (0.223 g, 0.258 mmol) were dissolved in 20 mL of  $CH_2Cl_2$  and stirred for 18 h at ambient temperature. The product precipitated as an orange microcrystalline solid, which was collected via filtration (0.450 g, 86% yield). The solid was recrystallized by the slow evaporation from a 1:1 solution of 1,2-difluorobenzene and toluene in 90% yield. Anal. Calcd for  $C_{66}H_{54}P_6B_2F_{40}Re \cdot C_{12}H_8F_4$ : C, 42.95%; H, 2.76%. Found: C, 43.10%; H, 3.02%.

 $[(dppm)_3Re](B(C_6F_5)_4)_2$  (13). Complex <u>6</u> (0.350 g, 0.173 mmol) and (4-BrC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>N<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> (0.200 g, 0.172 mmol) were dissolved in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> and stirred at ambient temperature for 24 h. The volatiles were removed from the resulting blue/purple solution, and the residue was triturated with 25 mL of Et<sub>2</sub>O. The residue was reprecipitated twice from CH<sub>2</sub>Cl<sub>2</sub>/hexane, and the dark blue product was collected via filtration (0.411 g, 88% yield). Anal. Calcd for C<sub>123</sub>H<sub>66</sub>P<sub>6</sub>B<sub>2</sub>F<sub>40</sub>Re: C, 54.72%; H, 2.47%. Found: C, 55.31%; H, 2.72%.

 $[(dmpb)_3 Re](B(C_6 F_5)_4)_2$  (<u>14</u>). Complex <u>7</u> (0.275 g, 0.189 mmol) and  $(4-BrC_6H_4)_3N^+B(C_6F_5)_4^-$  (0.218 g, 0.189 mmol) were dissolved in 20 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the mixture was stirred at ambient temperature for 3 h. Upon addition of  $CH_2Cl_2$  the solution turned immediately from dark blue to red. Removal of the volatiles and addition of 25 mL of Et<sub>2</sub>O to the residue followed by stirring for 1 h and standing for an additional 15 min caused the product to settle as a red oil. The Et<sub>2</sub>O layer was removed from the product oil, and the volatiles were removed. The resulting residue was suspended in hexane and stirred overnight at ambient temperature to precipitate the product as a red/ purple powder, which was collected via filtration (0.313 g, 78% yield). Anal. Calcd for C78H48P6B2F40Re·CH2Cl2: C, 42.67%; H, 2.27%. Found: C, 42.80%; H, 3.04%. Crystals suitable for single-crystal X-ray diffraction were grown from the  $[(dmpb)_3Re](SbF_6)_2$  salt, prepared from K<sup>+</sup>SbF<sub>6</sub><sup>-</sup> metathesis with (dmpb)<sub>3</sub>Re<sup>+</sup>I<sup>-</sup> in methylene chloride and subsequent oxidation in  $CH_3CN$  using  $NO^+SbF_6^-$ , then crystallization from CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>H<sub>5</sub>Cl.

**Computational Details.** All calculations were performed using Gaussian 09 Rev. A.02,<sup>86</sup> using the M06-L functional for geometry optimization and frequencies.<sup>87</sup> The Dunning correlation consistent basis sets cc-pVDZ were used for hydrogen and carbon; the diffuse basis set AUG-cc-pVDZ was used for phosphorus.<sup>88</sup> Figgen et al. energy-consistent pseudopotentials and correlation-consistent basis set for rhenium were used.<sup>89</sup> The NBO analysis (version 3) and accompanying spin-corrected Mayer bond order indices are implemented in Gaussian 09.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b01395.

Discussion of crystallographic data collection and refinement, tabulated crystallographic data, cyclic voltammograms, absorption spectra, luminescence spectra at room temperature and 77 K, quenching rate constant data. (PDF)

X-ray crystallographic data for all crystallographically characterized compounds. (CIF)

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#### Notes

The authors declare no competing financial interest.

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#### DEDICATION

Dedicated to B. Patrick Sullivan, in recognition of his contributions to inorganic photochemistry.

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