# ORGANOMETALLICS

# Tricarbonylrhenium(I) Complexes of Dinucleating Redox-Active **Pincer Ligands**

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S Supporting Information

ABSTRACT: Two homobimetallic tricarbonylrhenium(I) complexes of new redox-active dinucleating pincer ligands have been prepared to assess the impact of spacer size on the first oxidation potentials with respect to mononucleating analogues and on intramolecular electronic communication. The new pincer ligands feature two tridentate NNN- sites each composed of two pyrazolyl flanking donors and a diarylamido anchor that are either directly linked (to form a central benzidene core,  $H_2(L1)$ ) or



linked via a para-phenylene group (to form a para-terphenyldiamine core, H2(L2)). The bimetallic complexes of the deprotonated ligands,  $[fac-Re(CO)_3]_2(\mu-L1)$ , 1, and  $[fac-Re(CO)_3]_2(\mu-L2)$ , 2, were fully characterized in solution and the solid state including by single-crystal X-ray diffraction for 1. The electrochemical properties of each depended strongly on solvent and electrolyte. Complex 1 exhibits two one-electron oxidations in all electrolyte-containing solutions but with separations between first and second oxidation potentials,  $\Delta E_{1/2}$ , between 119 and 316 mV depending on conditions. On the other hand, cyclic voltammetry of 2 showed one two-electron oxidation in DMF with  $NBu_4PF_6$  as an electrolyte but two one-electron oxidations with a maximal separation in  $\Delta E_{1/2}$  of 96 mV in CH<sub>2</sub>Cl<sub>2</sub> with NBu<sub>4</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> as an electrolyte. The oxidized complexes 1<sup>n+</sup> and  $2^{n+}$  (n = 1, 2) were prepared by chemical oxidation and were studied spectroscopically (UV-vis/NIR, EPR). The mono-oxidized complex  $1^+$  behaves as a Robin-Day Class III species, while  $2^+$  is a Robin-Day Class II species that shows thermal valence trapping at 77 K by EPR spectroscopy. As suggested from theoretical studies using DFT methods, the oxidized complexes maintain considerable ligand radical character, so their electronic structures can be formulated as  $(CO)_3 Re^{I}(\mu - L^{n+})Re^{I}(CO)_3$  (*n* = 1 or 2).

## INTRODUCTION

Contemporary interest in metal complexes of redox-active ligands<sup>1</sup> is stimulated by their potential use in technological applications (redox flow batteries,<sup>2</sup> electrochromic materials<sup>3</sup>), in catalytic applications,<sup>4</sup> or simply by fundamental interest in bonding and electron transfer. In such complexes, the usual electrochemical and reaction chemistry mediated by the metal center is augmented by the ligand's added capacity to either accept or donate one electron. The electron accepting properties of the bipyridyl (bipy) moiety in  $[Ru(bipy)_3]^{2+5}$  or the electron donating behavior of the porphyrin in heme or other metalloporphyrin systems<sup>6</sup> are prominent examples. Clearly, for some reactions or electrochemical applications, the transfer of more than one electron onto or from a redoxactive ligand would be desirable. For this purpose, we have initiated investigations into metal complexes bound to ligands capable of multiple oxidations or reductions. One potentially attractive class of such multiply redox-active ligands would be organic (oligo)phenylenediamines of the form  $(RR'N)_2(\mu$ - $C_6H_4$ )<sub>n</sub>, where R = R' = alkyl, n = 1-7 or R = R' = aryl, n = 1-73. These organic compounds are well-known electron donors<sup>7</sup> and in certain cases have been implemented in various technological and molecular electronic applications.<sup>8</sup> The 3° amine derivatives undergo two successive one-electron oxidations at potentials that depend on the nitrogen's R, R'

groups and on the length of the intervening polyphenylene spacer.<sup>7d,9,10</sup> In contrast, the electrochemical properties of 2° diamine derivatives (with R = alkyl, aryl and R' = H) that may be suitable amido ligand precursors in metal complexes are less studied in organic chemistry because they are not well-behaved. These organic derivatives decompose on oxidation to form dinitroxyl radicals (R' = O) or intractable polymeric species.<sup>11</sup> However, in cases of ortho-phenylenediamines, replacement of hydrogen(s) with a metal (with R = alkyl, aryl, R' = metal) has indeed provided numerous robust complexes with interesting electronic properties and remarkable chemical reactivity.<sup>12–14</sup> Metal derivatives of para-substituted (poly)phenylenediamines are scarce<sup>15</sup> as they are expected to be highly reactive, moisturesensitive species like other simple metal diarylamides. We conjectured that the addition of Lewis donors at either orthopositions of an arylamine or the  $\beta$ - positions of an alkylamine could give stable dinucleating metal pincer derivatives like the known mononucleating diaryl-, dialkyl, or N-aryl-N-alkylamines.<sup>16</sup>

We have been examining the chemical and electrochemical properties of metal complexes of pincer-type ligands that have diarylamido anchors and pyrazolyl flanking donors.17-20 The

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Chart 1. Previously Studied Complex 0<sup>Me</sup> and the Three New Complexes in This Work<sup>19</sup>



electron-rich diarylamido group can act as a single-electron donor or as a Brønsted base. Further, the ligand's arylpyrazolyl arms confer structural flexibility to the metal complexes and can accommodate either *fac-* or *mer-* conformations,<sup>18,19</sup> or can even dissociate to open a reactive site on the metal.<sup>20</sup> We previously reported that *fac*-Re(CO)<sub>3</sub>(L0<sup>Me</sup>),  $0^{Me}$  (left, Chart 1, where X = Me)<sup>19b</sup>, and related derivatives<sup>19a</sup> showed a quasireversible one-electron oxidation near 0 V vs Fc/Fc<sup>+</sup>, a result that was intriguing because neither the free ligand nor the metal precursor (or (solvent)<sub>3</sub>Re(CO)<sub>3</sub><sup>+</sup> fragment) alone exhibits reversible oxidation behavior (especially at such a mild potential). We have now successfully prepared the dinucleating pincer complexes (middle and right, Chart 1) and herein report on the effect that the *para*-arylenediamine spacer has on their electronic properties and provide a comparison to those of their monometallic counterparts, *fac*-Re(CO)<sub>3</sub>(L0<sup>X</sup>).

### EXPERIMENTAL SECTION

**Syntheses.** General Considerations. Chemicals. Solvents for syntheses, spectroscopic characterization, or electrochemical studies were dried by conventional means and distilled under argon prior to use. Solvents used in organic workup or chromatographic separations were used as received from commercial sources. The compounds  $H(L0^{Br})$ ,<sup>17a</sup>  $Pd(PPh_3)_{4\nu}^{21}$  and  $Re(CO)_5Br^{22}$  were prepared by literature methods. All other chemicals were used as received from commercial sources.

Instrumentation and Characterization. Melting point determinations were made on samples contained in glass capillaries using an Electrothermal 9100 apparatus and are uncorrected. Midwest MicroLab, LLC (Indianapolis, IN), performed all elemental analyses. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian 400 MHz spectrometer. Chemical shifts were referenced to solvent resonances at  $\delta_{\rm H}$  7.26 and  $\delta_{\rm C}$  77.16 for CDCl<sub>3</sub>,  $\delta_{\rm H}$  2.05 for acetone- $d_6$ ,  $\delta_{\rm H}$  2.50 and  $\delta_{\rm C}$  39.51 for DMSO- $d_6$ , and  $\delta_{\rm H}$  2.75 and  $\delta_{\rm C}$  29.76 for DMF- $d_7$ . Electronic absorption (UV-vis/NIR) measurements were made on a Cary 5000 instrument. Abbreviations for NMR and UV-vis: br (broad), sh (shoulder), m (multiplet), ps (pseudo-), s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sept (septet). Solution magnetic moments were measured by the Evan's method.<sup>23</sup> IR spectra were recorded for samples as KBr pellets in the 4000-500 cm<sup>-1</sup> region on a Nicolet Magna-IR 560 spectrometer. Electrochemical measurements were collected under a nitrogen atmosphere for samples as 0.1 mM solutions in CH<sub>2</sub>Cl<sub>2</sub> with either 0.1 M NBu<sub>4</sub>PF<sub>6</sub> or 0.1 M  $NBu_4[B(C_6F_5)_4]$  as the supporting electrolyte or in DMF with 0.1 M NBu<sub>4</sub>PF<sub>6</sub>, as described in the main text. A three-electrode cell composed of a Ag/AgCl electrode (separated from the reaction medium with a semipermeable polymer membrane filter), a platinum working electrode, and a glassy carbon counter electrode was used for the voltammetric measurements. Data were collected at scan rates of 50, 100, 200, 300, 400, and 500 mV/s. With this set up, the ferrocene/ ferrocenium couple had an  $E_{1/2}$  value of +0.52 V in CH<sub>2</sub>Cl<sub>2</sub> and +0.55 V in DMF at a scan rate of 200 mV/s, consistent with the literature values.<sup>24</sup> Solid state magnetic susceptibility measurements were performed using a Johnson-Matthey MSB-MK1 instrument. Diamagnetic corrections were applied using tabulated values of Pascal's constants.<sup>25</sup> EPR spectra were obtained as solutions  $\sim 0.2$  mM in CH<sub>2</sub>Cl<sub>2</sub> using a Bruker ELEXYS E600 equipped with an ER4116DM

cavity resonating at 9.63 GHz, an Oxford instruments ITC503 temperature controller, and a ESR-900 helium flow cryostat. The spectra were recorded using 100 kHz field modulation unless otherwise specified. Spectra were simulated by using the EasySpin program.<sup>39</sup>

Precursors and Ligands.  $H(L0^{Ph})$ . A solution of 30 mL of C<sub>6</sub>H<sub>6</sub> and 10 mL of absolute ethanol that was purged with argon 15 min was transferred via cannula to a mixture of 0.797 g (2.022 mmol) of H(L0<sup>Br</sup>), 0.370 g (3.03 mmol) of PhB(OH)<sub>2</sub>, and 0.234 g (0.202 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub> under argon. Next, 10 mL of an argon-purged 2 M Na<sub>2</sub>CO<sub>3</sub> aqueous solution was added via cannula transfer. After the magnetically stirred biphasic mixture had been heated at 80 °C for 16 h under argon, the mixture was cooled to room temperature and was poured into 100 mL of H<sub>2</sub>O. The aqueous and organic fractions were separated. The aqueous layer was extracted with two 50 mL portions of ethyl acetate. The combined organic layers were dried over MgSO4 and filtered. After removing solvents under vacuum, the oily residue was subjected to column chromatography on silica gel using a 20 vol % solution of ethyl acetate in hexanes as an eluent. Solvent was removed from the second band ( $R_f = 0.45$ ) to give 0.630 g (80% yield) of H(L0<sup>Ph</sup>) as a colorless solid after drying under vacuum 1 h. Mp, 81-82 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.77 (dd, J = 2.4, 0.05 Hz, 1H,  $H_{\rm s}pz$ ), 7.75 (dd, J = 1.8, 0.5 Hz, 1H, H<sub>3</sub>pz), 7.73 (dd, J = 2.4, 0.5 Hz, 1H,  $H_{s}pz$ ), 7.70 (dd, J = 1.8, 0.5 Hz,  $\overline{1}H$ ,  $H_{3}pz$ ), 7.58–7.53 (m, 3H, Ar), 7.47–7.39 (m, 6H, Ar and NH), 7.31 (tt, J = 7.3, 1.9 Hz, 1H, Ar), 7.20 (d, J = 1.5 Hz, 1H, Ar), 7.09 (dd, J = 8.3, 1.9 Hz, 1H, Ar), 6.48 (t, J = 2.1 Hz, 1H, H<sub>4</sub>pz), 6.42 (t, J = 2.1 Hz, 1H, H<sub>4</sub>pz), 2.35 (s, 3H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta_{\rm C}$  140.8, 140.6, 137.1, 133.6, 133.2, 131.7, 131.1, 130.2, 130.0, 129.7, 128.9, 127.1, 126.9, 126.6, 125.9, 123.8, 120.3, 120.4, 117.6, 106.84, 106.77, 20.7 ppm.

N,N'-Di(p-tolyl)-4,4'-benzidine, IA. Under argon, 40 mL of dry deoxygenated toluene was added via cannula transfer to a mixture of 4.00 g (9.84 mmol) of 4,4'-diiodobiphenyl, 2.64 g (24.7 mmol, 2.5 equiv) of p-toluidine, 2.84 g (29.6 mmol, 3 equiv) of NaO<sup>t</sup>Bu, 0.6 mL (2 mol %) of P<sup>t</sup>Bu<sub>3</sub>, and 0.181 g (0.20 mmol, 2 mol %) of Pd<sub>2</sub>(dba)<sub>3</sub>. After the reaction mixture had been heated at reflux 15 h under argon, solvents were removed by vacuum distillation. The resulting solid was washed with 150 mL of deionized water, three 50 mL portions of Et<sub>2</sub>O, and then was vacuum-dried to afford 3.53 g of impure IA as a gray solid. The solid was added to 300 mL of ethyl acetate, and the mixture was heated at reflux 5 min, filtered hot, allowed to cool to room temperature 1 h, then placed in a -20 °C freezer overnight. The thin plate-like crystals were collected by filtration, washed with Et<sub>2</sub>O, and dried under vacuum. Additional crops of crystals were obtained by reducing the mother liquor by rotary evaporation to 50% volume and collecting the crystals after cooling, as above. A total of 2.65 g (74% yield) of IA was obtained as a lustrous ivory-colored solid. Solubility: ca. 0.014 M in ethyl acetate. Mp, 232–233 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta_{\rm H}$  8.07 (s, 2H, NH), 7.45 (d, J = 8.7 Hz, 4H), 7.06 (d, J = 8.8 Hz, <sup>H</sup> 4H), 7.05 (d, J = 8.8 Hz, 4H), 7.00 (d, J = 8.7 Hz, 4H), 2.23 (s, 6H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta_{\rm C}$  142.6, 140.7, 131.0, 129.6, 128.6, 126.4, 117.5, 116.3, 20.3 ppm.

N,N'-Di(2-bromo-p-tolyl)-2,2'-dibromo-4,4'-benzidine, **IB**. A solution of 0.59 mL (11 mmol, 4 equiv) of Br<sub>2</sub> in 20 mL of DMF was added dropwise to a cold (0 °C) solution of 1.04 g (2.84 mmol) of **IA** in 10 mL of DMF. After complete addition, the mixture was stirred at 0 °C for 1 h, the cold bath was removed, and the mixture was stirred an additional 4 h. Then, the supernatant of 10 mL of a saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was added. The resulting biphasic mixture

was poured into 100 mL of dilute NaHCO<sub>3</sub>, and the pale brown precipitate was collected by gravity filtration. The pale brown solid was washed with 100 mL of deionized water and was vacuum-dried to leave 1.76 g (91% yield) of **IB** as a beige solid. Mp, 198–199 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.74 (d, *J* = 2.1 Hz, 2H), 7.44 (br s, 2H), 7.35 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.07 (dd, *J* = 8.1, 1.5 Hz, 2H), 6.36(s, 2H, NH), 2.32 (s, 6H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta_{\rm C}$  139.96, 137.21, 133.79, 133.59, 133.28, 131.00, 129.03, 126.29, 119.87, 116.75, 115.49, 113.70, 20.65 ppm.

N,N'-Di(2-pyrazol-1-yl-p-tolyl)-2,2'-di(pyrazol-1-yl)-4,4'-benzidine,  $H_2(L1)$ . A 20 mL aliquot of dry, distilled, and argon-purged pxylenes was added by syringe to a mixture of 1.504 g (2.21 mmol) of IB, 1.055 g (15.50 mmol, 7 equiv) of pyrazole, 2.14 g (15.5 mmol) of K<sub>2</sub>CO<sub>3</sub>, and 0.50 mL (0.4 g, 4.58 mmol) of (N,N'-dimethylethylenediamine = DMED) previously placed under argon. Then, 0.200 g (1.05 mmol) of CuI was added under an argon blanket. After the resulting mixture had been heated at reflux 2 d under argon, the mixture was cooled to room temperature and solvent was removed by vacuum distillation. The solid residue was then dissolved in a biphasic mixture of 50 mL of ethyl acetate and 50 mL of H<sub>2</sub>O. The aqueous and organic layers were separated. The aqueous layer was extracted with three 25 mL portions of ethyl acetate. The combined organic layers were dried over MgSO4 and filtered. Volatiles were removed under vacuum to give a dark brown oil that was subjected to flash chromatography on silica gel. First, elution with hexanes removed residual (trace) xylene. Then, 3:1 hexane:ethyl acetate was used to remove unreacted and partially reacted starting materials. Finally, 1:1 hexanes:ethyl acetate was used to elute the desired band ( $R_f = 0.53$ ) which, after removing solvent under vacuum, gave 0.830 g (63%) of  $H_2(L1)$  as a pale brown solid. Mp, 85–86 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_H$  7.74 (m, 8H), 7.50 (s, 2H), 7.40 (s, 4H), 7.39 (d, J = 6.6 Hz, 2H), 7.20 (s, 2H), 7.09 (d, J = 8.1 Hz, 2H), 6.47, (t, J = 1.9 Hz, 2H, pz), 6.42 (t, J = 1.9 Hz, 2H, pz), 2.35 (s, 6H, CH<sub>3</sub>) ppm. <sup>1</sup>H NMR (acetone):  $\delta_{\rm H}$  9.27 (s, 2H, NH), 8.14 (dd, J = 2.5, 0.4 Hz, 2H, pz), 7.99 (dd, J = 2.4, 0.4 Hz, 2H, pz), 7.79 (d, J = 1.9 Hz, Ar), 7.75 (d, J = 1.8 Hz, Ar), 7.73 (d, J = 2.3 Hz, pz), 7.59 (dd, J = 8.6, 2.3 Hz, 2H, Ar), 7.43 (d, J = 8.6 Hz, 2H, Ar), 7.41 (dd, *J* = 8.3, 1.9 Hz, 2H, Ar), 6.51 (t, *J* = 2.1 Hz, 2H, pz), 6.47 (t, *J* = 2.1 Hz, 2H, pz), 2.33 (s, 6H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta_c$ 140.85, 140.66, 136.77, 133.70, 132.08, 131.64, 131.06, 130.22, 130.00, 128.95, 127.38, 126.27, 125.87, 123.19, 120.18, 117.88, 106.89, 106.80, 20.75 ppm.

 $H_2(L2)$ . An argon-purged (15 min) mixture of 35 mL of benzene and 12 mL of ethanol was added via cannula to a mixture of 1.217 g (3.09 mmol, 2.5 equiv) of H(L0<sup>Br</sup>), 0.205 g (1.23 mmol) of 1,4phenylenediboronic acid, and 0.028 g (0.25 mmol, 20 mol %) of Pd(PPh<sub>3</sub>)<sub>4</sub> previously placed under argon. Then 15 mL of an argonpurged 2 M Na<sub>2</sub>CO<sub>3</sub> aqueous solution was added by cannula and the mixture was heated at 80 °C for 15 h. Then, the organic layer was separated and the aqueous layer was washed with two 20 mL aliquots of ethyl acetate. The combined organic fractions were dried with anhydrous MgSO<sub>4</sub>, filtered, and evaporated to leave a brown solid. The solid was washed with two 20 mL portions of ethanol, 20 mL of Et<sub>2</sub>O, and was dried under vacuum to give 0.757 g (87% yield) of  $H_2(L2)$  as a pale yellow solid. Mp, 235–236 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_{\rm H}$  8.26 (s, 2H, NH), 7.78 (d, J = 2.4 Hz, 2H), 7.76 (d, J = 1.9 Hz, 2H), 7.73 (d, J = 2.4 Hz, 2H), 7.70 (d, J = 1.8 Hz, 2H), 7.60 (s, 4H, Ar), 7.59 (d, J = 2.1 Hz, 2H), 7.48 (dd, J = 8.6, 2.1 Hz, 2H), 7.42 (dd, J = 8.6, 1.9 Hz, 4H), 7.20 (d, J = 1.8 Hz, 2H), 7.10 (dd, J = 8.2, 1.7 Hz, 2H), 6.48 (t, J = 2.4 Hz, 2H), 6.42 (t, J = 2.3 Hz, 2H), 2.35 (s, 6H) ppm. <sup>13</sup>C NMR  $(CDCl_3)$ :  $\delta_C$  140.9, 140.7, 138.6, 137.3, 133.6, 132.6, 131.8, 131.3, 130.3, 130.1, 129.9, 129.0, 127.0, 126.8, 126.0, 123.7, 120.5, 117.7, 107.0, 106.9, 20.8 ppm.

*Metal Complexes.*  $Re(CO)_3(Me,Ph)$ ,  $\mathbf{0}^{Ph}$ . A mixture of 0.201 g (0.514 mmol) of  $H(L0^{Ph})$ , 0.209 g (0.514 mmol) of  $Re(CO)_5Br$ , 0.35 mL of 1.47 M (solution in MeOH, 0.514 mmol) NEt<sub>4</sub>OH and 15 mL of toluene was heated at reflux 12 h under argon. Solvents were removed by vacuum distillation. The yellow residue was washed with two 10 mL portions of methanol and then was dried under vacuum 2 h to give 0.252 g (74%) of  $\mathbf{0}^{Ph}$  as a yellow powder. Mp, 251–252 °C (Dec.). Anal. Calcd (Found) for  $Re_2C_{50}N_{10}H_{34}O_6$ : C, 50.90 (51.26);

H, 3.05 (3.11); N, 10.60 (10.87). IR (KBr):  $\nu_{\rm CO}$  2017, 1911, 1874. $^1{\rm H}$ NMR (DMF- $d_7$ ):  $\delta_H$ : 8.77 (d, J = 2.3 Hz, 1H, pz), 8.65 (d, J = 1.9 Hz, 1H, pz), 8.64–6.6 (m, 2H, pz), 8.00 (d, J = 6.7 Hz, 1H, Ar), 7.98 (d, J = 6.9 Hz, 1H, Ar), 7.94 (d, I = 2.0 Hz, 1H, Ar), 7.80 (d, I = 7.5 Hz, 2H, Ar), 7.65 (dd, J = 8.9, 2.0 Hz, 2H, Ar), 7.49-7.42 (m, 3H, Ar), 7.30 (t, J = 7.3 Hz, 2H, Ar), 6.82 (t, J = 2.4 Hz, 1H, pz), 6.76 (t, J = 2.4 Hz, 1H, pz), 2.38 (s, 3H) ppm. <sup>1</sup>H NMR (acetone- $d_6$ ):  $\delta_H$ : 8.50 (d, J =2.7 Hz, 1H, pz), 8.42 (d, J = 2.2 Hz, 1H, pz), 8.37(d, J = 2.5 Hz, 2H, pz), 7.96 (d, J = 4.8 Hz, 1H, Ar), 7.94 (d, J = 5.3 Hz, 1H, Ar), 7.78 (d, J = 2.2 Hz, 1H, Ar), 7.71 (br d, J = 7.4 Hz, 2H), 7.57 (dd, J = 8.8, 2.3Hz, 1H, Ar), 7.44–7.38 (br t, 2H), 7.35 (d, J = 1.4 Hz, 1H, Ar), 7.29– 7.24 (m, 2H, Ar), 6.72 (t, J = 2.5 Hz, 1H, pz), 6.52 (t, J = 2.5 Hz, 1H, pz), 2.37 (s, 3H) ppm. <sup>13</sup>C NMR (DMF- $d_7$ ):  $\delta_C$ : 197.3, 195.9, 195.8, 147.8, 146.2, 144.6, 144.1, 139.9, 132.8, 132.2, 132.1, 129.8, 129.2, 129.1, 128.9, 128.7, 126.7, 126.1, 125.9, 124.8, 121.5, 121.3, 116.6, 108.43, 108.42, 20.0 ppm. <sup>13</sup>C NMR (acetone-d<sub>6</sub>):  $\delta_{\rm C}$ : 197.5, 196.4, 196.1, 148.4, 147.0, 144.6, 144.1, 140.7, 132.8, 132.7, 132.2, 130.3, 129.8, 129.6, 129.5, 129.4, 127.1, 126.7, 126.5, 125.1, 122.3, 121.8, 117.2, 108.8, 108.7, 20.5 ppm. UV–vis  $\lambda_{max}$  nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>), DMF: 375 (26 500), 268 (31 000). Crystals suitable for single-crystal X-ray diffraction were grown by layering a CH2Cl2 solution with hexane and allowing solvents to diffuse 1 d.

 $(0^{Ph})(BF_4)$ . A 20 mL aliquot of dry, argon-purged CH<sub>2</sub>Cl<sub>2</sub> was added by syringe to a mixture of 0.0343 g (0.052 mmol) of  $0^{Ph}$  and 0.0061 g (0.052 mmol) of NOBF<sub>4</sub> under argon. After the resulting purple solution had been stirred 2 h, solvent was removed by vacuum. The purple solid was washed with 5 mL of Et<sub>2</sub>O and dried under vacuum to give 0.030 g (77%) of  $(0^{Ph})(BF_4)$  as a purple solid. Mp, > 350 °C dec  $\mu_{eff}$  (solid, 295 K) = 1.7  $\mu_{B}$ . IR (KBr):  $\nu_{CO}$  2033, 1906 cm<sup>-1</sup>. UV– vis (CH<sub>2</sub>Cl<sub>2</sub>): nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 773 (1800), 627 (1200), 395 (5340).

 $[Re(CO)_3]_2(\mu-L1)$ , 1. A mixture of 0.127 g (0.20 mmol) of H<sub>2</sub>(L1) and 0.164 g (0.40 mmol) of Re(CO)<sub>5</sub>Br in 10 mL of toluene was heated at reflux under argon 10 min. Then, 0.28 mL of a solution 1.47 M NEt<sub>4</sub>OH in MeOH (0.40 mmol) was added by syringe (while hot and under argon); a bright yellow solution formed immediately. After a few minutes, a yellow precipitate began forming. The mixture was heated an additional 12 h, then was cooled to room temperature. The yellow solid was collected by filtration, was washed with two 15 mL portions of MeOH, one 15 mL portion of Et<sub>2</sub>O, and was dried under vacuum 1 h. Yield: 0.211 g (89%). Mp, 260-261 °C (Dec.). Anal. Calcd (Found) for Re<sub>2</sub>C<sub>44</sub>N<sub>10</sub>H<sub>30</sub>O<sub>6</sub>: C, 45.28 (45.54); H, 2.59 (2.78); N, 12.00 (11.84). IR (KBr):  $\nu_{CO}$  2013, 1905, 1882 cm<sup>-1</sup>. <sup>1</sup>H NMR  $(DMF-d_7): \delta_H 8.74 (d, J = 2.7 Hz, 2H, pz), 8.64 (d, J = 2.4 Hz, 2H, pz),$ 8.62 (d, J = 2.26 Hz, 2H, pz), 8.61 (d, J = 2.6 Hz, 2H,pz), 7.98 (d, J = 8.3 Hz, 2H, Ar), 7.96 (d, J = 8.8 Hz, 2H, Ar), 7.74 (dd, J = 8.8, 2.1 Hz, 2H, Ar), 7.45 (s, 2H, Ar), 7.28 (dd, J = 8.3, 1.7 Hz, 2H, Ar), 7.21 (s, 2H, Ar), 6.82 (t, J = 2.5 Hz, pz), 6.77 (t, J = 2.4 Hz, 2H, pz), 2.37 (6H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ<sub>c</sub> 196.66, 195.55, 195.20, 146.02, 145.31, 144.16, 143.73, 132.48, 131.87, 130.81, 128.72, 128.50, 127.52, 124.72, 124.21, 120.26, 119.91, 116.40, 108.11, 108.06, 20.06. UV-vis  $\lambda_{max}$  nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>), CH<sub>2</sub>Cl<sub>2</sub>: 402 (22 400), 238 (36 350). Single crystals of 1.1.59DMF.0.41Et<sub>2</sub>O suitable for X-ray diffraction studies were grown by layering a 50% Et<sub>2</sub>O/MeOH mixture on a DMF solution and allowing solvents to diffuse 2 d.

 $1(BF_4)_2$ . In a manner like that described for  $(0^{\text{ph}})(BF_4)$  above, a mixture of 0.0353 g (0.030 mmol) of 2 and 0.0071 g (0.061 mmol) of NOBF<sub>4</sub> yielded 0.0341 g (84%) of  $1(BF_4)_2$  as a blue/black solid. Mp, > 350 °C dec  $\mu_{\text{eff}}$  (solid, 295 K) = 2.9  $\mu_{\text{B}}$ . IR (KBr):  $\nu_{\text{CO}}$  2028, 1936, 1914 cm<sup>-1</sup>. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): cm<sup>-1</sup> ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 654 (45 600), 552 (31 000), 227 (231 000).

**1**(*BF*<sub>4</sub>). A mixture of 0.0232 g (19.9  $\mu$ mol) of **1** and 0.0267 g (19.9  $\mu$ mol) of **1**(*BF*<sub>4</sub>)<sub>2</sub> in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> was stirred 30 min at room temperature; then solvent was removed to give 0.0361 g (72% yeld) of **1**(*BF*<sub>4</sub>) as a red solid.  $\mu_{\rm eff}$  (Evan's, CD<sub>2</sub>Cl<sub>2</sub>, 295 K) = 1.6  $\mu_{\rm B}$ . IR (KBr):  $\nu_{\rm CO}$  2011, 1900 cm<sup>-1</sup>. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>): cm<sup>-1</sup> ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 739 (53 500), 660 (4400), 535 (42 800).

 $[Re(CO)_3]_2(\mu-L2)$ , **2**. By using the method described for **1** above, a mixture of 0.115 g (0.163 mmol) of H<sub>2</sub>(L2), 0.132 g (0.33 mmol, 2 equiv) of Re(CO)<sub>5</sub>Br, 0.22 mL of 1.47 M (solution in MeOH, 0.33 mmol) NEt<sub>4</sub>OH, and 10 mL of toluene gave 0.121 g (60%) of **2** as a

yellow powder. Mp, 330 °C (Dec.). Anal. Calcd (Found) for  $C_{50}H_{34}N_{10}O_6Re_2$ : C, 48.30 (48.66); H, 2.76 (2.95); N, 11.27 (11.10). IR (KBr):  $\nu_{CO}$  2013, 1901, 1876 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMF- $d_7$ ):  $\delta_H$  8.94 (dd, J = 2.7, 0.7 Hz, 2H, pz), 8.82 (dd, J = 2.4, 0.7 Hz, 2H, pz), 8.79 (br d, J = 2.6 Hz, 4H, pz), 8.16 (d, J = 6.2 Hz, 2H, Ar), 8.15 (s, 2H, Ar), 8.14 (d, J = 5.5 Hz, 2H, Ar), 8.04 (s, 4H, Ar), 7.87 (dd, J = 8.9, 2.2 Hz, 2H, Ar), 7.62 (d, J = 1.9 Hz, 2H, Ar), 7.48 (dd, J = 8.5, 1.8 Hz, 2H, Ar), 6.99 (t, J = 2.5 Hz, 2H, pz), 6.92 (t, J = 2.5 Hz, 2H, pz), 2.55 (s, 6H) ppm. <sup>13</sup>C NMR (DMSO- $d_6$ ):  $\delta_c$  196.85, 195.37, 195.18, 146.77, 145.25, 144.19, 143.73, 136.96, 132.58, 131.94, 131.27, 129.14, 128.50, 128.42, 127.42, 126.05, 125.26, 124.40, 120.94, 120.46, 116.01, 108.25, 108.20, 20.19. UV-vis  $\lambda_{max}$  nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>), CH<sub>2</sub>Cl<sub>2</sub>: 403 (8300), 227 (10 300). Attempts to obtain crystals suitable for single-crystal X-ray diffraction by a number of conditions only produced microcrystalline solids.

**2(BF**<sub>4</sub>)<sub>2</sub>. By using the method described for (0<sup>Ph</sup>)(BF<sub>4</sub>), a mixture of 0.0345 g (0.028 mmol) of **2** and 0.0065 g (0.056 mmol) of (NO)(BF<sub>4</sub>) yielded 0.0329 g (84%) of **2(BF**<sub>4</sub>)<sub>2</sub> as a black solid. Mp, > 350 °C dec  $\mu_{\text{eff}}$  (solid, 295 K) = 2.7  $\mu_{\text{B}}$ . IR (KBr):  $\nu_{\text{CO}}$  2034, 1938, 1914 cm<sup>-1</sup>. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>): cm<sup>-1</sup> ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 817 (149 000), 227 (54 700).

Crystallography. X-ray intensity data from a yellow plate of 0<sup>Ph</sup> and a light-yellow prism of 1.1.59DMF.0.41Et<sub>2</sub>O were collected at 100.0(1) K with an Oxford Diffraction Ltd. Supernova diffractometer equipped with a 135 mm Atlas CCD detector using  $Mo(K\alpha)$  radiation. Raw data frame integration and Lp corrections were performed with CrysAlis Pro (Oxford Diffraction, Ltd.).<sup>26</sup> Final unit cell parameters were determined by least-squares refinement of 13 376 and 25 309 reflections of  $0^{\text{Ph}}$  and  $1.1.59\text{DMF}.0.41\text{Et}_2\text{O}$ , respectively, with I > 1.59DMF $2\sigma(I)$  for each. Analysis of the data showed negligible crystal decay during collection in each case. Direct methods structure solutions, difference Fourier calculations, and full-matrix least-squares refinements against F<sup>2</sup> were performed with SHELXTL.<sup>27</sup> Numerical absorption corrections based on Gaussian integration over a multifaceted crystal model were applied to the data in each experiment. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The X-ray crystallographic parameters and further details of data collection and structure refinements are given in Table S1.

#### RESULTS AND DISCUSSION

**Syntheses.** Schemes 1 and 2 outline the preparative routes to the new ligands,  $H_2(L1)$  and  $H_2(L2)$ , respectively.  $H_2(L1)$  is synthesized in a three-step sequence starting from 4,4-diiodobiphenyl (Scheme 1). Thus, *N*,*N*'-di-*p*-tolyl-*p*-benzidene was prepared in high yield by a Pd-catalyzed amination of the

Scheme 1. Preparation of  $H_2(L1)^a$ 







diiodoarene with toluidine. Subsequent bromination afforded the sparingly soluble tetrabromo derivative which was then subjected to CuI-catalyzed amination with pyrazole to give  $H_2(L1)$ . Attempts to produce  $H_2(L1)$  by Ni(0)-catalyzed homocoupling of  $H(L0^{Br})^{17a}$  (i.e., the compound on the left of Scheme 2) was unsuccessful; only starting materials were recovered.  $H_2(L2)$  was obtained in high yield by the Suzuki coupling reaction between *p*-benzenediboronic acid and 2 equiv of  $H(L0^{Br})$  (Scheme 2). The new mononucleating pincer ligand  $H(L0^{Ph})$  was prepared similarly by the Suzuki coupling method but used an equimolar ratio of  $H(L0^{Br})$  and PhB(OH)<sub>2</sub>.

The tricarbonylrhenium(I) complexes were prepared by heating a mixture of ligand,  $Re(CO)_5Br$ , and  $(NEt_4)(OH)$  (1) Re and 1 OH<sup>-</sup> per N-H bond on a given ligand) in toluene at reflux 12 h. The bimetallic complexes precipitate as bright yellow solids that can be purified by filtration and drying under vacuum. On the other hand, the monometallic complexes are appreciably soluble in toluene. So, solvent is removed by vacuum distillation and the yellow residue was washed with methanol to remove the byproduct  $(NEt_4)(Br)$ , and the analytically pure yellow solids  $0^x$  (x = Me, Ph) are obtained after drying under vacuum. The IR spectra for solid samples (ATR) or for KBr pellets of each  $0^{Ph}$ , 1, and 2 show CO stretching bands characteristic of the fac-Re(CO)<sub>3</sub> moiety similar to that reported for  $0^{Me}$ .<sup>19</sup> That is, each shows three bands (an A" and two A' modes) for the local  $C_s$  symmetric  $Re(CO)_3N_{Ar}(N_{nz})_2$  unit. Somewhat surprisingly, given the different electronic properties of the complexes discussed later, the substitution pattern of the pincer ligand has little impact on the CO stretching frequency; the average CO stretching frequencies are statistically equivalent ranging between 1930(2)and 1934(2) cm<sup>-1</sup>.

**Structures.** The *fac*-binding mode was confirmed by singlecrystal X-ray diffraction studies of  $0^{\text{Ph}}$  and 1.1.59DMF· 0.41Et<sub>2</sub>O, whose structures are given in Figures 1 and 2, respectively. Unfortunately, suitable crystals of 2 could not be grown despite exhaustive effort. The metrics of the ReN<sub>3</sub>C<sub>3</sub> moieties in each complex (Table 1) are nearly identical to those



Figure 1. Structure of  $0^{\text{ph}}$  with thermal ellipsoids drawn at 50% probability and hydrogen atoms removed for clarity.



Figure 2. Structure of  $1.1.59DMF \cdot 0.41Et_2O$  with solvate molecules and hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

reported earlier for  $0^{Me}$ . The average Re–N distance of 2.161(2) Å in  $0^{Me}$ , 2.164(3) Å in  $0^{Ph}$ , and 2.158(3) Å in 1 are the same, but the average Re–C distance of 1.928(3) Å in  $0^{Me}$  is slightly longer than 1.917(3) Å in  $0^{Ph}$  or 1.921(3) Å in 1. The C-O bond distances are rather unremarkable, averaging 1.15 Å, in line with other rhenium(I) carbonyls.<sup>19</sup> The amido nitrogen(s) of each  $0^x$  and 1 are similar, being nearly planar with a sum of angles about N1 (or N2) of 356° (but asymmetric such as to be an acute triclinic pyramid derived from an 8% folded trigonal plane<sup>28</sup>). Also, the six-membered ReN<sub>3</sub>C<sub>2</sub> chelate rings are not planar but have twist-boat conformations such that there is a  $40(3)^{\circ}$  dihedral angle between attached pz and aryl rings and with the rhenium atom folded along the  $\bar{N_{Ar}}\cdots N_{pz}$  hinge (e.g., N1…N11 or N1…N12 in  $0^{Ph}$ ). The dihedral angles between rings in the biphenyl moieties in  $0^{Ph}$  (19°) and 1 (20°) are similar. For the latter, the rhenium centers are located on opposite sides of the mean plane of the connecting biphenyl unit. The monometallic complexes  $0^{Me}$  and  $0^{Ph}$  are soluble in many organic solvents except MeOH, Et<sub>2</sub>O, and light alkanes. On the other hand, the bimetallic complexes 1 and 2 are freely soluble in dmso or DMF, but are only slightly soluble in CH<sub>2</sub>Cl<sub>2</sub>, and are insoluble in most other organic solvents. Thus, comparisons of solution properties between mono- and bimetallic complexes were limited to either DMF or (dilute) CH<sub>2</sub>Cl<sub>2</sub> solutions. The solution <sup>1</sup>H NMR spectra of the new complexes are in accord

with expectations based on solid state structures, or idealized models of the complexes as drawn in Chart 1. That is, there are two sets of resonances for pyrazolyl ring hydrogens for the inequivalent heterocycles as well as the predicted number of resonances for aryl and methyl hydrogens. Moreover, the <sup>13</sup>C NMR spectrum of each compound shows three resonances for the symmetrically inequivalent CO groups.

Theoretical Calculations. Before discussion of the experimental electronic properties, it will be useful to describe qualitative aspects of the molecular orbital diagrams found from DFT calculations; full details regarding theoretical calculations are given in the Supporting Information. Figures 3 and S7 display the frontier orbitals of 0<sup>Ph</sup>, obtained from calculations at the M06/Def2-SV(P) level of theory. For this low symmetry species, a coordinate system is adopted for convenience such as to have Re as the origin and the z-axis to be coincident with the Re-C bond that is *trans*- to the diarylamido nitrogen, N<sub>Ar</sub>. The x-axis is then arbitrarily assigned coincident with the Re-C bond that is trans- to the nitrogen of the pyrazolyl bound to the tolyl group,  $N_{pzMe}$ , and the y-axis is aligned with the final Re-C bond trans- to the nitrogen of the pyrazolyl bound to the biphenyl, N<sub>pzPh</sub>. In this way, the  $d_{vz}$  orbital participates in  $\pi$ interactions with the diarylamido nitrogen's p<sub>v</sub> orbital, and with two carbonyl  $\pi^*$  orbitals, one *trans*- to N<sub>Ar</sub> and the other *trans*to N<sub>pzPh</sub>. The d<sub>xz</sub> orbital participates in  $\pi$  interactions with  $\pi^*$ orbitals of carbonyl groups trans- to NAr and to NpzMe. Likewise, the  $d_{xy}$  orbital has  $\pi$  interactions with  $\pi^*$  orbitals of carbonyl groups trans- to the two rhenium-bound pyrazolyl nitrogens, N<sub>pzMe</sub> and N<sub>pzPh</sub>. The HOMO (second from left, Figure 3) is mainly a  $\pi_{\rm L}$  orbital<sup>29</sup> centered on the toluidinyl arm of the diarylamido fragment that is weakly mixed (in an antibonding fashion) with orbitals of the  $\text{Re}(d_{\nu z})$ -CO  $\pi$  interaction. The HOMO(-N) (N = 1-3) (N = 1 is shown to left of Figure 3, others in Figure S7) are mainly metal-centered orbitals with  $d\pi - p\pi$  bonding interactions involving the Re-CO fragments. The corresponding antibonding  $d\pi - p\pi$  interactions (associated with the Re-CO fragments) are found in LUMO(+N) (N = 11–13) (Figure S7). The LUMO and LUMO(+1) are  $\pi^*$ orbitals on the pincer scaffold (near and far right, Figure 3), while LUMO(+*N*) (*N* = 3, 4) are mainly  $\pi^*$  orbitals involving the carbonyl groups. The  $\sigma^*$  interactions involving  $d_{x^2-v^2}$  and  $d_{z^2}$ 

Table 1. Selected Bond Distances (Å) and Angles (deg) for 0<sup>Ph</sup> and 1·1.59DMF·0.41Et<sub>2</sub>O

	0 <sup>Ph</sup>	1.1.59DMF.0.41Et <sub>2</sub> O						
bond distances (Å)								
Re1–N1	2.157(3)	Re1–N1	2.160(2)	Re2-N2	2.162(2)			
Re1-N11	2.178(3)	Re1-N11	2.152(2)	Re2-N41	2.170(2)			
Re1-N21	2.158(3)	Re1-N21	2.163(2)	Re2-N51	2.143(2)			
Re1-C51	1.917(4)	Re1-C14	1.917(3)	Re2-C44	1.917(3)			
Re1-C52	1.913(4)	Re1-C15	1.923(3)	Re2-C45	1.927(3)			
Re1-C53	1.922(4)	Re1-C16	1.923(3)	Re2-C46	1.920(3)			
C51-O1	1.150(4)	C14-O1	1.151(4)	C44-O4	1.154(4)			
C52-O2	1.165(4)	C15-O2	1.155(4)	C45-O5	1.147(4)			
C53–O3	1.147(4)	C16-O3	1.154(4)	C46-O6	1.150(4)			
bond angles (deg)								
N1-Re1-N11	79.07(10)	N1-Re1-N21	79.20(9)	N2-Re2-N41	79.14(9)			
N1-Re1-N21	81.26(10)	N11-Re1-N1	80.87(9)	N51-Re2-N2	81.38(9)			
N21-Re1-N11	85.06(10)	N11-Re1-N21	84.48(9)	N51-Re2-N41	83.52(9)			
C52-Re1-C51	89.39(15)	C14-Re1-C15	89.80(14)	C44-Re2-C45	90.16(13)			
C51-Re1-C53	87.77(14)	C14-Re1-C16	90.68(13)	C44-Re2-C46	90.15(13)			
C52-Re1-C53	88.24(15)	C16-Re1-C15	89.01(12)	C46-Re2-C45	88.49(13)			



Figure 3. Frontier orbitals of 0<sup>Ph</sup> from DFT calculations (M06/Def2-SV(P)).

orbitals are much higher energy, found in LUMO (+N = 22 and 27).

Selected frontier orbitals for 1 and 2 are depicted in Figures 4, S8, and S9. The molecular orbitals of 1 and 2 are similar and



Figure 4. Frontier orbitals of 1 (left) and 2 (right) from DFT calculations (M06/Def2-SV(P)).

can be qualitatively derived from linear combinations of orbitals in  $0^{Ph}$  or  $0^{Me}$ . That is, the HOMO and HOMO(-1) in 1 and 2 are ligand-centered  $\pi_{\rm L}$  orbitals weakly mixed with bonding combinations of Re  $d_{yz}$  and CO  $\pi^*$  orbitals. However, the HOMOs in 1 and 2 are constructed from out-of-phase combinations of HOMOs of monomer units, as illustrated by examination of the phases of  $p_{y}$  orbitals on the diarylamido nitrogens, N<sub>Ar</sub> (second from bottom, Figure 4). The HOMO(-1) of each 1 and 2 is the in-phase-phase combination of monomer HOMOs (again seen by inspection of the phases of  $N_{Ar} p_{\nu}$  orbitals, bottom Figure 4). Similar to  $0^{Ph}$ , the LUMO and LUMO(+N) (N = 1-4) in both 1 and 2 are  $\pi^*$  orbitals centralized on the bridging ligand. Thus, the first oxidation of each could be predicted to be heavily ligand-centered, while the lowest energy absorption would have mainly  $\pi - \pi^*$  character mixed with, in order of decreasing contribution,  $n-\pi^*$ , and metal-ligand charge transfer (MLCT) character.

**UV**-vis. The electronic spectrum of each  $0^{\text{Ph}}$ , 1, and 2 in either CH<sub>2</sub>Cl<sub>2</sub> or DMF are similar to that reported earlier for  $0^{\text{Me}}$  in CH<sub>2</sub>Cl<sub>2</sub> with sets of three overlapping medium to high intensity (4000 <  $\varepsilon$  < 45 000 M<sup>-1</sup> cm<sup>-1</sup>) bands in the near-UV to blue range 330-450 nm that gives rise to the yellow color of the complexes; see Figure 5. TD-DFT calculations (Tables S5–S7) indicate these low energy bands arise due to HOMO to LUMO(+*N*) (*N* = 0-4) transitions which may be described as combinations of intraligand  $\pi$ - $\pi$ \*charge transfer (owing to spatial separation of orbitals), n- $\pi$ \*, and MLCT in character, as predicted above.



**Figure 5.** Electronic spectrum of 1 (blue solid line) and 2 (violet dashed line) in  $CH_2Cl_2$ . The nonzero long wavelength absorbance and relatively low  $\varepsilon$  for all bands in the spectra of 2 are due to the low solubility in this solvent (a suspension is formed).

Electrochemistry. The electrochemical properties of the rhenium complexes are summarized in Table 2, and cyclic voltammograms of CH<sub>2</sub>Cl<sub>2</sub> solutions of the new complexes are shown in Figure 6 (data for DMF solutions are found in Figure S1 and Table S1). The complex **0**<sup>Ph</sup> shows a single reversible one-electron oxidation wave at 0.57 V vs Ag/AgCl which is close to that at 0.55 V for  $0^{Me}$ , expectedly showing only a small dependence on the nature of the hydrocarbon (Me vs Ph) attached to the 4-aryl position of the ligand. Bimetallic complex 1 shows two reversible one-electron oxidation waves for  $1^+/1$ and  $1^{2+}/1^+$  couples. The first oxidation in 1 is 248 mV more negative than that for 0<sup>Ph</sup> under the same conditions (electrolyte) which reflects the electron-rich nature of the benzidene linker. The separation between oxidation waves,  $\Delta E_{i}$ in the voltammograms is typically used to measure the equilibrium constant for comproportionation,  $K_{com}$  (eq 1), and can provide a qualitative measure of the strength of electron

$$\mathbf{1} + \mathbf{1}^{2^+} \rightleftharpoons 2\mathbf{1}^+ \quad K_{\rm com} = (\mathbf{1}^+)^2 / [(\mathbf{1})(\mathbf{1}^{2^+})] \tag{1}$$

communication in a mixed valence species.<sup>30,31</sup> However, the value of  $\Delta E$  and hence  $K_{com}$  varies substantially depending on the experimental setup. For 1,  $\Delta E$  varies from 316 mV ( $K_{\rm com} \sim$  $10^5$ ) in medium polarity solvent CH<sub>2</sub>Cl<sub>2</sub> with a non-ion pairing electrolyte NBu<sub>4</sub> $[B(C_6F_5)_4]^{32}$  to only 119 mV ( $K_{com} \sim 10^2$ ) in the highly polar solvent DMF that contains an electrolyte with better ion pairing abilities NBu<sub>4</sub>PF<sub>6</sub>. The former setup with larger  $K_{\rm com}$  suggests that the one-electron oxidized species 1<sup>+</sup> would be near the Robin–Day<sup>33</sup> Class II/Class III border ( $K_{com}$  $\geq 10^6$ , Class III) for a mixed valence compound, while the latter, in electrolyte-containing DMF, suggests 1<sup>+</sup> to be a Class II mixed valence compound. Similar observations have been made for purely organic N,N,N,N-(tetraaryl)benzidene derivatives, which have varying  $\Delta E$ 's between 215 and 300 mV ( $K_{com}$ between  $10^3$  and  $10^4$ ) in electrolyte-containing CH<sub>2</sub>Cl<sub>2</sub>. Noteworthy, these organic (tetraaryl)benzidine cation radicals are fully delocalized (Class III) in CH<sub>2</sub>Cl<sub>2</sub> without electrolyte, based on spectroscopic measurements and theoretical studies.<sup>34–37</sup> For 2, the first oxidation potential is ca. 200 mV more positive than in 1, showing that this diamine is less electron-rich

Table 2. Electrochemical	Data from Cycl	c Voltammetry	Experiments	of Complexes	in CH <sub>2</sub> Cl <sub>2</sub> with	Various Supporting
Electrolytes						

complex	electrolyte	V vs Ag/AgCl <sup>a</sup> , $E_{ox1}$ ( $E_{sep}$ , mV) <sup>b</sup>	$E_{\text{ox2}} (E_{\text{sep}}, \text{ mV})^{b}$	$K_{\rm com}^{\ \ c}$
0 <sup>Me</sup>	NBu <sub>4</sub> PF <sub>6</sub>	0.552 (138)		
0 <sup>Ph</sup>	NBu <sub>4</sub> PF <sub>6</sub>	0.569 (148)		
1	NBu <sub>4</sub> PF <sub>6</sub>	0.321 (147)	0.549 (140)	$7.85 \times 10^{3}$
	$NBu_4[B(C_6F_5)_4]$	0.224 (69)	0.540 (73)	$2.51 \times 10^{5}$
2	NBu <sub>4</sub> PF <sub>6</sub>	0.519 <sup>d</sup>	$0.598^d (176)^e$	$2.24 \times 10^{1}$
	$NBu_4[B(C_6F_5)_4]$	0.408 (89)	0.504 (93)	$4.37 \times 10^{1}$

<sup>a</sup>Average values of  $(E_{pa} + E_{pc})/2$  from scan rates of 50, 100, 200, 300, 400, and 500 mV/s. <sup>b</sup>Peak potential separation  $(E_{pa} - E_{pc})$ . <sup>c</sup> $K_{com} = e^{(\Delta E \cdot F/RT)}$ , T = 295 K. <sup>d</sup>From square wave voltammogram. <sup>c</sup>Width of combined bands.



Figure 6. Left: Cyclic voltammograms of  $0^{Ph}$ , 1, and 2 in CH<sub>2</sub>Cl<sub>2</sub> with NBu<sub>4</sub>PF<sub>6</sub> as an electrolyte. Owing to low solubility of 2, the data were multiplied by a factor of 6 to be on scale. Right: Cyclic (blue) and square wave (red) voltammograms of 1 and 2 in in CH<sub>2</sub>Cl<sub>2</sub> with NBu<sub>4</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as an electrolyte.



**Figure 7.** X-band EPR spectra (experimental, top black lines) of  $2(BF_4)$  in  $CH_2Cl_2$  at 295 K (left) and 77 K (right). Instrumental parameters: 295 K: Freq = 9.463 GHz; Power = 1.6 mW, modulation 7 G; 77 K: Freq = 9.434 GHz; Power = 5.056 mW, modulation 3 G. Simulated spectra (red, bottom traces); see text.

than that in 1. Moreover,  $\Delta E$  is only about 100 mV ( $K_{\rm com} \sim 10^1$ ) in CH<sub>2</sub>Cl<sub>2</sub> with NBu<sub>4</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], which reduces to ~80 mV with NBu<sub>4</sub>PF<sub>6</sub>. In DMF, only one two-electron oxidation wave is observed at a potential (0.63 V) only slightly negative of those found for monometallic **0**<sup>x</sup> (x = Me, 0.65 V; x = Ph, 0.71 V). Thus, according to cyclic voltammetry, **2**<sup>+</sup> would be predicted to be a Robin–Day Class I mixed valence species in electrolyte-containing CH<sub>2</sub>Cl<sub>2</sub> and could not be formed in DMF in the presence of electrolyte. Thus, it appears from the current data and the literature of (tetraaryl)benzidine cation radicals that the electrochemical data only give the lower limit for electron communication in mixed valent species.

**Oxidation.** To further investigate the electronic behavior of 1 and 2, the complexes were each subjected to chemical oxidation. The reaction of each complex with 2 equiv of  $(NO)(BF_4)$  in  $CH_2Cl_2$  gave  $(1^{2+})(BF_4)_2$  and  $(2^{2+})(BF_4)_2$ , respectively. It is noteworthy that, while the starting materials have low solubility in  $CH_2Cl_2$ , the oxidized derivatives (both singly and doubly oxidized) are quite soluble. The doubly oxidized derivatives are paramagnetic in the solid at 295 K ( $\mu_{eff}$  2.8 ± 0.1  $\mu_B$ ) but are EPR silent both in solution at 295 K or as frozen glasses at 77 K. Each doubly oxidized complex is also

distinctly and deeply colored:  $(1^{2+})(BF_4)_2$  is blue, and  $(2^{2+})(BF_4)_2$  is green. These colors arise in part by characteristic pi-radical bands ( $\beta$ -HOMO(-N) to SOMO ( $\beta$ -LUMO) transitions) found in the visible region of the electronic spectrum:  $\lambda_{max} = 645 \text{ nm}$  ( $\varepsilon 41700 \text{ M}^{-1} \text{ cm}^{-1}$ ) for  $1^{2+}$ ,  $\lambda_{max} = 806 \text{ nm}$  ( $\varepsilon 15200 \text{ M}^{-1} \text{ cm}^{-1}$ ) for  $2^{2+}$ . The IR spectra of the dioxidized solids show a shift in the C–O stretching bands to higher frequency versus those for the non-oxidized counterparts, reflecting a lower capacity for metal–CO back-bonding in the former. The change in average energy of the C-O stretching bands on oxidation,  $\Delta \nu_{CO}(\text{avg})$ , was 28 cm<sup>-1</sup> on traversing from 1 (1933 cm<sup>-1</sup>) to  $1^{2+}$  (1963 cm<sup>-1</sup>) and 33 cm<sup>-1</sup> between 2 (1933 cm<sup>-1</sup>) and  $2^{2+}$  (1963 cm<sup>-1</sup>) to  $0^{\text{Ph}+}$  (1963 cm<sup>-1</sup>). As a means of comparison,  $\Delta \nu_{CO}(\text{avg})$  was  $\approx 100 \text{ cm}^{-1}$  on traversing CpRe(CO)<sub>3</sub> to CpRe(CO)<sub>3</sub><sup>+</sup>, a heavily rhenium-centered oxidation.<sup>38</sup>

**EPR.** With the dioxidized derivatives in hand, comproportionation reactions were used to study the properties of the singly oxidized derivatives,  $1^+$  and  $2^+$ . First, mixing equimolar solutions of EPR silent 1 or 2 with their EPR silent doubly oxidized counterparts ( $1^{2+}$  or  $2^{2+}$ ) produced EPR-active



**Figure 8.** Left: Spectrophotometric titration of **2** (bottom spectrum with black line) with  $2^{2+}$  (spectrum shown overlaid as a blue dashed line) to give  $2^+$  (top spectrum shown in green). Inset: Absorbance at 2000 nm as a function of added  $2^{2+}$ . Right: Deconvolution of low energy band into three Gaussian curves (black lines); see also Figure S7. The experimental spectrum is in blue. Sum of Gaussian fits is the red dashed line.

solutions of  $1^+$  or  $2^+$ . The left of Figure 7 shows the X-band EPR spectrum of a  $CH_2Cl_2$  solution of 2<sup>+</sup> recorded at 295 K. The eleven-line signal for the  $S = \frac{1}{2}$  species was adequately simulated<sup>39</sup> as axial with  $g_{x,y} = 2.011$  and  $g_z = 1.998$  and hyperfine coupling of the electron to two rhenium nuclei with  $A_{\text{Re1}} = 1.14 \text{ mT}, A_{\text{Re2}} = 1.25 \text{ mT} (I^{-185}\text{Re} (37.4\%))^{187}\text{Re}$  $(62.6\%) = \frac{5}{2}$ , indicating full delocalization of the electron. The 295 K spectrum of 1<sup>+</sup> (Figure S2) is simulated as axial with  $g_{x,y} = 2.011, g_z = 1.996, A_{Re1} = 1.16 \text{ mT}$ , and  $A_{Re2} = 1.04 \text{ mT}$ , values nearly identical to those of  $2^+$ . Interestingly, the spectrum of  $2^+$  at 77 K (right of Figure 7) is an inhomogeneously broadened six-line derivative signal  $(g_{iso} =$ 2.012;  $A_{\text{Re}} = 141$  MHz) that is very similar to that of monometallic  $(\mathbf{0}^{\text{Me}})^+$  (at 10 K,  $g_{\text{iso}} = 2.015$ ,  $A_{\text{Re}} = 124$  MHz) reported previously<sup>19b</sup> or that of  $(\mathbf{0}^{\text{Ph}})^+$  at 77 K ( $g_{\text{iso}} = 2.016$ ,  $A_{\text{Re}}$  = 146 MHz, Figure S3b). An alternate EPR model for the spectra of  $2^+$  at 77 K of a rhombic signal with  $g_{x,y,z} = 2.027$ , 1.998, 1.981 and hyperfine coupling of the electron to one nitrogen ( $A_{Nx,y,z}$  = 4.53, 4.43, 4.08 mT) and one rhenium  $(A_{Re,x,y,z} = 0.40, 0.38, 0.84 \text{ mT})$ , shown in the bottom right of Figure 7, could be fit to the spectrum but is less satisfactory since it gives nitrogen hyperfine coupling constants that are an order of magnitude higher than those of pure organic derivatives. Another possible model, with hyperfine coupling of the electron to two nitrogen atoms (which required two disparate A<sub>N</sub>'s and much larger anisotropic broadenings), was even less satisfactory (higher root-mean-square deviations from experimental data), while that with the electron coupled to two rhenium centers was wholly unsatisfactory. Thus, it appears most likely that the electron in  $2^+$  is localized on one end of the molecule at low temperature (i.e., is thermally valence-trapped). Unfortunately, the low temperature spectrum of  $1^+$  was not suitably structured for successful modeling (Figure S2b).

**NIR.** The identities of  $1^+$  and  $2^+$  were further supported by spectrophotometric titrations. That is, UV–vis/NIR spectra were recorded after substoichiometric quantities of doubly oxidized derivatives in CH<sub>2</sub>Cl<sub>2</sub> were added to dilute solutions of the appropriate non-oxidized derivatives **1** or to a suspension of **2** in CH<sub>2</sub>Cl<sub>2</sub>. As displayed for **2** in Figure 8 and for **1** in Figure S4, the spectrum shows the appearance of distinctive new bands for the singly oxidized species  $2^+$  (or  $1^+$ ) that stop growing in intensity when 1 equiv of doubly oxidized species is added to the solution of the appropriate charge-neutral compound. In each case, new bands are found in the NIR region that are

assigned as charge resonance for 1<sup>+</sup> and as intervalence charge transfer (IVCT) for  $2^+$ . The charge resonance assignment for bands in 1<sup>+</sup> is aligned with voluminous literature on Robin-Day Class III radical cations of benzidene<sup>34–37</sup> variants (like the aforementioned  $N_i N_i N' N'$ -tetraarylbenzidene derivatives). The assignment of an IVCT band for  $2^+$  is based on the EPR data that suggests Class II behavior. Such an assignment is bolstered by extrapolation of the electrochemical data to conditions without electrolyte and on results of time-dependent density functional theory (TD-DFT) calculations that show overlap between  $\beta$ -HOMO and  $\beta$ -LUMO and a highly solventdependent very low energy CT transition. Hush analysis of the NIR bands was used to extract information about electronic coupling.<sup>40</sup> The asymmetric, structured low-energy NIR bands in each experimental spectrum could be fit by deconvolution (right Figure 8 and Figure S5) as a sum of three Gaussianshaped curves of decreasing intensity separated by about 1300-1600  $\text{cm}^{-1}$  perhaps part of a vibronic progression (coupled with C = C/C = N stretching modes)<sup>41</sup> or due to conformational effects<sup>42</sup> (low energy rotamers for  $1^+$  and  $2^+$ ) or both. For  $1^+$ , the electronic coupling matrix element was determined directly from the experimental band maximum,  $H_{AB} = \nu_{max}/2 = 3715$ cm<sup>-1</sup>, a value in the range found for Robin–Day Class III tetraarylbenzidene derivatives.<sup>7,10,34–36</sup> The asymmetric IVCT band in the spectra of  $2^+$  was subject to Hush analyses using eqs 2 and 3<sup>40</sup> The transition dipole moment,  $\mu_{12}$ , was calculated by summing over the three Gaussian curves used to fit the IVCT band. The lowest

$$\mu_{12}(D) = 0.09584 \left( \int \varepsilon(v) \partial v / \nu_{max} \right)$$
(2)

$$H_{AB}(\rm cm^{-1}) = \mu_{12}\nu_{\rm max}/eR$$
(3)

energy component of the structured IVCT band from deconvolution gave  $\nu_{\text{max}}$  of 4376 cm<sup>-1</sup>. In eq 3,  $\mu_{12}$  was converted to non-SI units 1D =  $10^{-18}$  statC·cm. The elementary charge constant, *e*, is 4.803 ×  $10^{-10}$  statC. Finally, the effective charge separation distance, *R*, is in units of cm. The values for *R* in diamine cation radicals have been the subject of much scrutiny and values of  $^{2}/_{3}$  the nitrogen–nitrogen separation has given reasonable agreement with other experimental data.<sup>10b,43</sup> For 2<sup>+</sup>, a value of *R* ( $^{2}/_{3}$  N–N) = 9.47 ×  $10^{-8}$  cm (from geometry optimized structure) gave  $H_{AB}$  = 502 cm<sup>-1</sup>. As an estimated lower limit, the use of *R* (Re–Re)



Figure 9. Plots of spin density isosurfaces (magenta, 0.025 isovalue) for  $(0^{Ph})^+$  (top left),  $1^+$  (bottom left), and  $1^{2+}$  (S = 1, bottom right) with spin density values from Mulliken population analysis given in green.

= 16.43 × 10<sup>-8</sup> cm gave  $H_{AB}$  of 289 cm<sup>-1</sup>. In either case, the  $H_{AB}$  values are smaller than, but in line with, other Class II mixed valence species such as  $H_{AB}$  (<sup>2</sup>/<sub>3</sub> N–N) = 705 cm<sup>-1</sup> in *E,E*-1,4-bis{4-[di(4-*n*-butoxyphenyl)amino]styryl]-2,5-dicyanobenzene or  $H_{AB}$  (<sup>2</sup>/<sub>3</sub> N–N) = 735 cm<sup>-1</sup> in 1,4-bis{4-[di(4-methoxyphenyl)amino]phenylethynyl}benzene.<sup>35b</sup>

Theoretical. The results of DFT calculations are in qualitative agreement with experimental observations for the  $(\mathbf{0}^{\text{Ph}})^{n+}$ ,  $\mathbf{1}^{n+}$ ,  $\mathbf{2}^{n+}$  (n = 0, 1, or 2) series in that the redox events are mainly ligand-centered but are increasingly delocalized onto the rhenium centers with charge of the complex. Thus, the electronic structure of  $(0^{Ph})^+$  is best described as an oxidized ligand bound to rhenium(I)  $(0^{Ph+})Re^{I}(CO)_{3}$ . Examination of spin density isosurface shows a majority of the spin (82%) is located on the ligand, in particular the amido nitrogen atom and on the carbon atoms at the positions ortho- and para- to the amido nitrogen on the tolyl ring (top of Figure 9). Similarly,  $1^+$  and  $1^{2+}$  (or  $2^+$  and  $2^{2+}$ ) are best described as mainly ligand-centered radicals of the formulations: (OC)<sub>3</sub>Re<sup>I</sup>- $(L^+)$ -Re<sup>I</sup>(CO)<sub>3</sub> and  $(OC)_3$ Re<sup>I</sup>- $(L^{-2+})$ -Re<sup>I</sup>(CO)<sub>3</sub>, respectively. Mulliken population analyses (M06/def2-SV(P)) shows that the spin density of  $1^+$  is weighted disparately to one side of the complex, exemplified by different values for each atom of the rhenium amido fragment (Re1 0.17, N1 0.38; Re 2 0.02, N2 0.05, Figure 9, left). For  $1^{2+}$  (S = 1), the spin density is more evenly delocalized along the ligand fragment onto both rhenium atoms (Re1 0.22, N1 0.42; Re2 0.25, N2 0.40, Figure 9, right). Similar observations are found for  $2^+$  and  $2^{2+}$ .

# CONCLUSIONS

Two bimetallic rhenium complexes of new dinucleating pincer ligands have been prepared. Each of these new complexes exhibits solvent- and electrolyte-dependent electrochemical behavior. Complex 1, constructed from a benzidene core, exhibits two reversible one-electron oxidations. Complex 2, with a *p*-terphenylenediamine core, exhibits one two-electron oxidation in DMF but has two one-electron oxidations in  $CH_2Cl_2$ . The solvent- and electrolyte-dependent oxidation potentials in both 1 and 2 further underscore the difficulties in assigning Robin–Day classifications to mixed valent derivatives (in this case, the one-electron oxidations of 1 and 2

provided singly and doubly oxidized derivatives  $1^{n+}$  and  $2^{n+}$  (n = 1, 2) that permitted spectroscopic characterization and assignment of Robin–Day classes to the n = 1 cases. The complex 1<sup>+</sup> is a Robin–Day Class III mixed valence compound, whereas complex  $2^+$  is a Class II species that was thermally valence trapped at 77 K by EPR spectroscopy. Thus, the interjection of the additional benzene ring in  $2^+$  versus  $1^+$ profoundly dampens electronic coupling, reducing  $H_{AB}$  by nearly an order of magnitude. One could project that a pquarterphenylenediamine-linked pincer would be an electronically isolated, Robin-Day Class I species. Unfortunately, solubility issues have hindered the preparation of such a compound. Nonetheless, these results and prediction are on par with the recent studies on dialkylamine-capped oligo-phenylenes that show electronic saturation when three phenylenes bridge two nitrogen centers, which is a result of the disparate energy of nitrogens and the oligophenylene bridge.<sup>9</sup> It may be possible to increase the electronic communication in these dipincer systems by using more electron-deficient metals, favoring electron delocalization away from the bridge or by restricting rotation of the central arylene units, which are avenues for future study.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00013.

Electrochemical data, electronic absorption spectra, and details of computational studies (PDF) Molecular structures from DFT calculations (XYZ)

#### Accession Codes

CCDC 1590573 and 1590574 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### **Author Contributions**

All authors have approved the final version of this manuscript. **Notes** 

The authors declare no competing financial interest.

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