

bipyridine complexes arise solely from thermodynamic differences, the ratio k_{pz}^{is}/k_{bpy}^{is} should be 33, the same value as for the corresponding outer-sphere reaction. However, the distance between the metal centers is presumably different for inner-sphere and outer-sphere transition states. Calculations⁸ suggest that outer-sphere electron transfer corresponds to a distance of closest approach between metal centers of 7×10^{-8} cm in $[\text{Ru}(\text{NH}_3)_5\text{L}]^{3+}-[\text{Co}(\text{EDTA})]^{2-}$, independent of the nature of L when L = pyridine or 4,4'-bipyridine. In contrast, the metal to metal distances are very different in the $[(\text{NH}_3)_5\text{Ru}(\text{pz})\text{Co}(\text{EDTA})]^{3+}$ (6.9×10^{-8} cm) and $[(\text{NH}_3)_5\text{Ru}(\text{bpy})\text{Co}(\text{EDTA})]^{3+}$ (11.1×10^{-8} cm) inner-sphere transition states. In previous work² we found that the distance dependence of rate constants for intramolecular electron transfer in $[(\text{NC})_5\text{Fe}(\text{L})\text{Co}(\text{NH}_3)_5]$ and $[(\text{EDTA})\text{Ru}(\text{L})\text{Co}(\text{NH}_3)_5]^{3+}$ (L = pyrazine or a bipyridine) is given by eq 8,

$$\lambda_0 = e^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right) \quad (8)$$

the outer-sphere reorganization energy,²⁶ where a_1 and a_2 are the radii of the two reactants, r is the distance between the metal centers in the transition state, and D_{op} and D_s are the optical and static dielectric constant of the medium, respectively. On the basis of eq 8, the expected ratio of inner-sphere reactivities for pyrazine and 4,4'-bipyridine is 65 (to be compared with experimental values of 21 and 30 for $[(\text{NC})_5\text{Fe}(\text{L})\text{Co}(\text{NH}_3)_5]$ ²⁷ and $[(\text{EDTA})\text{Ru}(\text{L})\text{Co}(\text{NH}_3)_5]^{3+}$ ²⁸, respectively). On the basis of the thermody-

amic barrier and the distance effect, the calculated value of k_{pz}^{is}/k_{bpy}^{is} is 33×65 or 2.1×10^3 and $k_{bpy}^{is} = 2.5 \times 10^3 / (2.1 \times 10^3) = 1.2 \text{ M}^{-1} \text{ s}^{-1}$. Evidently, such small contribution of the inner-sphere path to the overall $[\text{Ru}(\text{NH}_3)_5(\text{bpy})]^{3+}-[\text{Co}(\text{EDTA})]^{2-}$ reaction ($k_{bpy}^{os} = 77 \text{ M}^{-1} \text{ s}^{-1}$) could not have been detected.⁸

Finally, it is of interest to compare the value of the rate constant 16.9 s^{-1} for intramolecular electron transfer in $[(\text{NH}_3)_5\text{Ru}^{II}(\text{pz})\text{Co}^{III}(\text{EDTA})]^{3+}$ measured in the present work with the value $8 \times 10^9 \text{ s}^{-1}$ reported previously¹² for intramolecular electron transfer in the very similar system $[(\text{NH}_3)_5\text{Ru}^{II}(\text{pz})\text{Ru}^{III}(\text{EDTA})]^{3+}$. Since the thermodynamic factors are probably not very different for the $\text{Ru}^{II}/\text{Co}^{III}$ and $\text{Ru}^{II}/\text{Ru}^{III}$ systems,²⁹ the difference in intramolecular electron-transfer rates reflects mostly the difference in rate constants for self-exchange in $[\text{Ru}(\text{EDTA})]^{2-/-}$ vs. $[\text{Co}(\text{EDTA})]^{2-/-}$. Undoubtedly,³⁰ a major portion of the difference in the rate constants for exchange is associated with the much smaller inner-sphere configuration changes in $[\text{Ru}(\text{EDTA})]^{2-/-}$ as compared to $[\text{Co}(\text{EDTA})]^{2-/-}$. Whether orbital symmetry considerations are also important in determining the difference in the rates of exchange remains to be seen.³¹

Registry No. I, 88440-69-1; $[\text{Ru}(\text{NH}_3)_5(\text{pz})]^{3+}$, 38139-16-1; $[\text{Co}(\text{EDTA})]^{2-}$, 14931-83-0.

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Reactivity of 2-(Diphenylphosphino)pyridine toward Complexes Containing the Quadruply Bonded Re_2^{6+} Core: Ortho Metalation and Redox Chemistry

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Abstract: The quadruply bonded dirhenium(III) complexes $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ and $\text{Re}_2\text{Cl}_6(\text{PR}_3)_2$ (R = Et or *n*-Bu) react in methanol with 2-(diphenylphosphino)pyridine (Ph_2Ppy) to afford complexes that are derivatives of the triply bonded dirhenium(II) core, Re_2^{4+} . The complex $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_3$ (I) is formed initially and is found to eliminate HCl to give the ortho-metalated complex $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$ (II), the first example of a reaction of this type occurring at a metal-metal multiple bond of the M_2L_8 type. Both chloride and hexafluorophosphate salts of the $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4]^{2+}$ dication (III) have been isolated (Cl^- , IIIa; PF_6^- , IIIb); III constitutes a rare example of a multiply bonded dimetal unit complexed by four neutral bridging ligands. $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4]\text{Cl}_2$ can be converted to either I or II under certain conditions. When acetone is used as the solvent, then $\text{Re}_2\text{Cl}_6(\text{PR}_3)_2$ reacts with Ph_2Ppy to give $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_2(\text{PR}_3)$ (R = Et, IVa; R = *n*-Bu, IVb), whereas with acetonitrile as the solvent, Ph_2Ppy converts $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ to the dirhenium(III) complex $\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-Ph}_2\text{Ppy})_2\text{Cl}_4$; i.e., substitution occurs but without concomitant reduction. The complexes II, IIIb, and IVa have been structurally characterized by X-ray crystallography. Compound II crystallizes in space group $P2_1/n$ with $a = 12.160$ (6) Å, $b = 21.418$ (7) Å, $c = 18.464$ (2) Å, $\beta = 99.04$ (3)°, and $Z = 4$. Complex IIIb forms crystals in space group $P2_1/c$ with $a = 24.316$ (3) Å, $b = 12.101$ (2) Å, $c = 27.070$ (3) Å, $\beta = 105.670$ (9)°, and $Z = 4$. Two acetone molecules per dimer unit are also present in the lattice. Compound IVa crystallizes in space group $P\bar{1}$ with $a = 10.683$ (2) Å, $b = 20.033$ (5) Å, $c = 10.544$ (3) Å, $\alpha = 102.29$ (3)°, $\beta = 107.69$ (2)°, $\gamma = 94.19$ (2)°, and $Z = 2$.

Monodentate tertiary phosphines form a variety of well-defined complexes with the halides of Nb, Ta, Mo, W, and Re that contain dimetal units with metal-metal bonds of order two (Nb and Ta), three (Re), or four (Mo, W, and Re).² In the case of Nb and

Ta, these complexes are chlorine-bridged molecules of stoichiometry $\text{M}_2\text{X}_6(\text{PR}_3)_4$, whereas the Mo, W, or Re species are either $\text{Re}_2\text{X}_6(\text{PR}_3)_2$ or $\text{M}_2\text{X}_4(\text{PR}_3)_4$ (M = Mo, W, or Re) and possess eclipsed M_2L_8 -type rotational geometries.² However, with

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the bidentate ligands $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1$ or 2) some interesting and important structural variations exist. Complexes of dimolybdenum and dirhenium have been identified³⁻⁶ that contain bridging $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) ligands and, of necessity, an eclipsed (or essentially eclipsed) rotational conformation of the two metal units about the metal-metal bond; the complexes $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$,^{3,4} $\text{Re}_2\text{Cl}_5(\text{dppm})_2$,⁶ and $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ ⁵ are examples of this. On the other hand, the introduction of a second methylene unit between the two phosphorus atoms of the ligand, as in $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe) and its closely related phosphine-arsine analogue $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$ (arphos), has been shown to give complexes of stoichiometry $\text{M}_2\text{X}_4(\text{dppe})_2$ and $\text{M}_2\text{X}_4(\text{arphos})_2$ that either contain nonbridging, chelating dppe (or arphos) ligands and an eclipsed rotational conformation or contain ligands that bridge the two metal centers and confer a staggered rotational geometry upon the complex.^{3,5,7-13} This situation has now been recognized for cases where $\text{M} = \text{Mo}$, W , or Re and $\text{X} = \text{Cl}$, Br , or I .

More recently, we have turned our attention to unsymmetrical neutral bridging ligands that might yield, in certain circumstances, unsymmetrical multiply bonded dimetal complexes in which the metal centers would exhibit different reactivities. One of the ligands we chose for these investigations was 2-(diphenylphosphino)pyridine (abbreviated Ph_2Ppy), which Balch and co-workers¹⁴⁻¹⁹ have demonstrated can be very effective in stabilizing well-defined homo- and heterobinuclear transition-metal complexes, particularly those of the group 8 metals. The extension of these studies to include multiply bonded pairs of atoms of the early transition series is especially noteworthy as judged by the recent results we have obtained on dirhenium complexes of this ligand. In the course of these investigations, we have isolated several derivatives containing the triply bonded Re_2^{4+} core,^{2,5,12,20,21} including one that possesses the stoichiometry $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$. This complex contains a novel tridentate bridging mode for this ligand in which ortho metalation has occurred at one of the phenyl rings. This is the first example of an ortho-metalation reaction involving a multiply bonded dimetal unit contained within a M_2L_8 skeleton. The syntheses, structures, and spectroscopic and electrochemical properties of five well-defined complexes of dirhenium containing the Ph_2Ppy ligand are described in this report.²²

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Experimental Section

Starting Materials. The complexes $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$,²³ $\text{Re}_2\text{Cl}_6(\text{P-}n\text{-Bu}_3)_2$,²⁰ and $\text{Re}_2\text{Cl}_6(\text{PET}_3)_2$ ²⁰ were prepared according to known literature procedures. Solvents used in the preparation of complexes were, unless otherwise stated, of commercial grade and thoroughly deoxygenated prior to use. Dichloromethane used in the electrochemical experiments was of the highest purity available commercially and used without further purification.

Reaction Procedures. All reactions were carried out in a nitrogen atmosphere by using standard vacuum line techniques. In several instances, reactions under reflux were carried out with a white birch boiling stick ("Puritan Applicator") added to the contents of the reaction flask. The boiling stick not only served to prevent bumping of the reaction mixture but often served as a means of nucleating crystal growth in the case of sparingly soluble products. Hereafter, the term "boiling stick" will be used to refer to such an item.

Preparation of the Ligand Ph_2Ppy . The preparation of this compound has been described previously in the literature.^{16,24} However, we have chosen to use a convenient modification as described herein. Tetrahydrofuran (THF) (200 mL) was freshly distilled from Na/benzophenone and transferred to a round-bottom flask containing Li(s) (1.5 g) that had been cut into small strips. A quantity of PPh_2Cl (22.1 g, 18.0 mL) was added dropwise with vigorous stirring over a 30-min period. The deep red solution was stirred for 12 h and then cooled to -5°C . 2-Bromopyridine (16.0 g, 10.0 mL) was added dropwise over a 1-h period and upon complete addition the solution was allowed to warm to room temperature and then refluxed for 0.5 h. The THF was removed by vacuum distillation and the solid residue extracted with diethyl ether. The ether extract was evaporated to dryness and the white solid recrystallized from hot methanol; yield 22 g (84%). The compound was identified on the basis of the following properties: mp $81\text{--}83^\circ\text{C}$ (lit.^{16,24} mp $84\text{--}85^\circ\text{C}$); mass spectrum, $M^+ = 263$; ^1H NMR, δ -4.03 (singlet).

A. Preparation of Complexes. (i) $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_3\cdot 0.5\text{CH}_2\text{Cl}_2$. A mixture of $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ (0.20 g, 0.18 mmol), Ph_2Ppy (0.23 g, 0.88 mmol), and methanol (10 mL) was refluxed for 17 h with stirring. The dark red solid was filtered off, washed with methanol and diethyl ether, and dried under vacuum. The compound was then recrystallized by dissolving a sample in dichloromethane and allowing it to slowly diffuse into methanol; yield 0.16 g (68%). Anal. Calcd for $\text{C}_{51.5}\text{H}_{43}\text{Cl}_5\text{N}_3\text{P}_3\text{Re}_2$: C, 45.94; H, 3.22; N, 3.13; Cl, 13.16. Found: C, 45.90; H, 3.30; N, 2.98; Cl, 12.58. The presence of lattice CH_2Cl_2 was confirmed by ^1H NMR spectroscopy.

If the proportions of Ph_2Ppy and $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ were increased to 6:1 and the reaction mixture was refluxed for 18 h, the above complex was again isolated in good yield (66%). However, prolonged reflux (ca. 48 h) produced the ortho-metalated complex $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$ (see iv) in ca. 70% yield as monitored by cyclic voltammetry.

(ii) $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_2(\text{P-}n\text{-Bu}_3)$. An acetone solution (15 mL) of $\text{Re}_2\text{Cl}_6(\text{P-}n\text{-Bu}_3)_2$ (0.20 g, 0.20 mmol) and Ph_2Ppy (0.30 g, 1.13 mmol) was refluxed for 4 h in the presence of a boiling stick. The dark purple crystals were filtered off, washed with diethyl ether, and dried under vacuum; yield 0.19 g (76%). In some instances, if the reaction filtrate was allowed to stand undisturbed in air, more of the complex slowly crystallized. Anal. Calcd for $\text{C}_{46}\text{H}_{55}\text{Cl}_4\text{N}_2\text{P}_3\text{Re}_2$: C, 44.45; H, 4.46; Cl, 11.41. Found: C, 44.99; H, 4.75; Cl, 11.43.

(iii) $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_2(\text{PET}_3)$. This complex was prepared from $\text{Re}_2\text{Cl}_6(\text{PET}_3)_2$ in 52% yield by using a procedure similar to that described for its tri-*n*-butylphosphine analogue. Its spectroscopic and electrochemical properties were very similar to those of $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_2(\text{P-}n\text{-Bu}_3)$ and its structure was determined by X-ray crystallography.

(iv) $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$. A mixture of $\text{Re}_2\text{Cl}_6(\text{P-}n\text{-Bu}_3)_2$ (0.30 g, 0.30 mmol), Ph_2Ppy (0.50 g, 1.90 mmol), and methanol (25 mL) was refluxed for 10 h in the presence of a boiling stick. The dark red crystals were filtered off, washed with methanol, and dried under vacuum; yield 0.13 g (34%). Anal. Calcd for $\text{C}_{51}\text{H}_{41}\text{Cl}_3\text{N}_3\text{P}_3\text{Re}_2$: C, 48.32; H, 3.26; Cl, 8.39. Found: C, 47.78; H, 3.33; Cl, 8.64. If the ligand-to-metal stoichiometry was reduced from 6:1 to 3:1, only $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_2$ was isolated; this is in accord with the results obtained upon reacting $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ with Ph_2Ppy using different reagent stoichiometries (vide supra).

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(v) $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4](\text{PF}_6)_2$. If the filtrate from (iv) is evaporated to an oil and the residue stirred in 50 mL of a 50:50 mixture of acetone and diethyl ether, then a green solid can be isolated. This product, which is believed to be $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4]\text{Cl}_2$, was dissolved in 25 mL of acetone containing an excess of KPF_6 , and its green PF_6^- salt was precipitated by the addition of an excess of water. This product was filtered off, washed with water, and dried under vacuum. The complex was recrystallized from acetone by the slow addition of diethyl ether; yield 0.19 g (35%). Anal. Calcd for $\text{C}_{68}\text{H}_{56}\text{Cl}_2\text{F}_{12}\text{N}_4\text{P}_8\text{Re}_2$: C, 45.72; H, 3.15; N, 3.14; Cl, 3.97. Found: C, 45.59; H, 3.51; N, 3.81; Cl, 4.32. This complex could also be isolated after short reaction times (ca. 2 h) from (i) in yields up to 40% as monitored by cyclic voltammetry.

An alternative (higher yield) synthesis of $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4](\text{PF}_6)_2$ is as follows. A methanol solution (50 mL) containing $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ (0.50 g, 0.44 mmol) and Ph_2Ppy (0.80 g, 3.04 mmol) was stirred at room temperature for 12 h. The reaction mixture was filtered, evaporated to dryness, treated with a saturated acetone solution of KPF_6 , and worked up as described above; yield 0.70 g (90%). However, if the original reaction solution is refluxed, then significant quantities of the ortho-metallated product $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$ are generated. For example, after 17 h the yields of $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4](\text{PF}_6)_2$ and ortho-metallated product were 52% and 41%, respectively.

(vi) $[\text{ReCl}_3(\text{Ph}_2\text{Ppy})]_n$. A solution containing $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ (0.30 g, 0.26 mmol) and Ph_2Ppy (0.28 g, 1.06 mmol) in acetonitrile (25 mL) was refluxed for 22 h in the presence of a boiling stick. The dark brown crystals were filtered off, washed with acetonitrile and diethyl ether, and dried under vacuum; yield 0.045 g (15%). Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{Cl}_3\text{NPRe}$: C, 36.73; H, 2.53; N, 2.52; Cl, 19.13. Found: C, 36.81; H, 2.46; N, 2.85; Cl, 18.66. This complex was the only characterizable rhenium-containing species we were able to isolate from this reaction.

B. Reactions of Dirhenium(II) Complexes. (i) **Reactions of $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_3$ with Ph_2Ppy .** A mixture of $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_3$ (0.05 g, 0.04 mmol) and Ph_2Ppy (0.019 g, 0.04 mmol) was refluxed with stirring in methanol (10 mL) for 11 h. The insoluble red product was found by cyclic voltammetry and spectroscopy to be the pure ortho-metallated complex $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$; yield 0.045 g (92%). When this same reaction was carried out for 21 h, using 1:4 proportions of reactants, the insoluble red ortho-metallated product was obtained as before (82% yield), but workup of the filtrate by the procedure described in A(v) afforded a small quantity of green $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4](\text{PF}_6)_2$; yield 9%.

(ii) **Reactions of $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_3$ with Pyridines.** Reaction of $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_3$ with pyridine or 4-methylpyridine in methanol, as in B(i), for 2 h produced the ortho-metallated complex in 72% yield.

(iii) **Reaction of $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4]\text{Cl}_2$ in Methanol.** When a methanol solution (15 mL) of $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4]\text{Cl}_2$ (0.16 g, 0.01 mmol) was refluxed for 8 h, a small quantity (0.06 g) of red solid precipitated. This was shown by cyclic voltammetry to be an approximately equimolar mixture of $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_3$ and $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$. When the reflux time was increased to 48 h, a product consisting exclusively of $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$ crystallized in high yield; yield 0.10 g (90%).

(iv) **Reaction of $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_2(\text{PET}_3)$ with Ph_2Ppy .** A mixture of $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_2(\text{PET}_3)$ (0.105 g, 0.09 mmol) and Ph_2Ppy (0.05 g, 0.19 mmol) was refluxed in methanol with stirring for 24 h. The resulting red solid was filtered off and the filtrate worked up as described in A(v). Cyclic voltammetry showed that the red green solid was the ortho-metallated complex; yield 0.07 g (43%). The green solid isolated from the filtrate was identified as $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4](\text{PF}_6)_2$ by cyclic voltammetry and spectroscopy; yield 0.02 g (9%).

Preparation of Single Crystals for Structure Determination. Crystals suitable for X-ray crystallographic studies were grown directly from the appropriate reaction solutions in the case of $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$ and $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_2(\text{PET}_3)$. Crystals of $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4](\text{PF}_6)_2$ were obtained by dissolving a sample of this complex in acetone and carefully layering diethyl ether over it. During a period of approximately 1 day, diffusion occurred slowly enough to permit satisfactory crystal growth.

X-ray Crystallography. Data collection on single crystals of complexes II, IIb, and IVa was carried out at room temperature ($25 \pm 3^\circ\text{C}$) with automated four-circle diffractometers (Enraf-Nonius CAD-4 or Syntex PI) equipped with Mo $K\alpha$ radiation. The general procedures for geometric and intensity measurements have been fully described previously.²⁵ Pertinent crystallographic parameters for all three structures are summarized in Table I, and details of the data collection and structure

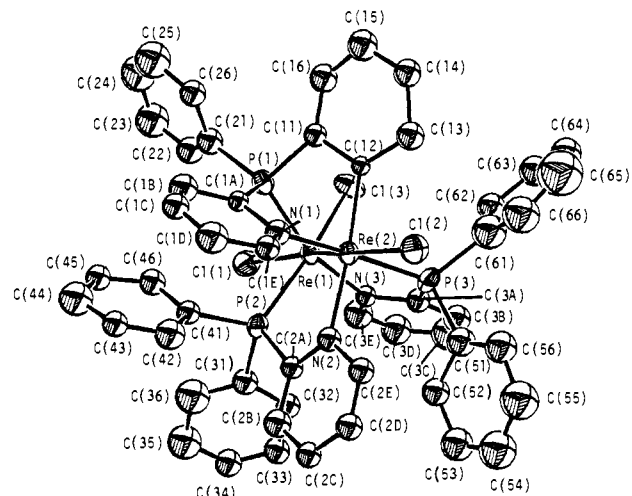


Figure 1. Complete molecular structure and atom-labeling scheme for $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$ (II).

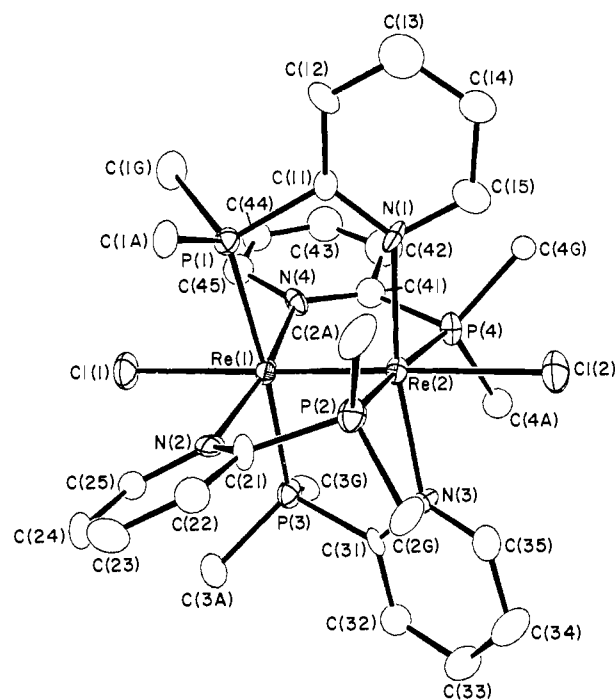


Figure 2. Structure of the cation $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4]^{2+}$ (IIb). For the sake of clarity, only the first carbon atom of each phenyl ring is illustrated.

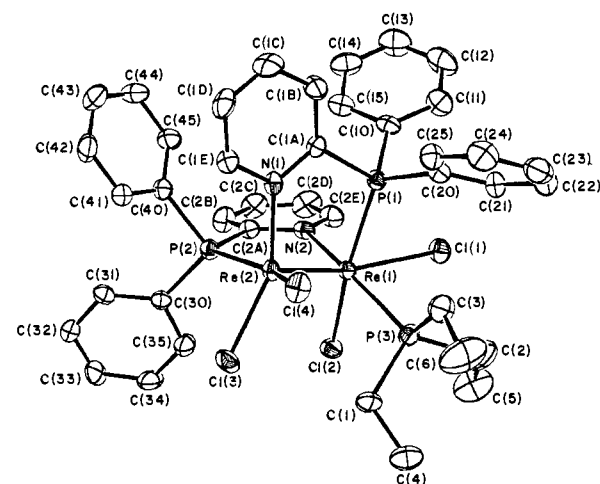


Figure 3. Complete molecular structure and atom-labeling scheme for the non-hydrogen atoms of $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_2(\text{PET}_3)$ (IVa).

(25) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. J. *Organomet. Chem.* **1973**, *50*, 227.

Table I. Crystal Data, Data Collection Parameters, and Least-Squares Residuals for $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$ (II), $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4](\text{PF}_6)_2 \cdot 2(\text{CH}_3)_2\text{CO}$ (IIIb), and $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_2(\text{PEt}_3)$ (IVa)

	II	IIIb	IVa
formula	$\text{Re}_2\text{Cl}_3\text{P}_3\text{N}_3\text{C}_{51}\text{H}_{41}$	$\text{Re}_2\text{Cl}_2\text{P}_6\text{F}_{12}\text{N}_4\text{C}_{68}\text{H}_{56} \cdot 2(\text{C}_3\text{H}_6\text{O})$	$\text{Re}_2\text{Cl}_4\text{P}_3\text{N}_2\text{C}_{40}\text{H}_{43}$
formula weight	1267.60	1902.52	1158.94
space group	$P2_1/n$	$P2_1/c$	$P1$
a , Å	12.160 (6)	24.316 (3)	10.683 (2)
b , Å	21.418 (7)	12.101 (2)	20.033 (5)
c , Å	18.464 (2)	27.070 (3)	10.544 (3)
α , deg	90	90	102.29 (3)
β , deg	99.04 (3)	105.670 (9)	107.69 (2)
γ , deg	90	90	94.19 (2)
V , Å ³	4749 (5)	7669 (4)	2078 (2)
Z	4	4	2
d_{calcd} , g/cm ³	1.773	1.648	1.852
crystal size, mm	0.02 × 0.12 × 0.13	0.05 × 0.14 × 0.30	0.05 × 0.18 × 0.25
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	54.7	36.14	63.06
data collection instrument	Syntex P1	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
radiation	Mo K α ($\lambda_\alpha = 0.71073$ Å)	Mo K α ($\lambda_\alpha = 0.71073$ Å); graphite monochromated	
scan method	$\omega - 2\theta$	$\omega - 2\theta$	ω
data collection range, 2θ , deg	$5^\circ \leq 2\theta \leq 50^\circ$	$5^\circ \leq 2\theta \leq 50^\circ$	$4^\circ \leq 2\theta \leq 50^\circ$
no. of unique data, $F_o^2 \geq 3\sigma(F_o^2)$	1956	4667	4736
no. of parameters refined	289	714	572
R^a	0.0502	0.0587	0.0311
R_w^b	0.0597	0.0668	0.0377
quality-of-fit indicator ^c	1.061	1.454	0.9830
largest shift/esd, final cycle	0.26	0.38	0.55

^a $R = \sum |F_o| - |F_c| / \sum |F_o|$. ^b $R_w = \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$; $w = 1/\sigma^2(|F_o|)$. ^c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obsd}} - N_{\text{parameters}})]^{1/2}$.

solutions and refinements are available as supplementary material. In each case, standard computational procedures²⁶ were followed and empirical absorption corrections²⁷ were applied.

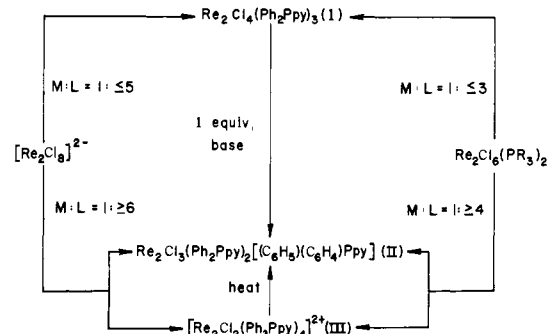
Tables II, III, and IV list the atomic coordinates, while Tables V, VI, and VII give important bond distances and angles for structures II, IIIb, and IVa, respectively. Complete tables of anisotropic thermal parameters, bond distances, bond angles, and structure factors are available as supplementary material. Figures 1, 2, and 3 illustrate the structures and atom-labeling schemes for the three complexes.

Physical Measurements. Infrared spectra were recorded as Nujol mulls with a Beckman IR-12 spectrophotometer (4000–400 cm⁻¹) and a Digilab FTS-20B spectrophotometer (500–50 cm⁻¹). Electronic absorption spectra between 800 and 1900 nm were recorded on a Cary 17D spectrophotometer and between 300 and 800 nm on a Hewlett-Packard 8450 spectrophotometer. Electrochemical experiments were performed with a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values [$(E_{p,a} + E_{p,c})/2$] were referenced against a saturated potassium chloride calomel electrode (SCE) at room temperature and were uncorrected for junction potentials. ³¹P{¹H} NMR spectra were recorded on 1:1 CDCl₃/CH₂Cl₂ solutions using a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock and aqueous 85% H₃PO₄ as an external standard. Positive chemical shifts were measured downfield from H₃PO₄. ¹H NMR spectra were also recorded on a Varian XL-200 spectrometer in CD₂Cl₂. Microanalyses were performed by Dr. C. S. Yeh and Dr. H. D. Lee of the Purdue University microanalytical laboratory and by Galbraith Laboratories, Inc., Knoxville, TN.

Results and Discussion

(a) Reaction Chemistry. The reactions of the quadruply bonded dirhenium(III) complexes $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ and $\text{Re}_2\text{Cl}_6(\text{PR}_3)_2$ ($R = \text{Et}$ or $n\text{-Bu}$) with 2-(diphenylphosphino)pyridine (Ph_2Ppy) are dominated by the reduction of the Re_2^{6+} core to give complexes derived from the triply bonded Re_2^{4+} core. The course of these reactions is markedly dependent upon the choice of solvent, the stoichiometry of the reactants, and the reaction time. This is shown in Scheme I, which summarizes most (but not all) of the

Scheme I. Reactions of $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ and $\text{Re}_2\text{Cl}_6(\text{PR}_3)_2$ ($R = \text{Et}$ or $n\text{-Bu}$) with Ph_2Ppy in Refluxing Methanol^a



^a The mole proportions of dirhenium starting complex (M) to Ph_2Ppy ligand (L) are denoted as $M:L$.

pertinent information that we have obtained for reactions carried out with methanol as the solvent. The reaction times can be found in the appropriate places in the Experimental Section, while the equivalents of Ph_2Ppy used in each reaction are so indicated in Scheme I.

In all instances, the reactions of $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ and $\text{Re}_2\text{Cl}_6(\text{PR}_3)_2$ with Ph_2Ppy lead to the formation of complexes that are derivatives of the Re_2^{4+} core. In this regard, they resemble those with the more basic monodentate tertiary phosphines PR_3 and PPhR_2 ($R = \text{alkyl}$ group) in which the triply bonded dirhenium(II) complexes $\text{Re}_2\text{Cl}_4(\text{PR}_3)_4$ and $\text{Re}_2\text{Cl}_4(\text{PPhR}_2)_4$ are formed.²⁰ However, the reactions are markedly dependent upon the reaction stoichiometry, especially with regard to the total number of equivalents of base, i.e., Ph_2Ppy , along with PR_3 in the case of $\text{Re}_2\text{Cl}_6(\text{PR}_3)_2$. If there is just sufficient base present to reduce the Re_2^{6+} core to Re_2^{4+} and complex the latter (see Scheme I), then $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_3$ (I) is the major product. When the equivalents of Ph_2Ppy used are increased, the ortho-metalated complex $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$ (II) is formed in good yield. It should be noted here that in the case of reactions where ortho metalation is favored, $\text{Re}_2\text{Cl}_6(\text{P-}n\text{-Bu}_3)_2$ was a superior starting material compared to $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$, since II was generated over shorter reaction times. This most likely reflects the fact that $\text{Re}_2\text{Cl}_6(\text{P-}n\text{-Bu}_3)_2$ is more easily reduced than $[\text{Re}_2\text{Cl}_8]^{2-}$, as evidenced by the relative ease of reducing elec-

(26) For structures II and IVa, calculations were done on the PDP-11/60 computer at B. A. Frenz and Associates, Inc., College Station, TX, with Enraf-Nonius SDP software. For structure IIIb, computing was done on a VAX-11/780 computer at the Department of Chemistry, Texas A & M University, using VAX-SDP software.

(27) North, A. C. T.; Phillips, D. C.; Matthews, F. S. *Acta Crystallogr., Sect. A* 1968, A24, 351.

Table II. Positional and Isotropic-Equivalent Thermal Parameters and Their Estimated Standard Deviations for Re₂Cl₃(Ph₂Ppy)₂[(C₆H₅)₂(C₆H₄)Ppy] (II)

atom	x	y	z	B, Å ²
Re(1)	0.2047 (1)	0.16493 (7)	0.34231 (7)	2.14 (2)
Re(2)	0.1751 (1)	0.19425 (7)	0.21894 (7)	2.23 (3)
Cl(1)	0.1893 (7)	0.1581 (5)	0.4798 (4)	3.8 (2)
Cl(2)	0.1828 (7)	0.2118 (4)	0.0823 (4)	3.7 (2)
Cl(3)	0.2609 (8)	0.0562 (4)	0.3552 (5)	3.9 (2)
P(1)	0.0234 (7)	0.1247 (5)	0.2983 (4)	3.0 (2)
P(2)	0.1539 (7)	0.2690 (4)	0.3627 (4)	2.5 (2)
P(3)	0.3682 (7)	0.1799 (4)	0.2248 (5)	2.9 (2)
N(1)	-0.001 (2)	0.216 (1)	0.197 (1)	2.9 (6) ^a
N(2)	0.194 (2)	0.297 (1)	0.229 (1)	2.6 (5) ^a
N(3)	0.376 (2)	0.175 (1)	0.369 (1)	2.3 (5) ^a
C(1A)	-0.062 (2)	0.183 (1)	0.242 (1)	1.9 (6) ^a
C(1B)	-0.175 (3)	0.195 (2)	0.244 (2)	3.7 (7) ^a
C(1C)	-0.219 (3)	0.240 (2)	0.193 (2)	3.0 (7) ^a
C(1D)	-0.165 (3)	0.273 (2)	0.150 (2)	4.3 (9) ^a
C(1E)	-0.052 (2)	0.257 (1)	0.151 (2)	2.6 (7) ^a
C(2A)	0.190 (2)	0.323 (1)	0.293 (1)	2.3 (7) ^a
C(2B)	0.202 (3)	0.389 (2)	0.304 (2)	3.6 (8) ^a
C(2C)	0.234 (2)	0.426 (1)	0.249 (2)	2.7 (7) ^a
C(2D)	0.239 (3)	0.399 (1)	0.182 (2)	3.0 (7) ^a
C(2E)	0.226 (2)	0.336 (2)	0.174 (2)	3.0 (7) ^a
C(3A)	0.446 (2)	0.172 (1)	0.316 (2)	2.8 (7) ^a
C(3B)	0.560 (3)	0.166 (2)	0.332 (2)	3.7 (7) ^a
C(3C)	0.620 (3)	0.161 (2)	0.403 (2)	6 (1) ^a
C(3D)	0.551 (3)	0.164 (2)	0.458 (2)	5.1 (9) ^a
C(3E)	0.437 (3)	0.173 (2)	0.441 (2)	4.6 (9) ^a
C(11)	0.042 (2)	0.073 (1)	0.225 (2)	2.4 (7) ^a
C(12)	0.118 (2)	0.102 (1)	0.183 (1)	1.7 (6) ^a
C(13)	0.147 (3)	0.069 (2)	0.120 (2)	3.5 (8) ^a
C(14)	0.090 (3)	0.008 (2)	0.102 (2)	3.4 (8) ^a
C(15)	0.019 (3)	0.017 (2)	0.144 (2)	4.2 (8) ^a
C(16)	0.008 (3)	0.013 (2)	0.203 (2)	3.6 (8) ^a
C(21)	-0.070 (3)	0.083 (2)	0.352 (2)	3.4 (8) ^a
C(22)	-0.049 (3)	0.074 (2)	0.424 (2)	3.7 (8) ^a
C(23)	-0.117 (3)	0.043 (2)	0.465 (2)	6 (1) ^a
C(24)	-0.206 (3)	0.013 (2)	0.424 (2)	6 (1) ^a
C(25)	-0.239 (3)	0.023 (2)	0.348 (2)	6 (1) ^a
C(26)	-0.166 (3)	0.056 (2)	0.310 (2)	3.2 (7) ^a
C(31)	0.232 (2)	0.312 (2)	0.445 (2)	3.3 (7) ^a
C(32)	0.345 (2)	0.316 (1)	0.451 (2)	3.1 (7) ^a
C(33)	0.400 (3)	0.355 (2)	0.510 (2)	3.6 (8) ^a
C(34)	0.343 (3)	0.378 (2)	0.558 (2)	3.8 (8) ^a
C(35)	0.231 (3)	0.377 (2)	0.554 (2)	6 (1) ^a
C(36)	0.173 (3)	0.338 (2)	0.497 (2)	6 (1) ^a
C(41)	0.009 (2)	0.286 (1)	0.371 (2)	2.6 (7) ^a
C(42)	-0.048 (3)	0.334 (2)	0.328 (2)	4.2 (8) ^a
C(43)	-0.159 (2)	0.347 (2)	0.333 (2)	3.0 (7) ^a
C(44)	-0.211 (3)	0.320 (2)	0.387 (2)	5 (1) ^a
C(45)	-0.152 (3)	0.271 (2)	0.427 (2)	3.0 (7) ^a
C(46)	-0.046 (3)	0.252 (2)	0.418 (2)	3.3 (7) ^a
C(51)	0.445 (3)	0.245 (2)	0.198 (2)	3.9 (8) ^a
C(52)	0.471 (3)	0.295 (2)	0.251 (2)	3.5 (8) ^a
C(53)	0.528 (3)	0.349 (2)	0.234 (2)	4.9 (9) ^a
C(54)	0.541 (3)	0.362 (2)	0.160 (2)	6 (1) ^a
C(55)	0.508 (3)	0.315 (2)	0.108 (2)	7 (1) ^a
C(56)	0.461 (3)	0.258 (2)	0.127 (2)	4.7 (9) ^a
C(61)	0.425 (3)	0.111 (2)	0.176 (2)	6 (1) ^a
C(62)	0.462 (3)	0.059 (2)	0.222 (2)	3.8 (8) ^a
C(63)	0.505 (3)	0.006 (2)	0.188 (2)	4.7 (9) ^a
C(64)	0.489 (3)	0.002 (2)	0.114 (2)	4.7 (9) ^a
C(65)	0.439 (4)	0.051 (2)	0.070 (3)	10 (2) ^a
C(66)	0.409 (3)	0.107 (2)	0.102 (2)	7 (1) ^a

^a Atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic-equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

trochemically the former species.^{28,29}

Complicating this picture is the observation that the dicationic species $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4]^{2+}$ (III), isolable as both its chloride

(IIIa) and PF_6^- (IIIb) salts, is also formed in significant quantities. This complication is best considered in the case of the reactions between $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ and Ph_2Ppy . With 1:5, 1:6, or 1:7 mole ratios of reagents, III is generated early on in these reactions. In the case of the 1:5 stoichiometric ratio, the yield of III then diminishes with increase in reaction time as the concentration of I builds up. For the 1:6 stoichiometry, this same situation holds with the exception that I is in turn converted to the ortho-metalated product II upon further reaction. With a further increase in the proportion of Ph_2Ppy (i.e., 1:7 mole proportions), the complex I does not precipitate, and it may be that under these conditions (i.e., an excess of ligand) III can be converted directly to II as the reaction proceeds. For both the 1:6 and 1:7 stoichiometries, appreciable amounts of III remain even after long reaction times (see Experimental Section). Thus, both I and III can be regarded as "intermediates" in the formation of II since both can be so converted under a variety of conditions. This has been independently verified through the observation that when I is reacted with 1 equiv of base (Ph_2Ppy , pyridine, or 4-methylpyridine) it is converted to II in high yield following the elimination of HCl. This confirms that I is a precursor to II. Under no circumstances have we been able to reverse this reaction (i.e., convert II to I) through the reaction of II with hydrogen chloride. Of further note is the thermal conversion of IIIa, i.e., $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4]\text{Cl}_2$, to II in refluxing methanol. Such a reaction for approximately 8 h gives an equimolar mixture of I and II, while after 48 h the product is exclusively the ortho-metalated product II.

The preceding reactions that we have discussed were, in all instances, carried out in methanol. Use of other solvent systems changes the reaction course. Thus, when acetone is the solvent, $\text{Re}_2\text{Cl}_6(\text{PR}_3)_2$ ($\text{R} = \text{Et}$ or $n\text{-Bu}$) reacts with Ph_2Ppy to form the dirhenium(II) complexes $\text{Re}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_2(\text{PR}_3)_4$ (IVa ($\text{R} = \text{Et}$) and IVb ($\text{R} = n\text{-Bu}$)). These complexes are formed irrespective of the reaction stoichiometries. However, when IVb is reacted with 1 or 2 equiv of Ph_2Ppy in refluxing methanol, then it is converted to II.

The identities of complexes II, IIIb, and IVa have been established by X-ray crystallographic studies (vide infra). Although we isolated I in a crystalline state, the crystals were of an insufficient quality to permit a structure solution by this means. However, we suspect it has a structure closely related to those of II and IVa. While the spectroscopic and electrochemical properties of all the complexes will be discussed in a later section (following presentation of the crystallographic structural details), one spectroscopic feature of I is noted here, namely, the appearance of a downfield shifted resonance at $\delta +9.98$ (doublet, 1 H) in its ¹H NMR spectrum (in CD_2Cl_2).³⁰ This spectral feature, which is absent in the spectrum of II, could be attributable to the "acidic" phenyl proton that is lost in the ortho-metalation reaction. In other words, the ortho hydrogen on a phenyl ring could be brought into close enough proximity to one of the rhenium atoms in I to cause a significant $\text{Re}\cdots\text{H}$ interaction, along the lines found previously in other systems.³¹ Alternatively, this downfield shift may result from the diamagnetic anisotropy associated with the $\text{Re}\cdots\text{Re}$ triple bond.³²

A quite different reaction product was obtained when $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ was reacted with Ph_2Ppy in acetonitrile. In this case, a diamagnetic rhenium(III) complex $[\text{ReCl}_3(\text{Ph}_2\text{Ppy})]_n$ was isolated in low yield. We have spectroscopic and electrochemical evidence that this species is $\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-Ph}_2\text{Ppy})_2\text{Cl}_4$ and therefore bears a close structural relationship to $\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Cl}_4$.¹⁴ The latter compound has now been structurally characterized,³³ so that all further discussion of $\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-Ph}_2\text{Ppy})_2\text{Cl}_4$ is best deferred until our studies on its

(30) The ¹H NMR spectra of these complexes are otherwise quite straightforward and, accordingly, further details will not be presented in this paper.

(31) Matsumoto, M.; Yoshioka, H.; Nakatsu, K.; Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1974**, *96*, 3323.

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(28) Reference 2, pp 62-64.

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Table III. Positional and Isotropic-Equivalent Thermal Parameters and Their Estimated Standard Deviations for $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4](\text{PF}_6)_2 \cdot 2(\text{CH}_3)_2\text{CO}$ (111b)

atom	x	y	z	B, Å	atom	x	y	z	B, Å
Re(1)	0.20726 (4)	0.03651 (8)	0.22170 (3)	2.23 (2)	C(4D)	0.134 (1)	-0.509 (2)	0.250 (1)	6.5 (7)
Re(2)	0.27233 (4)	-0.10174 (8)	0.22233 (4)	2.27 (2)	C(4E)	0.095 (1)	-0.456 (3)	0.211 (1)	7.8 (9) ^a
Cl(1)	0.1361 (3)	0.1949 (5)	0.2203 (2)	4.2 (2)	C(4F)	0.114 (1)	-0.364 (2)	0.187 (1)	6.9 (9)
Cl(2)	0.3440 (3)	-0.2649 (5)	0.2237 (3)	4.4 (2)	C(4G)	0.2173 (8)	-0.294 (2)	0.1161 (7)	2.3 (4) ^a
P(1)	0.2407 (3)	0.1451 (5)	0.1597 (2)	2.8 (1)	C(4H)	0.243 (1)	-0.394 (2)	0.1253 (8)	4.0 (6)
P(2)	0.3521 (3)	0.0047 (5)	0.2737 (2)	3.0 (2)	C(4I)	0.262 (1)	-0.448 (2)	0.086 (1)	5.0 (7)
P(3)	0.1678 (2)	-0.0566 (5)	0.2839 (2)	2.8 (1)	C(4J)	0.252 (1)	-0.406 (3)	0.038 (1)	6.3 (8)
P(4)	0.1997 (3)	-0.2229 (5)	0.1701 (2)	3.1 (2)	C(4K)	0.224 (1)	-0.297 (3)	0.030 (1)	6.2 (9)
N(1)	0.2908 (7)	-0.048 (1)	0.1515 (6)	3.0 (4)	C(4L)	0.206 (1)	-0.239 (2)	0.0684 (9)	5.2 (7)
N(2)	0.2637 (7)	0.127 (1)	0.2856 (6)	2.7 (4)	C(11)	0.2740 (8)	0.047 (2)	0.1250 (8)	2.8 (5)
N(3)	0.2663 (7)	-0.180 (1)	0.2952 (6)	2.8 (4)	C(12)	0.2833 (9)	0.078 (2)	0.0793 (8)	4.2 (6)
N(4)	0.1395 (6)	-0.030 (1)	0.1568 (6)	2.5 (4)	C(13)	0.314 (1)	0.005 (2)	0.057 (1)	5.4 (8)
C(1A)	0.2928 (9)	0.255 (2)	0.1821 (8)	3.1 (6)	C(14)	0.333 (1)	-0.097 (2)	0.0813 (9)	5.3 (7)
C(1B)	0.284 (1)	0.329 (2)	0.2184 (9)	3.8 (6)	C(15)	0.321 (1)	-0.122 (2)	0.1280 (9)	4.7 (7)
C(1C)	0.3219 (9)	0.414 (2)	0.235 (1)	4.2 (7)	C(21)	0.3207 (9)	0.115 (2)	0.2986 (8)	3.1 (5)
C(1D)	0.368 (1)	0.433 (2)	0.215 (1)	5.9 (8)	C(22)	0.357 (1)	0.191 (2)	0.3354 (9)	3.9 (6) ^a
C(1E)	0.376 (1)	0.361 (2)	0.176 (1)	5.2 (8)	C(23)	0.331 (1)	0.272 (2)	0.3602 (8)	4.3 (7)
C(1F)	0.339 (1)	0.268 (2)	0.1595 (9)	4.2 (6) ^a	C(24)	0.275 (1)	0.281 (2)	0.3498 (9)	3.8 (6)
C(1G)	0.1859 (9)	0.211 (2)	0.1079 (9)	3.7 (6)	C(25)	0.2398 (8)	0.207 (2)	0.3118 (8)	2.7 (5) ^a
C(1H)	0.1584 (9)	0.147 (2)	0.0658 (8)	3.7 (5) ^a	C(31)	0.2186 (9)	-0.159 (2)	0.3142 (7)	2.6 (5)
C(1I)	0.117 (1)	0.194 (2)	0.027 (1)	8.1 (9)	C(32)	0.2114 (9)	-0.216 (2)	0.3579 (8)	3.6 (5) ^a
C(1J)	0.098 (1)	0.296 (3)	0.0324 (9)	7.4 (9)	C(33)	0.253 (1)	-0.293 (2)	0.3837 (9)	4.5 (7)
C(1K)	0.123 (1)	0.367 (2)	0.076 (1)	7.7 (9)	C(34)	0.302 (1)	-0.310 (2)	0.3660 (9)	4.5 (7)
C(1L)	0.171 (1)	0.321 (2)	0.115 (1)	5.1 (7)	C(35)	0.308 (1)	-0.246 (2)	0.3210 (9)	3.8 (6)
C(2A)	0.4076 (8)	0.056 (2)	0.2459 (9)	4.0 (6)	C(41)	0.1408 (9)	-0.136 (2)	0.1414 (8)	3.5 (5) ^a
C(2B)	0.425 (1)	-0.023 (3)	0.216 (1)	6.3 (8)	C(42)	0.097 (1)	-0.173 (2)	0.097 (1)	6.0 (7) ^a
C(2C)	0.475 (1)	0.003 (3)	0.196 (1)	7.5 (9)	C(43)	0.048 (1)	-0.108 (2)	0.074 (1)	5.5 (7) ^a
C(2D)	0.501 (1)	0.111 (2)	0.2102 (9)	5.1 (6) ^a	C(44)	0.0511 (9)	-0.004 (2)	0.0938 (8)	3.7 (6) ^a
C(2E)	0.483 (1)	0.177 (2)	0.239 (1)	5.3 (8)	C(45)	0.0943 (9)	0.038 (2)	0.1312 (8)	3.8 (5) ^a
C(2F)	0.436 (1)	0.156 (2)	0.257 (1)	4.9 (7)	P(5)	0.3668 (3)	0.3099 (7)	0.0100 (3)	5.3 (2) ^a
C(2G)	0.3936 (8)	-0.062 (2)	0.3327 (8)	2.9 (6)	P(6)	0.1246 (4)	0.5451 (9)	0.4229 (4)	7.5 (2) ^a
C(2H)	0.441 (1)	-0.122 (2)	0.333 (1)	4.6 (7)	F(1)	0.3399 (8)	0.386 (2)	-0.0358 (7)	10.0 (6) ^a
C(2I)	0.471 (1)	-0.175 (3)	0.378 (1)	7 (1)	F(2)	0.3914 (8)	0.234 (2)	0.0576 (7)	9.5 (5) ^a
C(2J)	0.451 (1)	-0.169 (2)	0.423 (1)	5.7 (8)	F(3)	0.3136 (9)	0.329 (2)	0.0321 (8)	11.4 (6) ^a
C(2K)	0.407 (1)	-0.101 (2)	0.424 (1)	5.4 (7) ^a	F(4)	0.4129 (9)	0.281 (2)	-0.0149 (8)	12.5 (7) ^a
C(2L)	0.375 (1)	-0.051 (2)	0.3777 (8)	4.5 (7)	F(5)	0.3282 (8)	0.213 (2)	-0.0196 (7)	10.5 (6) ^a
C(3A)	0.1609 (8)	0.026 (2)	0.3387 (8)	3.0 (5)	F(6)	0.399 (1)	0.403 (2)	0.039 (1)	15.2 (8) ^a
C(3B)	0.2080 (9)	0.036 (2)	0.3833 (8)	3.8 (5) ^a	F(7)	0.069 (1)	0.586 (2)	0.3812 (9)	13.4 (7) ^a
C(3C)	0.204 (1)	0.109 (2)	0.4212 (9)	5.8 (8)	F(8)	0.0965 (9)	0.426 (2)	0.4179 (8)	12.0 (7) ^a
C(3D)	0.152 (1)	0.167 (2)	0.4186 (9)	7.2 (9)	F(9)	0.0942 (9)	0.575 (2)	0.4650 (8)	11.8 (7) ^a
C(3E)	0.106 (1)	0.153 (2)	0.375 (1)	6.5 (9)	F(10)	0.146 (1)	0.675 (2)	0.4253 (8)	12.8 (7) ^a
C(3F)	0.107 (1)	0.078 (2)	0.3341 (9)	4.9 (6) ^a	F(11)	0.175 (1)	0.517 (2)	0.464 (1)	15.9 (9) ^a
C(3G)	0.0983 (8)	-0.124 (2)	0.2634 (7)	3.0 (6)	F(12)	0.152 (1)	0.520 (2)	0.380 (1)	16.1 (9) ^a
C(3H)	0.0560 (9)	-0.061 (2)	0.2283 (8)	3.3 (5) ^a	O(1)	0.483 (2)	0.754 (3)	0.126 (1)	14 (1) ^a
C(3I)	-0.000 (1)	-0.107 (2)	0.2150 (8)	4.5 (7)	O(2)	-0.003 (1)	0.517 (2)	0.072 (1)	6.2 (6) ^a
C(3J)	-0.013 (1)	-0.206 (2)	0.2349 (9)	4.8 (7)	C(1)	0.459 (2)	0.677 (4)	0.104 (1)	5.2 (9) ^a
C(3K)	0.030 (1)	-0.265 (2)	0.2688 (9)	4.8 (7)	C(2)	0.429 (2)	0.619 (3)	0.128 (1)	4.8 (9) ^a
C(3L)	0.086 (1)	-0.224 (2)	0.2842 (9)	3.9 (6) ^a	C(3)	0.487 (2)	0.628 (4)	0.069 (2)	8 (1) ^a
C(4A)	0.171 (1)	-0.339 (2)	0.2018 (8)	3.6 (5) ^a	C(4)	-0.026 (2)	0.437 (3)	0.073 (1)	3.8 (9) ^a
C(4B)	0.212 (1)	-0.394 (2)	0.2399 (9)	4.7 (7)	C(5)	-0.076 (2)	0.396 (5)	0.030 (2)	12 (1) ^a
C(4C)	0.189 (1)	-0.483 (2)	0.263 (1)	5.9 (7)	C(6)	-0.014 (2)	0.360 (4)	0.114 (2)	8 (1) ^a

^a Atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic-equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

$\text{Ph}_2\text{PCH}_2\text{PPh}_2$ analogue are complete.³⁴

(b) **Crystal Structures.** $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$ (II). This molecule (see Figure 1) possesses C_1 symmetry. The two rhenium atoms, while being bound to different ligand atom types, both possess pseudooctahedral coordination symmetry. Two of the chlorine atoms, Cl(1) and Cl(2), are axially bound, one on each metal atom, to the Re_2^{4+} unit, while the third such ligand, Cl(3), occupies an equatorial position on Re(1). The two Ph_2Ppy ligands, containing P(2), N(2) and P(3), N(3), bridge the Re-Re

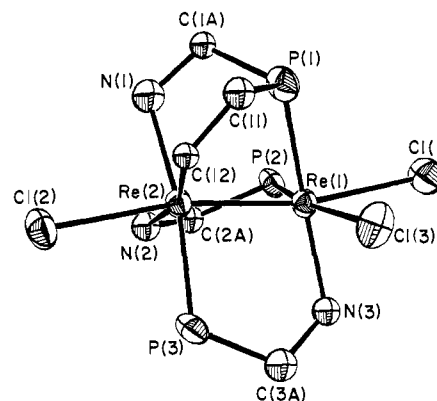


Figure 4. View of the central portion of $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$ (II), emphasizing the novel tridentate bonding mode of the ortho-metalated ligand.

(34) One other study of relevance to the present work is that in which we have attempted to prepare multiply bonded dimolybdenum complexes containing the Ph_2Ppy ligand. The reactions between this ligand and $\text{K}_4\text{Mo}_2\text{Cl}_8$, $(\text{NH}_4)_2\text{Mo}_2\text{Cl}_6$, $\text{Mo}_2\text{Cl}_4(\text{py})_4$, and $\text{Mo}_2\text{Cl}_4(\text{P-}n\text{-Bu}_3)_4$ in methanol, ethanol, or acetone lead, in all instances, to the precipitation of the blue-green complex $\text{Mo}_2\text{Cl}_4(\text{Ph}_2\text{Ppy})_2$ in very high yield ($\sim 95\%$). Its spectroscopic and electrochemical properties are in accord with its being, like $\text{Mo}_2\text{Cl}_4(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2$, a conventional derivative of Mo_2^{4+} with bridging Ph_2Ppy ligands and an eclipsed rotational conformation.^{3,4}

Table IV. Positional and Isotropic-Equivalent Thermal Parameters and Their Estimated Standard Deviations for Re₂Cl₄(Ph₂Ppy)₂(PEt₃)₂ (IVa)

atom	x	y	z	B, Å ²	atom	x	y	z	B, Å ²
Re(1)	0.32058 (3)	0.25307 (2)	-0.02006 (3)	2.873 (7)	C(31)	0.0755 (8)	-0.0404 (4)	-0.2208 (9)	4.1 (2)
Re(2)	0.16666 (3)	0.19188 (2)	0.03568 (3)	2.906 (7)	C(32)	0.1153 (9)	-0.1058 (5)	-0.232 (1)	5.2 (3)
Cl(1)	0.4629 (2)	0.3467 (1)	-0.0783 (2)	4.83 (5)	C(33)	0.246 (1)	-0.1074 (5)	-0.192 (1)	5.7 (3)
Cl(2)	0.4935 (2)	0.1819 (1)	-0.0099 (2)	4.20 (5)	C(34)	0.338 (1)	-0.0505 (5)	-0.148 (1)	6.2 (3)
Cl(3)	0.2577 (3)	0.1096 (1)	0.1523 (2)	5.12 (6)	C(35)	0.3004 (9)	0.0141 (5)	-0.139 (1)	5.3 (3)
Cl(4)	0.1393 (2)	0.2469 (1)	0.2477 (2)	5.34 (6)	C(40)	-0.0635 (8)	0.0871 (4)	-0.2584 (8)	3.8 (2)
P(1)	0.1726 (2)	0.3334 (1)	-0.0696 (2)	3.24 (5)	C(41)	-0.1419 (8)	0.0592 (5)	-0.1942 (9)	4.6 (2)
P(2)	0.1162 (2)	0.1056 (1)	-0.1691 (2)	3.27 (5)	C(42)	-0.279 (1)	0.0501 (5)	-0.252 (1)	6.4 (3)
P(3)	0.4537 (2)	0.3108 (1)	0.2214 (2)	4.36 (6)	C(43)	-0.336 (1)	0.0688 (6)	-0.370 (1)	7.7 (4)
N(1)	0.0022 (6)	0.2388 (3)	-0.0394 (6)	3.3 (1)	C(44)	-0.260 (1)	0.0957 (6)	-0.435 (1)	7.1 (3)
N(2)	0.2615 (6)	0.1976 (3)	-0.2386 (6)	3.3 (1)	C(45)	-0.1219 (9)	0.1053 (5)	-0.3798 (9)	5.1 (3)
C(1)	0.4963 (9)	0.2462 (5)	0.3239 (9)	5.0 (2)	H(1B)	-0.101 (6)	0.364 (3)	-0.176 (6)	3 (1) ^a
C(2)	0.612 (1)	0.3695 (8)	0.250 (1)	8.4 (4)	H(1C)	-0.293 (6)	0.312 (4)	-0.165 (7)	4 (2) ^a
C(3)	0.379 (1)	0.3759 (5)	0.322 (1)	5.8 (3)	H(1D)	-0.320 (6)	0.213 (3)	-0.102 (6)	2 (1) ^a
C(4)	0.616 (1)	0.2693 (7)	0.461 (1)	8.8 (4)	H(1E)	-0.097 (6)	0.184 (3)	0.015 (6)	3 (1) ^a
C(5)	0.711 (1)	0.3344 (9)	0.206 (1)	10.6 (5)	H(2B)	0.124 (7)	0.054 (4)	-0.440 (7)	5 (2) ^a
C(6)	0.433 (2)	0.392 (1)	0.478 (1)	12.4 (6)	H(2C)	0.219 (8)	0.076 (4)	-0.598 (8)	6 (2) ^a
C(1A)	0.0051 (7)	0.2951 (4)	-0.0888 (7)	3.4 (2)	H(2D)	0.344 (9)	0.203 (5)	-0.504 (9)	8 (3) ^a
C(1B)	-0.1079 (8)	0.3238 (5)	-0.140 (1)	5.0 (2)	H(2E)	0.365 (8)	0.279 (4)	-0.271 (8)	6 (2) ^a
C(1C)	-0.2273 (8)	0.2935 (6)	-0.142 (1)	5.8 (3)	H(11)	0.218 (8)	0.449 (4)	-0.178 (8)	6 (2) ^a
C(1D)	-0.2322 (8)	0.2380 (5)	-0.091 (1)	5.6 (3)	H(12)	0.172 (9)	0.467 (5)	-0.40 (1)	8 (3) ^a
C(1E)	-0.1183 (8)	0.2117 (4)	-0.0410 (8)	4.0 (2)	H(13)	0.021 (8)	0.370 (4)	-0.601 (8)	7 (2) ^a
C(2A)	0.1888 (7)	0.1346 (4)	-0.2867 (7)	3.4 (2)	H(14)	-0.013 (8)	0.273 (5)	-0.556 (9)	7 (3) ^a
C(2B)	0.1795 (9)	0.0910 (5)	-0.4117 (9)	5.2 (3)	H(15)	0.043 (6)	0.257 (3)	-0.344 (6)	3 (1) ^a
C(2C)	0.237 (1)	0.1148 (6)	-0.4982 (9)	5.7 (3)	H(21)	0.362 (6)	0.456 (3)	0.031 (6)	2 (1) ^a
C(2D)	0.304 (1)	0.1791 (6)	-0.4533 (9)	6.5 (3)	H(22)	0.393 (8)	0.559 (5)	0.182 (9)	7 (3) ^a
C(2E)	0.3177 (9)	0.2196 (5)	-0.3255 (9)	4.9 (2)	H(23)	0.253 (8)	0.585 (4)	0.321 (8)	6 (2) ^a
C(10)	0.1386 (7)	0.3551 (4)	-0.2374 (8)	3.9 (2)	H(24)	0.065 (6)	0.492 (3)	0.259 (6)	2 (1) ^a
C(11)	0.177 (1)	0.4178 (5)	-0.2550 (9)	5.8 (3)	H(25)	0.032 (5)	0.397 (3)	0.109 (5)	1 (1) ^a
C(12)	0.144 (1)	0.4282 (6)	-0.388 (1)	7.5 (3)	H(31)	-0.013 (6)	-0.039 (3)	-0.251 (7)	3 (2) ^a
C(13)	0.070 (1)	0.3765 (7)	-0.500 (1)	7.4 (3)	H(32)	0.035 (7)	-0.132 (4)	-0.281 (7)	5 (2) ^a
C(14)	0.031 (1)	0.3151 (6)	-0.483 (1)	6.4 (3)	H(33)	0.249 (8)	-0.138 (4)	-0.213 (8)	4 (2) ^a
C(15)	0.0644 (9)	0.3034 (5)	-0.3510 (9)	5.1 (2)	H(34)	0.412 (5)	-0.053 (3)	-0.115 (6)	2 (1) ^a
C(20)	0.1933 (8)	0.4174 (4)	0.0527 (8)	4.1 (2)	H(35)	0.378 (9)	0.055 (5)	-0.091 (9)	8 (3) ^a
C(21)	0.3008 (9)	0.4671 (5)	0.079 (1)	5.0 (3)	H(41)	-0.105 (7)	0.047 (4)	-0.113 (7)	4 (2) ^a
C(22)	0.322 (1)	0.5289 (5)	0.176 (1)	6.6 (3)	H(42)	-0.328 (5)	0.031 (3)	-0.213 (6)	2 (1) ^a
C(23)	0.238 (1)	0.5382 (6)	0.252 (1)	6.7 (3)	H(43)	-0.434 (8)	0.056 (5)	-0.407 (9)	7 (3) ^a
C(24)	0.132 (1)	0.4919 (6)	0.226 (1)	6.7 (3)	H(44)	-0.31 (1)	0.105 (6)	-0.50 (1)	10 (3) ^a
C(25)	0.1075 (9)	0.4309 (5)	0.1267 (9)	4.7 (2)	H(45)	-0.06 (1)	0.105 (8)	-0.45 (1)	17 (5) ^a
C(30)	0.1642 (8)	0.0190 (4)	-0.1770 (8)	3.7 (2)					

^a Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic-equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

bond and are oppositely directed, but cis to each other. The (C₆H₅)(C₆H₄)Ppy moiety serves as a tridentate ligand, doubly bridging the two metal atoms. This novel bonding mode is accomplished through ortho metalation by one of the phenyl groups, giving an Re(2)-C(12) bond, in addition to normal coordination by the phosphorus P(1) and nitrogen N(1) atoms. The resulting central position of the molecule (see Figure 4) contains four five-membered rings, all of which take on an envelope-type conformation and encompass the Re-Re bond.

Since the Re-Re bond is a triple bond, there is no barrier to rotation, and such a twist away from an eclipsed conformation does take place. The smallest torsional angles about the dimetal axis are P(1)-Re(1)-Re(2)-N(1) = 36.2°, P(2)-Re(1)-Re(2)-N(2) = 22.0°, N(3)-Re(1)-Re(2)-P(3) = 16.2°, and Cl(3)-Re(1)-Re(2)-C(12) = 32.2°, for an average torsional twist of 26.6°. Such a rotation appears to be necessary in order to prevent excessive strain in the three-point attachment of the ortho-metalated ligand.

Also, in order for ortho metalation to occur in this manner, the molecule adopts a rather skewed configuration. If the central portion of the structure is thought of as two distorted tetragonal pyramids (comprised of the four equatorial and one axial ligand atoms about each rhenium atom) joined together by the metal-metal bond, then clearly (see Figure 4) the basal planes of these two pyramids do not directly face each other. The dihedral angle between these two basal planes (the least-squares planes calculated for the four equatorial atoms of each Re atom) is 8.5°. The two axial Cl atoms (occupying the apical positions of the tetragonal pyramids) deviate by 13-18° from collinearity with the Re-Re bond. This skewed geometry introduces another interesting

structural feature, namely, the presence of three acute angles between the two Re atoms and the coordination sphere. These are Re(2)-Re(1)-P(1) = 76.8 (2)°, Re(2)-Re(1)-P(2) = 84.1 (2)°, and Re(1)-Re(2)-P(3) = 85.4 (2)°.

To our knowledge, structures II and IIIb (vide infra) are the first structurally characterized examples of triply bonded Re₂⁴⁺ dimers in which both Re atoms are coordinated to axial ligands. The rhenium-to-axial chloride bond distances in II, 2.578 (9) and 2.568 (9) Å, are notably longer than the rhenium-to-equatorial chloride bond distance (2.429 (9) Å) in this molecule, indicating weaker coordination. The Re-Re bond (2.336 (2) Å) in II is longer (by as much as 0.1 Å) than that in all previously characterized Re₂⁴⁺ dimers.^{2,35} This may be attributed to the axial chloride coordination and the skewed geometry of the molecule's core.

[Re₂Cl₂(Ph₂Ppy)₄](PF₆)₂·2(CH₃)₂CO (IIIb). The cation of this complex (see Figure 2) consists of an Re₂⁴⁺ unit bridged by four Ph₂Ppy ligands and axially bonded to two chlorine atoms. The bridging groups are arranged such that each one is cis to another one that is oppositely directed (i.e., the P and N atoms are staggered with respect to each other). Presumably, this staggering is required by the steric demands of these bulky ligands. Although no crystallographic symmetry is imposed on the cation, it does possess virtual C₂ symmetry with a 2-fold axis coincident with the Re-Re bond (ignoring the small deviations from 180° in the Re-Re-Cl angles).

Table V. Selected Bond Distances (Å) and Angles (deg) for $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)_3(\text{C}_6\text{H}_4)\text{Ppy}]$ (II)

Distances			
Re(1)–Re(2)	2.336 (2)	P(2)–C(2A)	1.84 (3)
–Cl(1)	2.578 (9)	–C(31)	1.90 (3)
–Cl(3)	2.429 (9)	–C(41)	1.82 (3)
–P(1)	2.388 (9)	P(3)–C(3A)	1.80 (3)
–P(2)	2.359 (10)	–C(51)	1.79 (4)
–N(3)	2.08 (2)	–C(61)	1.91 (4)
Re(2)–Cl(2)	2.568 (9)	N(1)–C(1A)	1.39 (3)
–P(3)	2.354 (9)	–C(1E)	1.31 (4)
–N(1)	2.17 (3)	N(2)–C(2A)	1.31 (4)
–N(2)	2.22 (3)	–C(2E)	1.42 (4)
–C(12)	2.16 (3)	N(3)–C(3A)	1.39 (4)
P(1)–C(1A)	1.84 (3)	–C(3E)	1.41 (4)
–C(11)	1.80 (3)	C(11)–C(12)	1.43 (4)
–C(21)	1.85 (4)		
Angles			
Re(2)–Re(1)–Cl(1)	162.0 (2)	Re(1)–P(1)–C(11)	105 (1)
–Cl(3)	110.6 (2)	–C(21)	127 (1)
–P(1)	76.8 (2)	C(1A)–P(1)–C(11)	97 (1)
–P(2)	84.1 (2)	–C(21)	107 (2)
–N(3)	101.6 (7)	C(11)–P(1)–C(21)	106 (2)
Cl(1)–Re(1)–Cl(3)	85.0 (3)	Re(1)–P(2)–C(2A)	113 (1)
–P(1)	96.3 (3)	–C(31)	118 (1)
–P(2)	80.5 (3)	–C(41)	119 (1)
–N(3)	89.7 (7)	C(2A)–P(2)–C(31)	97 (1)
Cl(3)–Re(1)–P(1)	85.3 (3)	–C(41)	106 (1)
–P(2)	165.3 (3)	C(31)–P(2)–C(41)	102 (1)
–N(3)	79.6 (7)	Re(2)–P(3)–C(3A)	115 (1)
P(1)–Re(1)–P(2)	98.3 (3)	–C(51)	117 (1)
–N(3)	163.3 (7)	–C(61)	121 (1)
P(2)–Re(1)–N(3)	98.1 (7)	C(3A)–P(3)–C(51)	96 (2)
Re(1)–Re(2)–Cl(2)	166.9 (2)	–C(61)	101 (2)
–P(3)	85.4 (2)	C(51)–P(3)–C(61)	103 (2)
–N(1)	103.6 (7)	Re(2)–N(1)–C(1A)	113 (2)
–N(2)	100.7 (7)	–C(1E)	128 (2)
–C(12)	92.4 (6)	C(1A)–N(1)–C(1E)	119 (3)
Cl(2)–Re(2)–P(3)	82.8 (3)	Re(2)–N(2)–C(2A)	119 (2)
–N(1)	88.5 (7)	–C(2E)	124 (2)
–N(2)	85.3 (7)	C(2A)–N(2)–C(2E)	117 (3)
–C(12)	84.0 (8)	Re(1)–N(3)–C(3A)	121 (2)
P(3)–Re(2)–N(1)	170.5 (7)	–C(3E)	125 (2)
–N(2)	92.1 (6)	C(3A)–N(3)–C(3E)	112 (3)
–C(12)	99.3 (8)	P(1)–C(1A)–N(1)	112 (2)
N(1)–Re(2)–N(2)	83.5 (9)	P(2)–C(2A)–N(2)	114 (3)
–C(12)	83 (1)	P(3)–C(3A)–N(3)	112 (2)
N(2)–Re(2)–C(12)	163 (1)	P(1)–C(11)–C(12)	108 (2)
Re(1)–P(1)–C(1A)	111 (1)	Re(2)–C(12)–C(11)	116 (2)

Each metal atom has approximate octahedral coordination symmetry, with two trans P and two trans N atoms in equatorial sites and one Cl atom and the other Re atom in axial positions. Despite these similar environments, the two Re–Cl bond lengths [Re(1)–Cl(1) = 2.575 (5) Å, Re(2)–Cl(2) = 2.628 (6) Å] differ by more than 0.05 Å. There appears to be no reasonable explanation for this other than steric effects introduced by the bulky Ph₂Ppy ligands. The nonbonded distances between the axial chlorides and their adjacent phenyl and pyridine groups are essentially identical for Cl(1) and Cl(2), indicating that if Cl(2) were any closer to Re(2), then it would experience greater nonbonded repulsion from neighboring atoms than Cl(1) would experience. The similarity in length between the Re(1)–Cl(1) bond in this cation and the average Re–Cl axial bond (2.573 [5] Å) in molecule II supports the theory that the Re(2)–Cl(2) bond is elongated due to steric crowding.

As in structure II, the central portion of IIIb contains four five-membered rings, each incorporating the Re–Re bond and adopting an envelope conformation. This leads to rotation about the metal–metal axis with smallest torsional angles of P(1)–Re(1)–Re(2)–N(1) = 16.6°, N(2)–Re(1)–Re(2)–P(2) = 16.2°, P(3)–Re(1)–Re(2)–N(3) = 16.2°, and N(4)–Re(1)–Re(2)–P(4) = 17.0°, for an average twist of 16.5°.

As mentioned in the Abstract, structure IIIb is a rare example of a multiply bonded dimetal unit bridged by four neutral ligands. Indeed, we are aware of only one other such complex in which

Table VI. Selected Bond Distances (Å) and Angles (deg) for $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4](\text{PF}_6)_2 \cdot 2(\text{CH}_3)_2\text{CO}$ (IIIb)

Distances			
Re(1)–Re(2)	2.300 (1)	P(2)–C(2A)	1.82 (2)
–Cl(1)	2.575 (5)	–C(2G)	1.83 (2)
–P(1)	2.436 (5)	–C(21)	1.76 (2)
–P(3)	2.429 (5)	P(3)–C(3A)	1.84 (2)
–N(2)	2.19 (2)	–C(3G)	1.82 (2)
–N(4)	2.210 (15)	–C(31)	1.79 (2)
Re(2)–Cl(2)	2.628 (6)	P(4)–C(4A)	1.88 (2)
–P(2)	2.428 (6)	–C(4G)	1.84 (2)
–P(4)	2.433 (6)	–C(41)	1.78 (2)
–N(1)	2.18 (2)	N(1)–C(11)	1.36 (2)
–N(3)	2.227 (15)	–C(15)	1.40 (3)
P(1)–C(1A)	1.82 (2)	N(2)–C(21)	1.34 (2)
–C(1G)	1.83 (2)	–C(25)	1.41 (2)
–C(11)	1.83 (2)	N(3)–C(31)	1.41 (2)
		–C(35)	1.34 (2)
		N(4)–C(41)	1.36 (2)
		–C(45)	1.40 (3)
Angles			
Re(2)–Re(1)–Cl(1)	178.5 (1)	C(1A)–P(1)–C(1G)	104 (1)
Re(2)–Re(1)–P(1)	92.3 (1)	C(1A)–P(1)–C(11)	106.1 (9)
Re(2)–Re(1)–P(3)	93.3 (1)	C(1G)–P(1)–C(11)	103 (1)
Re(2)–Re(1)–N(2)	94.4 (4)	Re(2)–P(2)–C(2A)	120.6 (8)
Re(2)–Re(1)–N(4)	96.1 (4)	Re(2)–P(2)–C(2G)	115.7 (6)
Cl(1)–Re(1)–P(1)	86.3 (2)	Re(2)–P(2)–C(21)	105.1 (8)
Cl(1)–Re(1)–P(3)	88.0 (2)	C(2A)–P(2)–C(2G)	102.4 (9)
Cl(1)–Re(1)–N(2)	85.0 (4)	C(2A)–P(2)–C(21)	110 (1)
Cl(1)–Re(1)–N(4)	84.5 (5)	C(2G)–P(2)–C(21)	101 (1)
P(1)–Re(1)–P(3)	174.4 (2)	Re(1)–P(3)–C(3A)	116.4 (7)
P(1)–Re(1)–N(2)	91.1 (4)	Re(1)–P(3)–C(3G)	120.3 (7)
P(1)–Re(1)–N(4)	87.9 (4)	Re(1)–P(3)–C(31)	106.7 (7)
P(3)–Re(1)–N(2)	88.1 (4)	C(3A)–P(3)–C(3G)	102.1 (8)
P(3)–Re(1)–N(4)	91.9 (4)	C(3A)–P(3)–C(31)	102.2 (9)
N(2)–Re(1)–N(4)	169.5 (6)	C(3G)–P(3)–C(31)	107 (1)
Re(1)–Re(2)–Cl(2)	177.9 (1)	Re(2)–P(4)–C(4A)	119.2 (8)
Re(1)–Re(2)–P(2)	93.4 (1)	Re(2)–P(4)–C(4G)	117.0 (6)
Re(1)–Re(2)–P(4)	92.5 (1)	Re(2)–P(4)–C(41)	105.8 (8)
Re(1)–Re(2)–N(1)	94.7 (4)	C(4A)–P(4)–C(4G)	102.2 (9)
Re(1)–Re(2)–N(3)	96.0 (4)	C(4A)–P(4)–C(41)	106 (1)
Cl(2)–Re(2)–P(2)	88.1 (2)	C(4G)–P(4)–C(41)	105 (1)
Cl(2)–Re(2)–P(4)	86.0 (2)	Re(2)–N(1)–C(11)	128 (1)
Cl(2)–Re(2)–N(1)	86.7 (5)	Re(2)–N(1)–C(15)	118 (1)
Cl(2)–Re(2)–N(3)	82.6 (5)	C(11)–N(1)–C(15)	115 (2)
P(2)–Re(2)–P(4)	174.0 (2)	Re(1)–N(2)–C(25)	122 (1)
P(2)–Re(2)–N(1)	91.4 (5)	Re(1)–N(2)–C(25)	119 (1)
P(2)–Re(2)–N(3)	87.2 (4)	C(21)–N(2)–C(25)	118 (2)
P(4)–Re(2)–N(1)	87.6 (5)	Re(2)–N(3)–C(31)	121 (1)
P(4)–Re(2)–N(3)	92.8 (5)	Re(2)–N(3)–C(35)	120 (2)
N(1)–Re(2)–N(3)	169.3 (6)	C(31)–N(3)–C(35)	120 (2)
Re(1)–P(1)–C(1A)	119.7 (7)	Re(1)–N(4)–C(41)	121 (1)
Re(1)–P(1)–C(1G)	116.9 (7)	Re(1)–N(4)–C(45)	120 (1)
Re(1)–P(1)–C(11)	106.2 (7)	C(41)–N(4)–C(45)	119 (2)

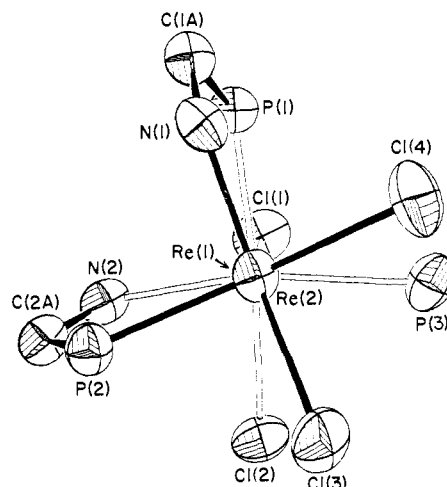
there are three-atom bridges, namely, the triply bonded Mo₂–Cl₂[F₂PN(CH₃)PF₂]₄ dimer.³⁶ This molecule also contains two axial Cl atoms and a long Mo–Mo bond (2.457 (1) Å). The Re–Re bond length (2.300 (1) Å) in IIIb is shorter than that in structure II but is still longer than those in the Re₂X₄L₄-type molecules.

Re₂Cl₄(Ph₂Ppy)₂(PEt₃) (IVa). This molecule (see Figure 3) possesses C₁ symmetry and consists of an Re₂⁴⁺ core with two cis, oppositely directed bridging Ph₂Ppy ligands; one axial chloride ligand, Cl(1) on Re(1); three equatorial Cl ligands, one on Re(1) and two on Re(2); and one PEt₃ group bonded to Re(1). As in structure II, the axial Cl atom is weakly coordinated with respect to the equatorial Cl atoms and is far from being collinear with the Re–Re axis. There is one acute angle [Re(2)–Re(1)–P(1) = 89.42 (5)°] between the two Re atoms and bound ligand atoms. The Re–P distance for the PEt₃ ligand is over 0.1 Å longer than those for the Ph₂Ppy ligands. There also appears to be a trans-effect lengthening³⁵ of Re–N bond distances: N(1) is trans to

(36) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 1918.

Table VII. Selected Bond Distances (Å) and Angles (deg) for Re₂Cl₄(Ph₂Ppy)₂(PEt₃) (IVa)

Distances			
Re(1)-Re(2)	2.270 (1)	N(2)-C(2A)	1.341 (11)
-Cl(1)	2.616 (2)	-C(2E)	1.364 (11)
-Cl(2)	2.406 (2)	P(1)-C(1A)	1.829 (8)
-P(1)	2.365 (2)	-C(10)	1.846 (9)
-P(3)	2.480 (3)	-C(20)	1.841 (10)
-N(2)	2.206 (7)	P(2)-C(2A)	1.818 (8)
Re(2)-Cl(3)	2.355 (2)	-C(30)	1.838 (9)
-Cl(4)	2.387 (2)	-C(40)	1.832 (9)
-P(2)	2.346 (2)	P(3)-C(1)	1.853 (10)
-N(1)	2.076 (7)	-C(2)	1.890 (13)
N(1)-C(1A)	1.342 (11)	-C(3)	1.880 (11)
-C(1E)	1.354 (11)		
Angles			
Re(2)-Re(1)-Cl(1)	166.37 (6)	Re(1)-P(1)-C(1A)	109.2 (3)
-Cl(2)	103.79 (6)	-C(10)	117.8 (3)
-P(1)	89.42 (5)	-C(20)	121.2 (3)
-P(3)	94.65 (6)	C(1A)-P(1)-C(10)	99.2 (4)
-N(2)	97.4 (2)	-C(20)	102.3 (4)
Cl(1)-Re(1)-Cl(2)	89.65 (8)	C(10)-P(1)-C(20)	103.9 (4)
-P(1)	77.50 (8)	Re(2)-P(2)-C(2A)	110.5 (3)
-P(3)	84.08 (9)	-C(30)	123.7 (3)
-N(2)	87.0 (2)	-C(40)	110.7 (3)
Cl(2)-Re(1)-P(1)	165.40 (8)	C(2A)-P(2)-C(30)	101.5 (4)
-P(3)	85.07 (9)	-C(40)	106.0 (4)
-N(2)	80.5 (2)	C(30)-P(2)-C(40)	102.8 (4)
P(1)-Re(1)-P(3)	100.25 (9)	Re(1)-P(3)-C(1)	110.6 (4)
-N(2)	92.0 (2)	-C(2)	116.8 (5)
P(3)-Re(1)-N(2)	162.9 (2)	-C(3)	118.0 (4)
Re(1)-Re(2)-Cl(3)	112.00 (7)	C(1)-P(3)-C(2)	108.1 (6)
-Cl(4)	113.55 (7)	-C(3)	105.3 (5)
-P(2)	91.62 (6)	C(2)-P(3)-C(3)	96.6 (6)
-N(1)	100.0 (2)	Re(2)-N(1)-C(1A)	124.7 (5)
Cl(3)-Re(2)-Cl(4)	85.1 (1)	-C(1E)	119.3 (6)
-P(2)	87.30 (9)	C(1A)-N(1)-C(1E)	116.0 (8)
-N(1)	147.9 (2)	Re(1)-N(2)-C(2A)	121.8 (5)
Cl(4)-Re(2)-P(2)	154.75 (9)	-C(2E)	121.1 (7)
-N(1)	80.7 (2)	C(2A)-N(2)-C(2E)	115.9 (8)
P(2)-Re(2)-N(1)	93.5 (2)		

Figure 5. Illustration of the central part of Re₂Cl₄(Ph₂Ppy)₂(PEt₃) (IVa), emphasizing the staggered conformation. The view is straight down the Re-Re axis so that Re(1) is hidden by Re(2). Re(1)-ligand bonds are shown in outlined form for clarity.

a Cl ligand, Cl(3), and Re(2)-N(1) = 2.076 (7) Å, while N(2) is trans to the PEt₃ ligand and Re(1)-N(2) = 2.206 (7) Å.

Once again, the Re-Re bond is rotated away from an eclipsed configuration (see Figure 5), the torsional angles being N(2)-Re(1)-Re(2)-P(2) = 13.9°, Cl(2)-Re(1)-Re(2)-Cl(3) = 19.9°, P(3)-Re(1)-Re(2)-Cl(4) = 28.2°, and P(1)-Re(1)-Re(2)-N(1) = 12.0°, for an average twist of 18.5°. The Re-Re bond length in IVa (2.270 (1) Å) is shorter than that in both II and IIIb as one would expect from only one axial Cl atom vs. two.

(c) **Spectroscopic and Electrochemical Properties.** The IR spectra of the complexes I-IV are not especially noteworthy,

although the striking similarity between the spectra of IVa and IVb, including the low-frequency region from 500 to 200 cm⁻¹ (with $\nu(\text{Re}-\text{Cl})$ at 317 (± 1) (s) and 294 (m) cm⁻¹), is support for their possessing the same structure. This is also apparent in the case of the electronic absorption spectra of IVa and IVb (λ_{max} (nm) in CH₂Cl₂ at 560 sh, ~ 520 ($\epsilon \sim 6000$), and 420 ($\epsilon \sim 5000$)), which are likewise very similar and which, in turn, resemble the spectrum of I (λ_{max} (nm) in CH₂Cl₂ at 550 sh, 490 (ϵ 6200), and 400 (ϵ 5600).

Complexes I, II, IVa, and IVb exhibit very similar electrochemical properties. Voltammetric half-wave potentials vs. SCE for 0.2 M tetra-*n*-butylammonium hexafluorophosphate-dichloromethane solutions were measured by the cyclic voltammetry technique (Table VIII). For complexes I and II two couples are observed in the potential range +0.20 to +1.20 V, each corresponding to a one-electron oxidation (as determined by coulometry), which is characterized by $i_{p,c}/i_{p,a} = 1$ and a constant $i_p/\nu^{1/2}$ ratio for sweep rates between 50 and 400 mV/s. The potential separation between the anodic and cathodic peaks, ΔE_p , was close to 75 mV for a sweep rate of 200 mV/s and increased slightly with increase in sweep rate. These observations are in accord with these being quasi-reversible electron-transfer processes. The electrochemical properties of IVa and IVb are similar to those of I and II with the exception that the second oxidation of IVa and IVb is clearly electrochemically irreversible ($i_{p,c}/i_{p,a} < 1$).

The electrochemical redox behavior of I, II, IVa, and IVb shows a striking resemblance to that exhibited by triply bonded di-

Table VIII. Cyclic Voltammetric Data for Dichloromethane Solutions of Dirhenium(II) Complexes^a

compd	$E_{1/2}(\text{ox}(2))$	$E_{1/2}(\text{ox}(1))$	$E_{1/2}(\text{red}(2))$	$E_{p,c}(\text{red}(2))$
Re ₂ Cl ₄ (Ph ₂ Ppy) ₃ (I)	+1.20 (80)	+0.41 (80)		
Re ₂ Cl ₃ (Ph ₂ Ppy) ₂ [(C ₆ H ₅)(C ₆ H ₄)Ppy] (II)	+1.06 (70)	+0.24 (70)		
[Re ₂ Cl ₂ (Ph ₂ Ppy) ₄](PF ₆) ₂ (IIIb)		+1.38 (100)	-0.82 (100)	-1.60
Re ₂ Cl ₄ (Ph ₂ Ppy) ₂ (PEt ₃) (IVa)	+1.15 ^b	+0.27 (90)		
Re ₂ Cl ₄ (Ph ₂ Ppy) ₂ (P- <i>n</i> -Bu) ₃ (IVb)	+1.19 ^b	+0.27 (80)		

^a $E_{1/2}$ values in volts vs. SCE using a Pt-bead electrode in dichloromethane with 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. Values of $E_{p,a} - E_{p,c}$ (in mV) at sweep rates of 200 mV/s are given in parentheses. ^b $E_{p,a}$ values.

Table IX. ³¹P{¹H} NMR Spectral Data for Dirhenium(II) Complexes

compd	³¹ P chem shifts, δ^a	² J _{P-P}	³ J _{P-P}
Re ₂ Cl ₄ (Ph ₂ Ppy) ₃ (I)	-6.50, ^b -5.45, ^b -0.37 ^b	11.1	6.7, 4.9
Re ₂ Cl ₃ (Ph ₂ Ppy) ₂ [(C ₆ H ₅)(C ₆ H ₄)Ppy] (II)	-25.81, ^b -0.88, ^b +14.66 ^b	16.3	9.3, 6.9
[Re ₂ Cl ₂ (Ph ₂ Ppy) ₄](PF ₆) ₂ (IIIb)	+11.76 ^c		
Re ₂ Cl ₄ (Ph ₂ Ppy) ₂ (PEt ₃) (IVa)	-25.48, ^d -7.24, ^d +13.68 ^d		
Re ₂ Cl ₄ (Ph ₂ Ppy) ₂ (P- <i>n</i> -Bu) ₃ (IVb)	-29.71, ^b -8.31, ^b +13.73 ^b	10.0	7.0, 3.9

^a Recorded in 1:1 CDCl₃/CH₂Cl₂; aqueous 85% H₃PO₄ used as an external standard. ^b Doublet of doublets. ^c Sharp singlet; $\delta(\text{PF}_6^-)$ for this complex is at δ -144.76 (heptet, $J_{P-F} = 712$ Hz). ^d Broad singlet, which is presumably an unresolved doublet of doublets.

rhodium(II) complexes of the type $\text{Re}_2\text{Cl}_4(\text{L-L})_2$ containing bridging ligands L-L (where L-L = $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1$ or 2) or $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{AsPh}_2$),^{33,37} for which the two one-electron oxidations correspond to the configuration changes $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2 \rightarrow (\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1 \rightarrow (\sigma)^2(\pi)^4(\delta)^2(\delta^*)^0$. Such a similarity in turn supports the formulation of the Ph_2Ppy complexes as being authentic derivatives of Re_2^{4+} .³⁸

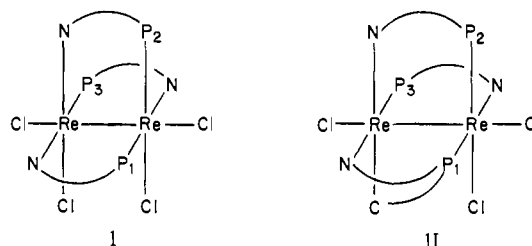
One species whose electrochemical properties do not at first sight appear to fit into the scheme of things is $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4]^{2+}$ (Table VIII). The chloride salt of this dication (IIIa) has the same redox chemistry as $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4](\text{PF}_6)_2$ (IIIb) (Table VIII), with the exception that the cyclic voltammogram of IIIa also shows an additional irreversible oxidation at $E_{\text{pa}} \sim +1.2$ V associated with the oxidation of free chloride ion. While there is no doubt whatsoever that III is an authentic derivative of the Re_2^{4+} core, the fact that its electrochemical redox behavior is so different from that of the other compounds listed in table VIII calls for comment. It is apparent that the first one-electron oxidation (at +1.38 V) has shifted to quite high positive potentials and that the second oxidation is now beyond the potential range of our measurements (approximately +1.6 to -1.6 V in dichloromethane). With the increase in difficulty of oxidizing this species there is an expected concomitant increase in the ease of reducing it; accessible reductions are now observed at -0.8 and -1.6 V vs. SCE (Table VIII). Apparently, there is an increase in the effective positive charge at the dirhenium core of this cation relative to the situation with the other derivatives, so that both the HOMO (δ^*) and LUMO (π^*) orbitals drop in energy, making oxidation (from δ^*) more difficult and reduction (through addition of electrons to π^*) much more favorable.

A final characterization study that merits comment concerns the $^{31}\text{P}\{^1\text{H}\}$ spectra of these complexes (Table IX). The complex IIIb shows a single phosphine phosphorus resonance at $\delta +11.76$; this is expected since it contains four equivalent phosphine phosphorus atoms. The other complexes (Table IX) display three resonances, each of which corresponds to a doublet of doublets, thereby demonstrating the inequivalency of the three phosphorus atoms. This inequivalency has of course been proven in the case of II and IVa by single-crystal structure analyses, so that these structures are apparently retained in solution. Of further note is the small magnitude of the coupling constants (<17 Hz), which would seem to preclude in the case of I (and also of course in the case of II, IVa, and IVb any trans P-Re-P bonding.³⁹ For the ortho-metallated complex II, the resonance at $\delta -25.81$ may be assigned to P(1) of the ortho-metallated ligand since this should be the most shielded.⁴⁰ On the basis of coupling constant considerations, we assign the resonance at $\delta -0.88$ to the atom P(2), which is cis to this, while the resonance at $\delta +14.66$ is attributed to P(3), which is bound to the adjacent rhenium center. It would be expected that the largest coupling would occur between the

cis phosphorus atoms, which makes $^2J_{\text{P}_1-\text{P}_2} = 16.3$ Hz, and thus the smallest would be the three-bond coupling constants, $J_{\text{P}_1-\text{P}_3} = 9.3$ Hz and $^3J_{\text{P}_2-\text{P}_3} = 6.9$ Hz.

Decoupling experiments showed that for IVb the resonance at $\delta -29.71$ is assignable to the P of the tri-*n*-butylphosphine ligand. It is reasonable to attribute the largest coupling constant to the two-bond coupling between it and the P atom of the bridging Ph_2Ppy ligand that is cis to it ($^2J_{\text{P-P}} = 10.0$ Hz), leaving the two small coupling constants to the three-bond coupling (Table IX).

Since the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of I, like those of II and IVa, consists of three doublets of doublets and coupling indicative of cis phosphorus atoms only (see Table IV), is it likely to have a structure (represented schematically as I below) that resembles closely the one for II.



(d) **Summarizing Remarks.** The reactions of $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ and $\text{Re}_2\text{Cl}_6(\text{PR}_3)_2$ ($\text{R} = \text{Et}$ or *n*-Bu) with Ph_2Ppy are, in the field of multiple-bond chemistry,² especially noteworthy for three reasons. (1) Not only are these reactions shown to afford a new class of ligand-bridged triply bonded dirhenium(II) complexes but in the case of $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppy}]$ we have the first example of an ortho-metallation reaction occurring at a metal-metal multiple bond of the M_2L_8 type. (2) In all instances, the dirhenium(II) complexes that were isolated and characterized possess axial, albeit weak, Re-Cl bonds; the existence of significant axial Re-L bonding interactions had not previously been recognized for complexes possessing the Re_2^{4+} core. (3) With the isolation of salts of the $[\text{Re}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_4]^{2+}$ cation, we have a very rare example of a multiply bonded dimetal unit complexes by *four neutral bridging* ligands; the isoelectronic and novel dimolybdenum(I) complex $\text{Mo}_2\text{Cl}_2[\text{F}_2\text{PN}(\text{CH}_3)\text{PF}_2]_4$ constitutes the only previous example of this.³⁶

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Registry No. I, 85650-36-8; II, 85665-22-1; IIIa, 88453-20-7; IIIb, 88495-16-3; IVa, 88495-17-4; IVb, 88495-18-5; $[\text{ReCl}_3(\text{Ph}_2\text{Ppy})_n]$, 88453-21-8; $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$, 14023-10-0; $\text{Re}_2\text{Cl}_6(\text{P-}n\text{-Bu})_2$, 38832-70-1; $\text{Re}_2\text{Cl}_6(\text{PET}_3)_2$, 19584-31-7; Ph_2Ppy , 37943-90-1; PPh_2Cl , 1079-66-9; Re, 7440-15-5; 2-bromopyridine, 109-04-6; pyridine, 110-86-1; 4-methylpyridine, 108-89-4.

Supplementary Material Available: Complete tables of anisotropic thermal parameters, bond distances, bond angles, and structure factor data, along with details of the data collection and structure solution and refinement for the three complexes II, IIIb, and IVa (80 pages). Ordering information is given on any current masthead page.

(37) Brant, P.; Glicksman, H. D.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 3203.

(38) We note that these Ph_2Ppy complexes as well as the compounds $\text{Re}_2\text{Cl}_4(\text{L-L})_2$, are appreciably more air stable than their analogues $\text{Re}_2\text{Cl}_4(\text{PR}_3)_4$, which contain monodentate tertiary phosphines. These differences correlate very nicely with the differences in $E_{1/2}$ values for the two one-electron oxidations; the values for $\text{Re}_2\text{Cl}_4(\text{PR}_3)_4$ occur at much lower potentials.^{29,37}

(39) Kunz, R. W.; Pregosin, P. E. ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes; Springer-Verlag: Berlin, 1979; p 32.

(40) Reference 39, pp 47-55.