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# Ligand Exchange or Reduction at Multiply Bonded Dimetal Units of Molybdenum and Rhenium by 2,6-Bis(diphenylphosphino)pyridine

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Reaction of 2,6-bis(diphenylphosphino)pyridine (bdppp or $(Ph_2P)_2Py$)) with $K_4Mo_2Cl_8$ in refluxing methanol gives $Mo_2Cl_4(bdppp)_2$ (**1**) with retention of the quadruple Mo−Mo bond. However, the quadruply bonded octachlorodirhenate(III) anion, $Re_2Cl_8^{2-}$, reacts with bdppp under similar conditions to afford $Re_2Cl_4(bdppp)_2$ (**2**), which has a triply bonded dirhenium(II) core, $Re_2^{4+}$. An intermediate species, $[Bu^n_4N][Re_2Cl_7(bdppp)]$ (**3**), containing an $Re_2^{6+}$ core and only one bridging bdppp ligand has also been isolated. The crystal structures of complexes **1**−**3** have been investigated by X-ray crystallography. In all cases the potentially tridentate bdppp acts as a bidentate ligand using one N and one of the P atoms, leaving the second phosphorus atom noncoordinated. The crystallographic parameters for these structures are as follows: $Mo_2Cl_4(bdppp)_2\cdot 2CH_2Cl_2$ (**1**$\cdot 2CH_2Cl_2$), monoclinic space group $P2_1/c$ with $a = 15.475(2)$ Å, $b = 11.5958(7)$ Å, $c = 16.7637\ (6)$ Å, $\beta = 98.178(5)°$, $Z = 2$; $Re_2Cl_4(bdppp)_2$ (**2**), monoclinic space group $P2_1/n$ with $a = 16.173(2)$ Å, $b = 11.285(1)$ Å, $c = 28.771\ (4)$ Å, $\beta = 96.17(1)°$, $Z = 4$; $[Bu^n_4N][Re_2Cl_7(bdppp)]\cdot CH_2Cl_2$ (**3**$\cdot CH_2Cl_2$), triclinic space group $P\bar{1}$ with $a = 16.054(2)$ Å, $b = 18.562(3)$ Å, $c = 20.205\ (6)$ Å, $\alpha = 89.71(2)°$, $\beta = 73.21(1)°$, $\gamma = 73.47(2)°$, $Z = 4$.

## Introduction

2,6-Bis(diphenylphosphino)pyridine (bdppp or $(Ph_2P)_2Py$) is a neutral tridentate ligand (Chart 1) that has been used in the synthesis of many novel di- and polynuclear complexes.[1] The ability of bdppp to interact with metals in a variety of binding modes has been demonstrated. Altogether three different coordination types (Chart 2) have been found so far in all crystallographically characterized compounds. Most of the reported complexes[1a−g] display the first binding mode (Chart 2a). Of particular interest are the doubly bridged compounds with an $[M_2\{\mu\text{-}(Ph_2P)_2Py\}_2]$ core (M = Rh,[1a] Pt,[1b] Cu,[1c] and Fe[1d]) and triply bridged molecules with an $[M_2\{\mu\text{-}(Ph_2P)_2Py\}_3]$ core (M = Cu,[1c] Au[1e]). Crystal structures are characterized by long metal−metal separations over a range of 4.74−8.21 Å and by a relatively open central cavity which is capable of binding an additional metal atom or ion. An example is provided by the complexation of tin(II) chloride by a dirhodium macrocycle.[1h] The resulting compound has an $[RhSnRh\{\mu\text{-}(Ph_2P)_2Py\}_2]$ core containing two ligands bound in the second coordination mode (Chart 2b) whereby a nitrogen atom is connected to the tin atom. The same type of structure has been suggested[1d] for $[FeHgFe\{\mu\text{-}(Ph_2P)_2Py\}_2]$, but this claim has not yet been supported by a crystallographic study.

**Chart 1**

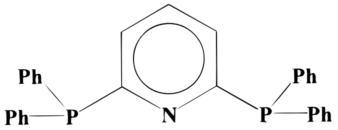
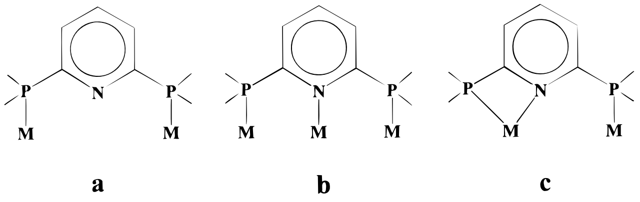


**Chart 2**



The rhodium complex containing the $[Rh_4\{\mu\text{-}(Ph_2P)_2Py\}_2]$ core is the only tetranuclear example of the second type of coordination mode (Chart 2b) with two ligands trans to one another and aligned by one unit translation.[1f] In this complex, the almost linear chain of four rhodium atoms is also supported by two bridging Cl and one CO group.

A third coordination type (Chart 2c), which features chelation by a phosphorus atom and the nitrogen together with the formation of a bridge to the second phosphorus atom, was found[1i] in the dirhodium cation $[Rh_2(\mu\text{-I})\{(\mu\text{-}Ph_2P)_2Py\}_2(\mu\text{-}CO)]^+$.

The metal−metal separation for the last two coordination modes is still long (2.57−2.92 Å). Therefore, it was of interest to study the behavior of the $(Ph_2P)_2Py$ ligand in reactions with

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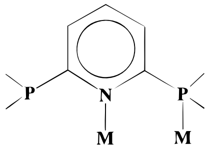
**Chart 3**



dinuclear units containing short metal−metal bonds, for example with the quadruply bonded $Mo_2Cl_8^{4-}$ and $Re_2Cl_8^{2-}$ anions. This study reveals still another coordination mode for the bdppp ligand (Chart 3) in which the metal atoms are bridged by the ligand through P and N atoms, leaving the remaining phosphorus atom noncoordinated.

The synthesis, structures, and spectroscopic and electrochemical properties of a molybdenum compound and two rhenium complexes containing the $(Ph_2P)_2Py$ ligand are described in this paper.

## Experimental Section

**General Procedures.** All syntheses and purifications were carried out under a $N_2$ atmosphere using standard Schlenk techniques. All solvents were freshly distilled under $N_2$ from suitable drying agents. Aldrich, Inc., supplied $[Bu^n{}_4N]_2Re_2Cl_8$; 2,6-bis(diphenylphosphino)pyridine[1d] and $K_4Mo_2Cl_8$[2] were synthesized using literature methods. Dichloromethane-$d_2$ was obtained from Cambridge Isotope Laboratories.

**Physical Measurements.** Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A stream of nitrogen was bubbled through the solution during the measurements. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the Ag/AgCl electrode at room temperature ($E_{1/2} = +0.47$ V for the ferrocenium/ferrocene couple). Voltammetric experiments were carried out on a Bioanalytical Systems Inc. electrochemical analyzer, Model 100; the scan rate was 100 mV/s at the Pt disk electrode. The IR spectra were performed in the range 4000−400 $cm^{-1}$ on a Perkin-Elmer 16PC FT-IR spectrometer using KBr pellets. The $^1H$ and $^{31}P\ \{^1H\}$ NMR data were recorded at room temperature on a UNITY-plus 300 multinuclear spectrometer operated at 300 and 121.4 MHz, respectively. Reference standards were $^1H$, $CH_2Cl_2$ (5.32 ppm), and $^{31}P$, 85% $H_3PO_4$ (0.00 ppm). Elemental analyses were done by Canadian Microanalytical Services, Ltd.; they were satisfactory.

**Synthesis of $Mo_2Cl_4(bdppp)_2\cdot 2CH_2Cl_2$ ($1\cdot 2CH_2Cl_2$).** In a 100 mL round-bottom flask, 0.164 g (0.260 mmol) of $K_4Mo_2Cl_8$ and 1.60 g (3.51 mmol) of bis(diphenylphosphino)pyridine were suspended in 25 mL of methanol. The mixture was refluxed for 5−6 h. Upon heating, the color of the mixture changed from red to lime green. After refluxing, the green solid was collected by filtration and washed repeatedly with warm $H_2O$, followed by methanol. Excess bdppp was removed by washing the product with small portions of toluene. Yield: 0.289 g (0.235 mmol, 90.5%). Crystals were grown by diffusion of hexanes into a concentrated $CH_2Cl_2$ solution. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 7.72 (mult), 7.45 (mult), and 7.25 (mult) ppm. $^{31}P$ NMR ($CD_2Cl_2$): $\delta$ +36.19 (s) and −9.60 (s) ppm. IR (KBr, $cm^{-1}$): 3052 (w), 1585 (w), 1566 (m), 1544 (m), 1483 (s), 1433 (vs), 1365 (m), 1189 (m), 1138 (w), 1087 (s), 1027 (m), 1014 (m), 998 (m), 795 (m), 744 (vs), 691 (vs), 518 (vs).

**Synthesis of $Re_2Cl_4(bdppp)_2$ (2).** A suspension containing $[Bu^n{}_4N]_2Re_2Cl_8$ (0.1845 g, 0.15 mmol) and bdppp (0.3440 g, 0.75 mmol) in 20 mL of methanol was refluxed for 15 h. A green solid was collected by filtration, washed with methanol (2 × 10 mL) and with small portions of toluene, and then dried. Yield: 0.175 g (0.12 mmol, 77.1%). Dark-green plate-shaped crystals were obtained by diffusion from a $CH_2Cl_2$ solution after layering with hexanes. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 7.94 (mult), 7.47 (mult), and 7.24 (mult) ppm. IR (KBr, $cm^{-1}$): 1584 (w), 1572 (w), 1560 (w), 1479 (s), 1433 (vs), 1350 (vs), 1263 (w), 1191 (m), 1169 (m), 1088 (s), 1027 (m), 1006 (m), 998 (m), 800 (m), 790 (m), 754 (s), 738 (s), 690 (vs), 664 (s), 575 (m), 552 (m), 530 (s), 518 (s), 503 (s), 493 (s), 476 (w), 446 (m), 417 (m). CV ($CH_2Cl_2$, 22 °C, V vs Ag/AgCl): $E_{1/2}$ (ox) (1) = −0.07, $E_{1/2}$ (ox) (2) = +0.85.

**Synthesis of $[Bu^n{}_4N][Re_2Cl_7(bdppp)]\cdot CH_2Cl_2$ ($3\cdot CH_2Cl_2$).** A suspension of $[Bu^n{}_4N]_2Re_2Cl_8$ (0.2375 g, 0.20 mmol) and bdppp (0.4503 g, 1.00 mmol) in 25 mL of methanol was stirred for 2 h at room temperature; the color of the solution changed to green-brown. The solution was filtered, and the solvent was removed under reduced pressure, leaving a green residue, which was washed with small portions of toluene (2 × 5 mL), followed by hexanes (2 × 10 mL), and dried. Yield: 0.094 g (0.07 mmol, 34.6%). Green plate-shaped crystals were obtained after a few days from $CH_2Cl_2$ solutions layered with hexanes; they were always contaminated by a small amount of crystals of $[Bu^n{}_4N]_2Re_2Cl_8$, which were separated manually. IR (KBr, $cm^{-1}$): 1617 (w), 1585 (w), 1570 (w), 1543 (w), 1482 (s), 1434 (vs), 1379 (m), 1368 (m), 1263 (w), 1233 (w), 1192 (m), 1152 (s), 1091 (s), 1070 (w), 1024 (s), 998 (m), 925 (w), 879 (m), 809 (m), 785 (w), 740 (vs), 689 (vs), 531 (s), 512 (s), 488 (s), 466 (s), 442 (m). CV ($CH_2Cl_2$, 22 °C, V vs Ag/AgCl): $E_{1/2}$ (red) (1) = + 0.03, $E_{1/2}$ (red) (2) = −0.75.

**X-ray Crystallographic Procedures.** Single crystals of **1**−**3** were obtained as described above. Unit cell determinations and data collections followed routine procedures and practices of this laboratory.[3] Oscillation photographs of principal axes were taken to confirm Laue class and axial lengths. All data were corrected for Lorentz and polarization effects. The intensities for **1** and **3** were corrected for absorption using a local adaptation of the program SORTAV.[4]

All calculations were done on a DEC Alpha running VMS. The coordinates of the heavy atoms for all of the structures were found in direct methods *E*-maps using the structure solution program SHELXTL.[5] The positions of the remaining atoms were located by a combination of least-squares refinements and difference Fourier maps using the SHELXL-93 program.[6] Details on data collection and structure refinement for **1**−**3** are summarized in Table 1.

**$Mo_2Cl_4(bdppp)_2\cdot 2CH_2Cl_2$.** A green block-shaped crystal of size 0.20 × 0.10 × 0.05 mm was mounted and placed in a cold nitrogen stream (−31 °C) on a Nonius FAST diffractometer equipped with an area detector and monochromated Mo K$\alpha$ radiation ($\lambda = 0.710\ 73$ Å). Indexing revealed a primitive monoclinic cell. On the basis of systematic absences, the space group was uniquely determined to be $P2_1/c$. Complex **1** crystallizes with two interstitial dichloromethane molecules per dimolybdenum unit. All of the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms, except those from the solvent molecule, were found in a difference map and also refined. A final difference map was essentially featureless.

**$Re_2Cl_4(bdppp)_2$.** A green plate-shaped crystal with dimensions 0.20 × 0.18 × 0.10 mm was selected and fixed on the tip of a quartz fiber with grease. It was then placed in a nitrogen stream at −100 °C in a CAD-4S diffractometer equipped with monochromated Mo K$\alpha$ radiation. Indexing based on 25 reflections in the range $20° < 2\theta < 28°$ resulted in a primitive monoclinic cell. No significant decay was found during the data collection. An empirical absorption correction based on azimuthal scans of 6 reflections with their $\psi$ angles near 90° was applied (0.5471−0.9986). The analysis of the systematic absences unambiguously assigned the space group as $P2_1/n$. Anisotropic displacement parameters were used for all non-hydrogen atoms. Hydrogen atoms were included in the structure factor calculations at idealized positions and were allowed to ride on the corresponding carbon atoms. The final difference Fourier map showed no peaks higher than 1 e/Å$^3$.

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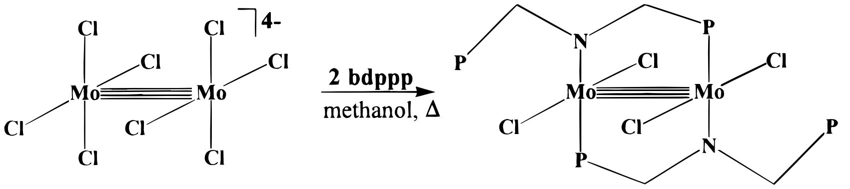
**Table 1.** Crystallographic Data for $Mo_2Cl_4(bdppp)_2{\cdot}2CH_2Cl_2$ (**1**·$2CH_2Cl_2$), $Re_2Cl_4(bdppp)_2$ (**2**), and $[Bu^n_4N][Re_2Cl_7(bdppp)]{\cdot}CH_2Cl_2$ (**3**·$CH_2Cl_2$)

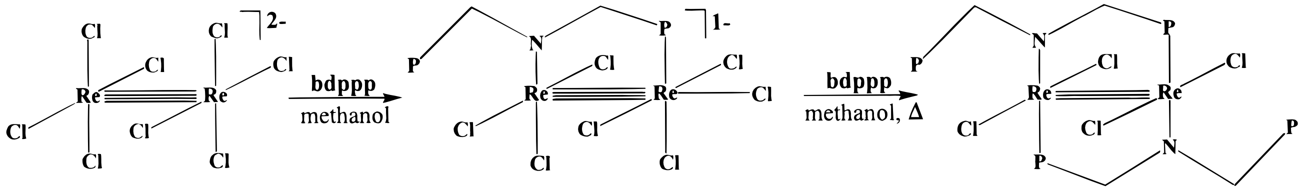
| | **1**·$2CH_2Cl_2$ | **2** | **3**·$CH_2Cl_2$ |
|---|---|---|---|
| formula | $Mo_2P_4N_2Cl_8C_{60}H_{50}$ | $Re_2P_4N_2Cl_4C_{58}H_{46}$ | $Re_2P_2N_2Cl_9C_{46}H_{61}$ |
| fw | 1898.38 | 1409.05 | 1395.36 |
| space group | $P2_1/c$ (No. 14) | $P2_1/n$ (No. 14) | $P\bar{1}$ (No. 2) |
| *a*, Å | 15.475(2) | 16.173(2) | 16.054(2) |
| *b*, Å | 11.5958(7) | 11.285(1) | 18.562(3) |
| *c*, Å | 16.7637(6) | 28.771(4) | 20.205(6) |
| α, deg | | | 89.71(2) |
| *β*, deg | 98.178(5) | 96.17(1) | 73.21(1) |
| *γ*, deg | | | 73.47(2) |
| *V*, $Å^3$ | 2977.6(4) | 5221(1) | 5507(2) |
| *Z* | 2 | 4 | 4 |
| $\rho_{calc.}$, g $cm^{-3}$ | 1.560 | 1.793 | 1.683 |
| $\mu$, $mm^{-1}$ | 0.929 | 5.002 | 4.920 |
| radiation ($\lambda$, Å) | Mo Kα (0.710 73) | Mo Kα (0.710 73) | Mo Kα (0.710 73) |
| temp, °C | −31 | −100 | −60 |
| R1,[a] wR2[b] [$I > 2\sigma(I)$] | 0.0518, 0.1341 | 0.0372, 0.0766 | 0.0816, 0.1859 |
| R1,[a] wR2[b] (all data) | 0.0807, 0.1479 | 0.1072, 0.0961 | 0.1189, 0.2217 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

**Scheme 1**



**Scheme 2**



**$[Bu^n_4N][Re_2Cl_7(bdppp)]{\cdot}CH_2Cl_2$.** All of the crystals were very weak diffractors; a green plate with dimensions 0.18 × 0.08 × 0.05 mm was selected. Indexing and refinement of 238 reflections gave a primitive triclinic cell. Space group $P\bar{1}$ was chosen and confirmed by the successful refinement of the structure. Both tetrabutylammonium cations and the $CH_2Cl_2$ solvent molecules were highly disordered. Thus, only the non-hydrogen atoms of two crystallographically independent dirhenium complexes and those of one of the $[Bu^n_4N]^+$ cations were refined anisotropically. All hydrogen atoms were included in the structure calculations but were not refined. The final difference map contained some peaks associated with solvent molecules.

## Results and Discussion

**Reaction Chemistry.** The dimolybdenum complex **1**, isolated in crystalline form with two molecules of $CH_2Cl_2$, was synthesized by refluxing a mixture of $K_4Mo_2Cl_8$ and bdppp in methanol (Scheme 1). The conversion to $Mo_2Cl_4(bdppp)_2$ proceeds in 90% yield. The analogous rhenium complex $Re_2Cl_4(bdppp)_2$ (**2**) was obtained using $[Bu^n_4N]_2Re_2Cl_8$ as a starting material and by following a similar route (Scheme 2). This reaction not only results in a ligand substitution but also is accompanied by reduction of rhenium(III) to rhenium(II). It is worth mentioning that reduction of $Re_2Cl_8^{2-}$ by phosphines has often been observed, especially when refluxing alcohols were used as reaction media.[7,8] Prolonging the reaction time also favors the formation of complexes containing the $Re_2^{4+}$ core. The actual reducing mechanism of this process is still not defined. Nevertheless, it has been found that the use of other solvents[9] or "mild" reaction conditions may prevent or slow down the reduction processes.[10] In this work, when we reacted $Re_2Cl_8^{2-}$ with bdppp in methanol at room temperature and stopped the reaction after 1.5−2 h, we isolated the rhenium(III,III) complex **3**, $[Bu^n_4N][Re_2Cl_7(bdppp)]$; it was soluble in methanol in contrast to **2**. Complex **3** has one bridging bdppp ligand and can be regarded as an intermediate in the formation of the doubly bridged rhenium(II,II) complex **2**.

The identities of compounds **1**, **2**, and **3** have been established by X-ray crystallographic studies and further confirmed by their properties. Thus, complexes **2** and **3** exhibit typical electrochemical behavior for $Re_2^{4+}$ and $Re_2^{6+}$ cores, respectively. For **2** two couples are observed at −0.07 and +0.85 V, each corresponding to a reversible one-electron oxidation, while the CV of **3** shows a reversible one-electron reduction at +0.03 V and an irreversible reduction at −0.75 V.

**Description of Structures.** $Mo_2Cl_4(bdppp)_2{\cdot}2CH_2Cl_2$ (**1**·$2CH_2Cl_2$) crystallizes in the monoclinic space group $P2_1/c$; there are two dimolybdenum molecules and four dichloromethane molecules per unit cell. $Re_2Cl_4(bdppp)_2$ (**2**) forms crystals in the monoclinic space group $P2_1/n$ with four dirhenium molecules

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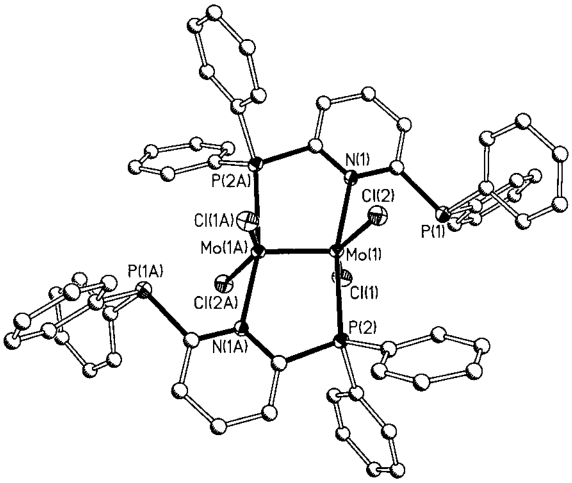

**Figure 1.** Perspective drawing of $Mo_2Cl_4(bdppp)_2$ in $\mathbf{1}\cdot 2CH_2Cl_2$. Atoms are represented by their thermal ellipsoids at the 40% probability level. Carbon atoms are shown as arbitrarily sized spheres and for clarity are not labeled. Hydrogen atoms are omitted.

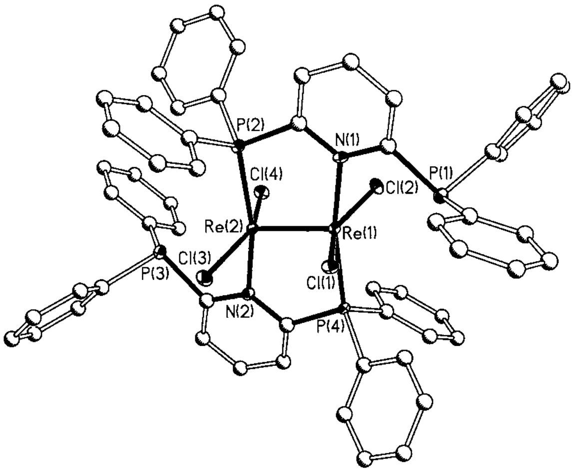

**Figure 2.** Perspective drawing of $Re_2Cl_4(bdppp)_2$ (**2**). Atoms are represented by their thermal ellipsoids at the 40% probability level. Carbon atoms are shown as arbitrarily sized spheres and for clarity are not labeled. Hydrogen atoms are omitted.

per unit cell. The molecular structures **1** and **2** are very similar (Figures 1 and 2). Both are composed of two trans bdppp ligands bridging the dinuclear metal units in a head-to-tail arrangement through one phosphorus and one nitrogen atom of each ligand, forming an $M_2P_2N_2$ framework; each metal center also has two equatorial chloride ligands. The molecule of $Mo_2Cl_4(bdppp)_2$ (**1**) (Figure 1) has a crystallographically imposed inversion center located at the midpoint of the Mo−Mo bond, whereas in the $Re_2Cl_4(bdppp)_2$ molecule (Figure 2) the two halves of the structure are crystallographically independent.

The metal−metal distance of 2.149(1) Å in **1** is in the normal range for Mo−Mo quadruple bonds.[11a] The bond distances for the bridging ligand Mo−P (2.544(2) Å) and Mo−N (2.228(5) Å) are similar to those found in an analogous dimolybdenum complex with monosubstituted pyridine, $Mo_2(NCS)_4((Ph_2P)Py)_2$,[12] which are 2.545(2) and 2.228(5) Å, respectively. The Mo−P and Mo−Cl distances in **1** (Table 2) may also be compared with those in the class of $\beta$-isomers $Mo_2Cl_4(P\text{-}P)_2$[13] (P-P = dmpm, bis(dimethylphosphino)methane; dppm, bis(diphenylphosphino)methane; tdpm, tris(diphenylphosphino)methane; and dmdppm, dimethyl(diphenylphosphino)methane) that have the same trans arrangement of bridging diphosphine ligands with one bridgehead atom. The corresponding distances in **1** fall in the ranges found for the $\beta$-isomers, 2.54−2.66 Å for the Mo−P and 2.39−2.41 Å for the Mo−Cl. Molecule **1** has a totally eclipsed conformation, similarly to $Mo_2Cl_4(dmpm)_2$ and $Mo_2Cl_4(dppm)_2$, but unlike $Mo_2(NCS)_4((Ph_2P)Py)_2$ where the twist angle, P−Mo−Mo−N, is 10.8°.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for $Mo_2Cl_4(bdppp)_2$ in $\mathbf{1}\cdot 2CH_2Cl_2$ and $Re_2Cl_4(bdppp)_2$ (**2**)

| | **1** | **2** | |
|---|---|---|---|
| M−M | 2.149(1) | 2.2342(6) | |
| M−N | 2.228(5) | 2.109(9) | 2.097(9) |
| M−Cl | 2.411(2) | 2.374(3) | 2.384(3) |
| M−Cl | 2.402(2) | 2.362(3) | 2.377(3) |
| M−P | 2.544(2) | 2.397(3) | 2.388(2) |
| M•••P[a] | 3.259(2) | 3.113(3) | 2.980(3) |
| M−M−N | 106.1(1) | 102.2(3) | 102.8(3) |
| M−M−Cl | 103.56(5) | 101.70(7) | 100.42(7) |
| M−M−Cl | 106.97(5) | 105.91(7) | 105.47(8) |
| M−M−P | 87.18(5) | 88.91(8) | 90.14(8) |
| M−M−P[a] | 161.94(5) | 160.41(6) | 162.63(6) |
| N−M−P | 166.6(1) | 168.9(3) | 166.8(3) |
| Cl−M−Cl | 149.29(6) | 151.6(1) | 153.1(1) |

[a] Noncoordinated P atom.

The Re−Re distance in **2** (2.2342(6) Å) matches well those of other similar doubly bridged Re(II)−Re(II) species containing a Re−Re triple bond.[11b] The average Re−P (2.393(3) Å), Re−N (2.103(9) Å), and Re−Cl (2.374(3) Å) distances are shorter than those of the Mo complex **1** (Table 2) as typically found in analogous rhenium and molybdenum (or tungsten) compounds. Unfortunately, the crystal structure of the dirhenium complex with two trans (diphenylphosphino)pyridine ($Ph_2PPy$) ligands is still unknown, so we cannot make direct comparison to the metal-to-ligand distances in **2**. Both Re−P and Re−Cl bond distances seem normal if compared to those of the $\beta$-isomers of $Re_2Cl_4(P\text{-}P)_2$[14] (P-P = dppm and dppa, bis(diphenylphosphino)amine). However, it is well-known that the latter possess staggered conformations; this contrasts to the ligand arrangement in **2**, which is essentially eclipsed. The torsion angles for this triply bonded Re complex **2** (1.1−9.3°) are a little bit larger than for the quadruply bonded Mo analogue **1**.

We can now turn to the central point of the discussion, namely, the coordination mode of the $(Ph_2P)_2Py$ ligand. In **1** and **2** the ligand, 2,6-bis(diphenylphosphino)pyridine, exhibits a structural feature never seen before: it bridges over the M−M multiply bonded units through the phosphorus and nitrogen atoms, while the remaining phosphorus atom does not coordinate to any metal atom. This appears to be due to the short metal−metal separations found in the multiply bonded dimetal units and the limited flexibility of the bdppp ligand. Another contributing factor is the reluctance of the $Mo_2^{4+}$ units to attach axial ligands.[15]

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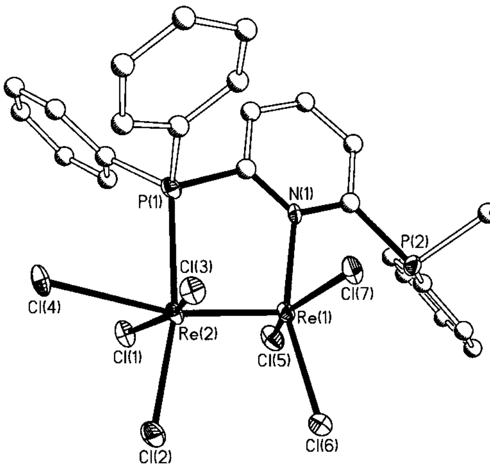

**Figure 3.** Perspective drawing of one crystallographically independent anion $[Re_2Cl_7(bdppp)]^-$. Atoms are represented by their thermal ellipsoids at the 40% probability level. Carbon atoms are shown as arbitrarily sized spheres and for clarity are not labeled. Hydrogen atoms are omitted.

The Mo•••P distances on both ends of molecule **1** are 3.259(2) Å, and the angles Mo−Mo−P are 161.94(5)°. Recently, similar molybdenum complexes bridged by dpmp ligands (dpmp = bis((diphenylphosphino)methyl)phenylphosphine), *trans*-$[Mo_2(O_2CR)_2(dpmp)_2](BF_4)_2$ (R = Me, Bu$^t$, Ph), were reported[16] to have the same type of coordination mode. The Mo•••P separations vary from 3.234 to 3.446 Å, indicative of the absence of any bonding interaction. Additional evidence of the nonbonding character of this separation in **1** is the fact that the distance from the Mo(1) atom to the P(2A) atom connected to the other side of the dimolybdenum unit (Figure 1) is even shorter (3.248 Å).

In the case of the rhenium complex **2** these distances are significantly different at both ends of molecule: the Re(2)−P(3) distance is 2.980(3) Å, while the Re(1)−P(1) distance is longer (3.113(3) Å). This shortening of the Re•••P separations is in accord with the longer M−M distances and shorter M−L distances in the rhenium compound **2** when compared to the molybdenum complex **1**. Still the Re(2)•••P(2) contact cannot be considered a bonding interaction. There is no dpmp analogue of complex **2**. All known rhenium complexes with dpmp ligands of the formula $[Re_2Cl_3(dpmp)_2]X$ (X = Cl, $PF_6$)[17] possess a structure in which the triphosphine is doubly bridging the dimetal unit with the central phosphorus atom coordinated to one rhenium atom, and both terminal phosphorus atoms coordinated to the other rhenium atom. This can be attributed to the greater flexibility of the methylene-bridged triphosphine ligands compared to the $(Ph_2P)_2Py$.[1i]

Complex **3** crystallizes in the space group $P\bar{1}$ with two pairs of crystallographically independent dirhenium anionic molecules per unit cell. There are also four highly disordered tetrabutylammonium cations and dichloromethane molecules. The dirhenium anion $[Re_2Cl_7(bdppp)]^-$ (Figure 3) is the first example of a compound with only one bdppp ligand bridging a dimetal unit. The ligand coordination mode is of the same type as for the molecules **1** and **2** (Chart 3) with one noncoordinated phosphorus atom "blocking", but not binding to, one of the axial positions of the dirhenium unit. The average Re•••P separation (for two molecules) is 3.136(5) Å with a Re−Re−P angle of 160.2(1)°. The other axial position of the $Re_2^{6+}$ unit is occupied by a chlorine atom. Thus the two rhenium atoms have coordination numbers 5 and 6, for Re(1) and Re(2), respectively (Figure 3). The axial chloride has a relatively weak interaction with the Re center as reflected by a bond length of 2.641(5) Å, which is ca. 0.3 Å larger than the other Re−Cl distances in **3** (average 2.325(5) Å).

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for Two Crystallographically Independent Molecules $[Bu^n_4N][Re_2Cl_7(bdppp)]$ in **3**$\cdot CH_2Cl_2$

| | | |
|---|---|---|
| Re−Re | 2.275(1) | 2.280(1) |
| Re−P | 2.487(5) | 2.460(5) |
| Re−N | 2.15(2) | 2.15(2) |
| Re−$Cl_{ax}$ | 2.646(5) | 2.636(5) |
| Re−$Cl_{transP}$ | 2.348(6) | 2.353(5) |
| Re−$Cl_{transN}$ | 2.299(6) | 2.290(6) |
| Re−$Cl_{transCl}$ | 2.326(5), 2.345(5), 2.307(5), 2.330(5) | 2.328(6), 2.336(5), 2.314(5), 2.333(6) |
| Re•••P[a] | 3.140(5) | 3.132(5) |
| Re−Re−P | 88.2(1) | 88.0(1) |
| Re−Re−N | 102.4(4) | 100.6(4) |
| Re−Re−$Cl_{ax}$ | 166.0(1) | 165.5(1) |
| Re−Re−P[a] | 160.6(1) | 159.7(1) |

[a] Noncoordinated P atom.

The Re−Re distances (2.275(1) and 2.280(1) Å) in the two molecules are among the longest known for quadruply bonded dirhenium species.[11c] They are even longer than that in the triply bonded complex **2**. The reason for the elongation must be the presence of an axial chloride ligand in **3**. This phenomenon was also observed in $Re_2(DMF)_4L_2$,[18] which have Re−Re bond lengths of 2.276 and 2.305 Å for L = Cl and OMe, respectively. Other examples are the complexes $(Ph_4As)_2Re_2(NCS)_8\cdot 2L$[19] with rhenium−rhenium distances of 2.270 Å for L = $(CH_3)_2O$ and 2.296 Å for L = $C_5H_5N$.

The Re−$Cl_{ax}$ distances in **3** (Table 3) are comparable to those in other dirhenium complexes having axial chlorides, e.g., $Re_2Cl_5(dppm)_2$[20] (2.575 Å), $Re_2Cl_5(NO)(dmpm)_2$[21] (2.621 Å), and $Re_2(DMF)_4Cl_2$ (2.527 Å).[18] The rest of the metal−ligand bond lengths in $[Re_2Cl_7(bdppp)]^-$ are very similar to the corresponding distances in **2**. However, there is a clear trans influence in **3** but not in **2**. The Re−P and Re−N bonds in **3** are trans to the Re−Cl bonds, while in **2** the former are trans to the Re−N and Re−P bonds and all Re−Cl bonds are trans to other Re−Cl bonds. That led to the slight elongation of the Re−P and Re−N distances for **3** but not to the doubly bridged complex **2**. Also, there are three sets of Re−Cl bond lengths among them: those trans to N atoms are the shortest, while those trans to P atoms are the longest. Like $Re_2Cl_4(bdppp)_2$ (**2**), the molecule of **3** is slightly twisted from the eclipsed configuration although the L−Re−Re−L torsion angles are all less than 12°.

## Conclusions

Dimolybdenum(II) and dirhenium(II) complexes $M_2Cl_4(bdppp)_2$ (**1**, **2**) were obtained by refluxing quadruply bonded $Mo_2Cl_8^{4-}$ and $Re_2Cl_8^{2-}$ anions with bdppp in methanol. A rare example of a quadruply bonded $Re_2^{6+}$ unit bridged by only one neutral ligand $[Bu^n_4N][Re_2Cl_7(bdppp)]$ (**3**) was found to be an intermediate in the latter process. In all cases coordination of the bdppp ligand to multiply bonded units with short metal−metal separations dictates the novel type of bonding for this

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ligand: a bidentate coordination through the nitrogen and only one phosphorus atom with the second phosphine unit remaining noncoordinated.

We believe that the new compounds obtained in this work could serve as precursors for the synthesis of polynuclear bimetallic complexes containing metal−metal bonds. One of the possible ways to achieve this goal is to use mononuclear chlorides of Co and Sn, for example, capable of coordinating through the dangling phosphine end. These studies are currently under way.

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**Supporting Information Available:** Three X-ray files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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