Table VI the experimental data are summarized for benzonorbornadiene (**14**), urazole **4**, and PTAD.

Control Experiments. Thermal Stability of Urazole 30: A 50-mg (0.24 mmol) sample of urazole **30** was sublimed at 0.1 torr through a hot tube kept at ca. 400 °C. The urazole **30** was recovered unchanged.

Acetone Trapping: A sample of 0.30 g (2.10 mmol) of benzonorbornadiene (**14**) was allowed to react with 0.37 g (2.1 mmol) of PTAD in 50 mL of absolute acetone as solvent at ca. 30 °C for 3 days. Only rearranged urazole **4** was detected as product.

Galvinoxyl Trapping: A sample of 0.20 g (2.0 mmol) of norbornene (**16**) was allowed to react with 0.15 g (0.86 mmol) of PTAD in the presence of 0.15 g (0.36 mmol) of galvinoxyl in 30 mL of methylene chloride at ca. 25 °C. Only rearranged urazole **5** was detected as product.

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Multiply Bonded Dimetal Complexes Containing Bis(diphenylphosphino)methane Bridges: Complexes Possessing Rhenium-Rhenium Double Bonds and a Tungsten-Tungsten Single Bond

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Abstract: The quadruply bonded dirhenium(III) complex $(n\text{-}Bu_4N)_2Re_2Cl_8$ reacts with bis(diphenylphosphino)methane (dppm) in dichloromethane to produce the complex $Re_2Cl_6(dppm)_2$ (I). The structurally analogous complex $Re_2Cl_6(Ph_2Ppy)_2$ (II) has been isolated from the reaction between $(n\text{-}Bu_4N)_2Re_2Cl_8$ and Ph_2Ppy in acetonitrile. When primary alcohols (ROH) are used as solvents, $(n\text{-}Bu_4N)_2Re_2Cl_8$ reacts with dppm to form the alkoxide complexes $Re_2Cl_5(OR)(dppm)_2$ (R = CH_3, IIIa; R = CH_2CH_3, IIIb; R = $CH_2CH_2CH_3$, IIIc). When the quadruply bonded complex $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$ is used in place of $(n\text{-}Bu_4N)_2Re_2Cl_8$, then the reaction with dppm in methanol yields $Re_2Cl_4(dppm)_2$, while with diethyl ether as the solvent $Re_2Cl_5(dppm)_2$ is formed. All of the preceding complexes exhibit well-defined electrochemical properties. Electrolysis of dichloromethane solutions of $Re_2Cl_4(dppm)_2$, containing an excess of Cl^-, at a potential of +0.60 V vs. SCE first generates $Re_2Cl_5(dppm)_2$, which is in turn converted to $Re_2Cl_6(dppm)_2$. This potential (+0.60 V) is sufficient to oxidize $Re_2Cl_4(dppm)_2$ to its monocation and, following the conversion of the latter to $Re_2Cl_5(dppm)_2$ upon its reaction with Cl^-, also to convert $Re_2Cl_5(dppm)_2$ to $[Re_2Cl_5(dppm)_2]^+$, which in turn reacts with Cl^-. The complexes I and IIIb have been structurally characterized by X-ray crystallography and shown to have structures which conform to the notion that these molecules possess rhenium-rhenium double bonds as predicted by Hoffmann. Using the bidentate ligand bis(diphenylphosphino)amine (dppa), we have prepared the complexes $Re_2Cl_6(dppa)_2$, $Re_2Cl_4(dppa)_2$, and $Re_2Cl_4(PMePh_2)_2(dppa)$ and the $[ReCl_2(dppa)_2]^+$ cation (either as the Cl^- or PF_6^- salt). The spectroscopic and electrochemical properties of the dirhenium species show a very close similarity to those of their dppm analogues, implying a close similarity of structure. To further explore the influence of replacing a terminal Cl ligand by OR on the M-M bond length we have also examined the structure of $W_2(\mu\text{-O-}i\text{-Pr})_2(\text{O-}i\text{-Pr})_6Cl_2$ and compare it with that of $W_2(\mu\text{-OEt})_2(OEt)_4Cl_4$. Again the OR for Cl replacement causes a lengthening of the M-M bond. $Re_2Cl_6(dppm)_2$ crystallizes in the monoclinic space group $C2/c$ with cell parameters a = 23.083 (3) Å, b = 10.866 (3) Å, c = 23.253 (5) Å, β = 124.25 (2)°, Z = 4. The structure of $Re_2Cl_5(OC_2H_5)(dppm)_2$ was solved and refined in the orthorhombic space group $Pn2_1a$ with cell parameters a = 24.099 (8) Å, b = 18.225 (4) Å, c = 12.565 (4) Å. $W_2(\text{O-}i\text{-Pr})_8Cl_2$ forms monoclinic crystals in space group $C2/m$ with a = 17.706 (4) Å, b = 12.034 (2) Å, c = 9.727 (2) Å, β = 123.74 (2)°, Z = 2.

Four important types of substitution reactions that can occur in the reaction chemistry of the octahalodirhenium(III) anion, $[Re_2X_8]^{2-}$, are as follows: (1) simple substitution where the quadruple bond is retained; (2) nonreductive substitution where the multiple bond is retained but is reduced to an order lower than 4; (3) reductive substitution where the multiple bond is retained but is of an order lower than 4; and (4) substitution where complete disruption of the metal-metal bond occurs. Tertiary phosphine complexes, in particular, comprise some of the best defined and most thoroughly studied examples of these types of substitution reactions.[2]

Recently we renewed our interest in the nature of the substitution products that arise when bidentate bridging ligands are used because of the range of interesting derivatives that are formed upon reacting the $[Re_2Cl_8]^{2-}$ anion with the Ph_2Ppy ligand.[3] One such derivative was of stoichiometry $[ReCl_3(Ph_2Ppy)]_n$ and was isolated from the reaction of $[Re_2Cl_8]^{2-}$ with Ph_2Ppy in acetonitrile.[3b] Its spectroscopic and electrochemical properties indicated that it bore a close structural relationship to the previously reported

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(1) (a) Purdue University. (b) Texas A&M University.

(2) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; and references therein.

(3) (a) Barder, T. J.; Tetrick, S. M.; Walton, R. A.; Cotton, F. A.; Powell, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 4090. (b) Barder, T. J.; Cotton, F. A.; Powell, G. L.; Tetrick, S. M.; Walton, R. A. *Ibid.* **1984**, *106*, 1323.

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complex $Re_2Cl_6(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$),[2,4] a molecule that has proven to be of special interest in its own right. Although the structure of $Re_2Cl_6(dppm)_2$ had not at the time been definitively established, it was proposed from XPS data[4] that it possessed the chlorine-bridged structure $Re_2(\mu\text{-}Cl)_2Cl_4(\mu\text{-}dppm)_2$. Later, Shaik and Hoffmann[5] predicted from a theoretical study of this and other d^4–d^4 M_2L_{10} type complexes that, because of the strong tendency for dppm to bridge dimetal units, the structure of $Re_2Cl_6(dppm)_2$ could be rationalized in terms of a rhenium–rhenium double bond ($\sigma^2\pi^2\delta^2\delta^{*2}$ configuration). If so, then the preparations of the complexes $Re_2Cl_6(dppm)_2$ and $Re_2Cl_6(Ph_2Ppy)_2$ from $[Re_2Cl_8]^{2-}$ provide unusual examples of substitution reactions of type 2.

The complex $Re_2Cl_6(dppm)_2$ is of further interest in that it constitutes a member of the series $Re_2Cl_4(dppm)_2$,[4] $Re_2Cl_5(dppm)_2$,[6] and $Re_2Cl_6(dppm)_2$ that are formally related to one another by one-electron oxidation (or reduction) changes with concomitant gain (or loss) of Cl^-.

In order to clarify the structural chemistry of these systems we have succeeded in solving the crystal structure of $Re_2Cl_6(dppm)_2$. Furthermore, in the course of exploring the synthetic routes that afford this complex, we have isolated a series of complexes $Re_2Cl_5(OR)(dppm)_2$ in which one of the terminal chloride ligands of $Re_2Cl_6(dppm)_2$ has been replaced by an alkoxide. The crystallographic details of both $Re_2(\mu\text{-}Cl)_2Cl_4(dppm)_2$ and $Re_2(\mu\text{-}Cl)_2Cl_3(OEt)(dppm)_2$ are reported along with our results on the electrochemistry of the series of complexes $Re_2Cl_n(dppm)_2$ (n = 4–6). In addition, the synthesis and characterization of several new dirhenium complexes containing the ligand $Ph_2PNHPPh_2$ (dppa) (which is electronically and sterically related to dppm) are also reported. In view of the observation that replacement of one terminal ligand in $Re_2Cl_6(dppm)_2$ by an alkoxide ion causes the Re=Re bond to become ca. 0.05 Å longer, we determined the structure of $W_2(\mu\text{-}O\text{-}i\text{-}Pr)_2(O\text{-}i\text{-}Pr)_6Cl_2$ for comparison with that of $W_2(\mu\text{-}OEt)_2(OEt)_4Cl_4$ (which we have previously reported[7]) to see if this effect is general.

Experimental Section

Starting Materials. The systematic names of the bidentate ligands, together with their abbreviations are as follows: (a) bis(diphenylphosphino)methane, dppm; (b) bis(diphenylphosphino)amine, dppa. The ligand dppa was prepared by the procedure of Nöth et al.[8] The complexes $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$,[9] $Re_2Cl_4(PMe_2Ph)_4$,[9] $(n\text{-}Bu_4N)_2Re_2Cl_8$,[10] and $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$[11] were prepared according to established literature procedures.

Solvents used in the preparation of complexes were, unless otherwise stated, of commercial grade and were thoroughly deoxygenated prior to use. The dichloromethane used in the electrochemical experiments was of the highest purity commercially available and was used without further purification.

Reaction Procedures. All reactions were carried out in a nitrogen atmosphere by using standard vacuum line techniques.

(A) Preparation of dppm Complexes. (i) **$Re_2Cl_6(dppm)_2\cdot{}^2/_3CH_2Cl_2$.** A solution of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.20 g, 0.18 mmol) and dppm (0.25 g, 0.65 mmol) in dichloromethane (5 mL) was refluxed for 16 h. The resulting dark purple crystals were filtered off, washed with diethyl ether, and dried under vacuum; yield 0.18 g (73%). Anal. Calcd for $C_{50.67}H_{45.33}Cl_{7.33}P_4Re_2$: C, 42.86; H, 3.24; Cl, 18.43. Found: C, 42.9; H, 3.32; Cl, 18.4.

If this same reaction is carried out in acetonitrile or acetone, purple solids can also be isolated which exhibit the same spectroscopic and electrochemical properties as the above complex but they are obtained in lower yields.

(ii) **$Re_2Cl_5(OMe)(dppm)_2$.** A mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.20 g, 0.18 mmol) and dppm (0.20 g, 0.52 mmol) was refluxed in a mixture of *reagent grade* methanol (10 mL) and *dry* diethyl ether (10 mL) for 30 min with rapid stirring. The purple solid was filtered off and dissolved in a 5:1 (v/v) toluene–dichloromethane mixture (50 mL) and the resulting solution allowed to stand for 2 h. The extract was filtered to remove any $Re_2Cl_6(dppm)_2$ and the filtrate evaporated to dryness. The resulting solid was recrystallized from dichloromethane by the slow addition of diethyl ether; yield 0.22 g (93%). Anal. Calcd for $C_{51}H_{47}Cl_5OP_4Re_2$: C, 45.39; H, 3.51. Found: C, 44.6; H, 3.31.

(iii) **$Re_2Cl_5(OEt)(dppm)_2$.** A mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.30 g, 0.26 mmol) and dppm (0.30 g, 0.78 mmol) was refluxed for 1 h with rapid stirring in a mixture of *reagent grade* ethanol (20 mL) and dichloromethane (5 mL). The purple solid was filtered off and worked up as described in A(ii); yield 0.20 g (56%). Anal. Calcd for $C_{52}H_{49}Cl_5OP_4Re_2$: C, 45.81; H, 3.62. Found: C, 45.2; H, 3.50.

We were also able to isolate the analogous *n*-propoxide and *n*-butoxide products in 77% and 44% yields, respectively, using this procedure but substituting the appropriate *reagent grade* primary alcohol for ethanol. These complexes exhibit spectroscopic and electrochemical properties similar to those of the methoxide and ethoxide products, thereby establishing the homology between them. We found that the use of reagent grade alcohol solvents is apparently very important since when the drier spectroscopic grade solvents were used the yield of the corresponding alkoxide product decreased dramatically, with a concomitant increase in the formation of $Re_2Cl_5(dppm)_2$. It appears that small (but critical) amounts of water in the reaction mixtures play a significant role in ways not yet understood in dictating the product distribution.

Under no circumstances were we able to detect the formation of any significant quantities of alkoxide products when secondary alcohols were used. The major product formed in these reactions was $Re_2Cl_6(dppm)_2$.

(iv) **$Re_2Cl_5(dppm)_2\cdot(C_2H_5)_2O$.** A solution of $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$ (0.20 g, 0.20 mmol) and dppm (0.30 g, 0.78 mmol) in dry diethyl ether (15 mL) was refluxed for 1.5 days with stirring. The brown solid was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.11 g (39%). Anal. Calcd for $C_{54}H_{54}Cl_4OP_4Re_2$: C, 46.58; H, 3.91. Found: C, 45.8; H, 4.08. Its spectroscopic and electrochemical properties were identical with those of an authentic sample of this complex prepared by a different method.[6] The presence of lattice diethyl ether was confirmed by ^1H NMR spectroscopy on a $CDCl_3$ solution of this paramagnetic complex (δ +3.52 ($-CH_2-$) and +1.23 ($-CH_3$)).

(v) **$Re_2Cl_4(dppm)_2$.** A methanol solution (30 mL) containing $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$ (0.50 g, 0.51 mmol) and dppm (0.50 g, 1.3 mmol) was refluxed for 15 min with stirring. The resulting purple solid was filtered off and washed with diethyl ether. The complex can be recrystallized from dichloromethane by the slow addition of methanol; yield 0.50 g (77%). Anal. Calcd for $C_{50}H_{44}Cl_4P_4Re_2$: C, 46.81; H, 3.46. Found: C, 46.3; H, 3.66. This procedure represents a superior method for the preparation of this complex over that reported previously.[4]

(B) Preparation of dppa Complexes. (i) **$Re_2Cl_6(dppa)_2$.** A solution of $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$ (0.20 g, 0.20 mmol) and dppa (0.30 g, 0.78 mmol) in freshly distilled (over Na/benzophenone) benzene (10 mL) was refluxed without stirring for 30 min. The dark purple crystals that separated were filtered off, washed with methanol to remove the yellow $[ReCl_2(dppa)_2]Cl$ impurity and then with diethyl ether, and dried under vacuum; yield 0.17 g (62%). Anal. Calcd for $C_{48}H_{42}Cl_6N_2P_4Re_2$: C, 42.52; H, 3.12. Found: C, 43.0; H, 3.57.

(ii) **$Re_2Cl_4(dppa)_2\cdot2.5C_6H_6$.** A solution containing $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ (0.30 g, 0.26 mmol) and dppa (0.30 g, 0.78 mmol) in freshly distilled (over Na/benzophenone) benzene (15 mL) was refluxed without stirring for 4 h. The resulting blue-purple crystals were filtered off, washed with diethyl ether, and dried under vacuum; yield 0.16 g (42%). Anal. Calcd for $C_{63}H_{57}Cl_4N_2P_4Re_2$: C, 51.11; H, 3.88; Cl, 9.58. Found: C, 51.4; H, 3.93; Cl, 9.71.

(iii) **$Re_2Cl_4(PMe_2Ph)_2(dppa)$.** A solution containing $Re_2Cl_4(PMe_2Ph)_4$ (0.30 g, 0.27 mmol) and dppa (0.30 g, 0.78 mmol) in freshly distilled (over Na/benzophenone) toluene (10 mL) was refluxed without stirring for 16 h. The dark blue-purple crystals were filtered off, washed with diethyl ether, and dried under vacuum; yield 0.31 g (93%). Anal. Calcd for $C_{40}H_{43}P_4NCl_4Re_2$: C, 40.86; H, 3.69. Found: C, 41.4; H, 3.99.

(iv) **$[ReCl_2(dppa)_2]Cl$.** A solution containing $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.20 g, 0.18 mmol) and dppa (0.30 g, 0.78 mmol) in acetone (7 mL) was refluxed for 30 min. The orange solid that precipitated was filtered off and washed with diethyl ether. The solid was then extracted with 10 mL of methanol and filtered to remove any purple $Re_2Cl_6(dppa)_2$. The yellow filtrate was treated with diethyl ether (20 mL) and then maintained at 0 °C for 4 days. The yellow-orange crystals were filtered off and washed with diethyl ether; yield 0.08 g (43%). Anal. Calcd for $C_{48}H_{42}Cl_3NP_4Re$: C, 54.23; H, 3.98. Found: C, 53.5; H, 4.23.

The PF_6^- salt of this cation can be generated by dissolving the chloride salt in acetone containing an excess of KPF_6. An excess of water was

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[4] Ebner, J. R.; Tyler, D. R.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 833.

[5] Shaik, S.; Hoffmann, R.; Fisel, R. C.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555.

[6] Cotton, F. A.; Shive, L. W.; Stults, B. R. *Inorg. Chem.* **1976**, *15*, 2239.

[7] Cotton, F. A.; DeMarco, D.; Kolthammer, B. W. S.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 3048.

[8] Nöth, H.; Meinel, L. *Z. Anorg. Allg. Chem.* **1967**, *349*, 225.

[9] Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1975**, *14*, 1987.

[10] Barder, T. J.; Walton, R. A. *Inorg. Chem.* **1982**, *21*, 2510.

[11] San Filippo, J., Jr. *Inorg. Chem.* **1972**, *11*, 3140.

Table I. Crystallographic Parameters

formula	$Re_2Cl_6(dppm)_2$: $Re_2Cl_6P_4C_{50}H_{44}$	$Re_2Cl_5(OEt)(dppm)_2$; $Re_2Cl_5P_4O_1C_{52}H_{49}$	$W_2Cl_2O_8C_{24}H_{56}$
formula weight	1353.9	1363.5	911.32
space group	$C2/c$	$Pn2_1a$	$C2/m$
systematic absences	hkl: $h + k = 2n$; $h0l$: $l = 2n$	$0kl$: $k + l = 2n$; $hk0$: $h = 2n$	hkl: $h + k = 2n$
a, Å	23.083 (3)	24.099 (8)	17.706 (4)
b, Å	10.866 (3)	18.255 (4)	12.034 (2)
c, Å	23.253 (5)	12.565 (4)	9.727 (2)
β, deg	124.25 (2)		123.74 (2)
V, Å^3	4756 (2)	5534 (2)	1723.5 (9)
Z	4	4	2
d_{calcd}, g/cm^3	1.891	1.636	1.756
crystal size, mm	0.3 × 0.2 × 0.2	0.1 × 0.1 × 0.05	0.2 × 0.2 × 0.2
μ(Mo Kα), cm^{-1}	56.65	48.23	70.07
data collection instrument	Syntex P$\bar{1}$	CAD-4	Syntex P$\bar{1}$
radiation (monochromated incident beam)	Mo Kα	Mo Kα	Mo Kα
orientation reflections, number, range (2θ), deg	15, $17 \leq 2\theta \leq 26$	25, $18 \leq 2\theta \leq 28$	15, $23 \leq 2\theta \leq 31$
temp, °C	room temp	room temp	room temp
scan method	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
data collection range, 2θ, deg	5–50; $+h, +k, \pm l$	5–45; $+h, +k, +l$	5–50; $+h, +k, \pm l$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	2810	3273	1145
no. of parameters refined	288	556	91
trans factors, max, min	1.0, 0.51	1.0, 0.81	1.0, 0.82
R^a	0.036	0.053	0.026
$R_w{}^b$	0.045	0.063	0.034
quality of fit indicator^c	1.267	1.485	0.8
largest shift/esd, final cycle	0.01	0.62	0.01
largest peak, e/Å^3	1.2	1.4	0.9

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

added to this solution to precipitate orange $[ReCl_2(dppa)_2]PF_6$, which can be recrystallized from acetone–diethyl ether.

(C) Preparation of $W_2(\mu$-O-i-Pr$)_2$(O-i-Pr$)_6Cl_2$. Pale green cuboidal crystals of this compound were obtained as a byproduct in a reaction between W_2(O-i-Pr$)_6py_2$ and (n-Bu_4N)Cl. Optimum conditions for the synthesis of this compound have not been established. The relatively easy oxidation of Mo^{III} and W^{III} alkoxides is, of course, well-known[12] and in that sense the formation of this compound is not particularly surprising.

Preparation of Single Crystals for Structure Determination. Crystals of $Re_2Cl_6(dppm)_2$ that were suitable for X-ray crystallographic studies were grown by layering an acetone solution of dppm over a dichloromethane solution containing (n-$Bu_4N)_2Re_2Cl_8$. During a period of several days, diffusion occurred slowly enough to permit satisfactory crystal growth. The procedure used to grow crystals of $Re_2Cl_5(OEt)(dppm)_2$ consisted of dissolving a sample of the complex in dichloromethane (20 mL) and then adding diethyl ether (100 mL) and allowing the solution to stand for 2 days. Suitable crystals of $W_2(\mu$-O-i-Pr$)_2$(O-i-Pr$)_6Cl_2$ were obtained directly as described above.

X-ray Crystallography. For each of the three compounds a single crystal was either mounted on the tip of a glass fiber (the Re compounds) or embedded in epoxy cement inside a glass capillary (the W compound). All basic information pertaining to the crystallography is summarized in Table I. The solution and refinement of the structure were accomplished in each case by applying conventional procedures that have been described in general terms elsewhere.[13] No unusual problems were encountered. A detailed account of the procedures is available as supplementary material.

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 were recorded on Cary 17D and IBM 9420 spectrophotometers. Electrochemical experiments were performed by using 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 uncorrected for junction potentials. $^{31}P\{^1H\}$ NMR spectra were recorded on 1:1 $CDCl_3/CH_2Cl_2$ solutions with a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock using aqueous 85% H_3PO_4 as an external standard. Positive chemical shifts were measured downfield from H_3PO_4. ^1H NMR spectra were recorded on CD_2Cl_2 solutions with Varian XL-200 and Nicolet NT-470 Fourier transform spectrometers. Magnetic susceptibility measurements were performed by Dr. Thomas J. Smith, Kalamazoo College, using a Cahn/Ventron Faraday Susceptibility Balance; the complex $Hg[Co(NCS)_4]$ was used as the calibrating standard while diamagnetic corrections were estimated from Pascal's constants.

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) Synthesis and Preliminary Characterization of $Re_2Cl_6(dppm)_2$ and $Re_2Cl_5(OR)(dppm)_2$ (R = Me, Et, n-Pr, and n-Bu).

In an earlier paper[4] we described the preparation of purple materials with a stoichiometry approximating to $[ReCl_3(dppm)]_n$ from the reactions of (n-$Bu_4N)_2Re_2Cl_8$ with dppm in acetonitrile and in methanol (the latter containing a trace of hydrochloric acid).[14] Primarily on the basis of X-ray photoelectron spectroscopic measurements we concluded that this complex most likely possesses a structure containing both dppm and chloride bridges, viz., $Re_2(\mu$-Cl$)_2Cl_4(dppm)_2$.[4] However, clouding this structural issue was some question as to the purity of the products isolated from acetonitrile and a puzzling (and unexplained) feature in the IR spectrum of the products from methanol, namely, a quite intense band at 1060 cm^{-1} that was not seen in the related spectra of the products isolated from acetonitrile. Soon thereafter, we were able to report[6] that the reaction between (n-$Bu_4N)_2Re_2Cl_8$ and dppm in acetone produced both $Re_2Cl_6(dppm)_2$ and $Re_2Cl_5(dppm)_2$, the latter complex being fully characterized through an X-ray crys-

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[12] Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

[13] (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. (c) North, A. C. T.; Phillips, D. C.; Mathews, F. A. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351. (d) Calculations were done on a VAX 11/780 computer with software from the Enraf-Nonius VAX-SDP package. (e) Data for $Re_2Cl_5(OEt)(dppm)_2$ were collected by Molecular Structure Corporation, College Station, TX.

[14] In the case of the reaction in acetonitrile, this product contained one CH_3CN of "solvation" per rhenium atom.[4]

Table II. Selected Spectral Data for Dirhenium Complexes

	electronic absorption maxima,[a] nm	infrared spectra[b]
$Re_2Cl_6(dppm)_2 \cdot {}^2/_3CH_2Cl_2$ (I)	1435 (300), 516 (1700)	355 m, *312 s, 282 m, 273 sh*
$Re_2Cl_6(Ph_2Ppy)_2$ (II)	1525 (500), 516 (2200), 430 (7500)	366 m-w, *325 sh, 317 s, 285 m*
$Re_2Cl_5(OR)(dppm)_2$		
R = CH_3 (IIIa)	545 (2500), 400 sh	350 m, *307 s, 283 m, 274 sh*
R = CH_2CH_3 (IIIb)	550 (2500), 400 sh	350 s, *306 s, 276 m-s*
R = $CH_2CH_2CH_3$ (IIIc)	545 (2800), 400 sh	350 s, *308 s, 292 m, 274 s*
$Re_2Cl_6(dppa)_2$	1520 (500), 645 sh, 530 (1400)	357 m, *312 s, 280 m*
$Re_2Cl_5(dppm)_2 \cdot (C_2H_5)_2O$	1530 (1700), 440 (1500)	*316 m, 291 s*
$Re_2Cl_4(dppm)_2$	680 sh, 510 (500), 420 sh	*336 s, 304 s*
$Re_2Cl_4(dppa)_2 \cdot 2.4C_6H_6$	635 (400), 510 (500), 440 sh	*334 s, 306 s*
$Re_2Cl_4(PMe_2Ph)_2(dppa)$	560, 425	*311 s, 280 s*
$[ReCl_2(dppa)_2]PF_6$	470 (1800), 425 (2500), 400 sh, 350 sh	*333 vs*

[a] Recorded on CH_2Cl_2 solutions; molar extinction coefficients given in parentheses. [b] Recorded on Nujol mulls; w = weak; m = medium; s = strong; vs = very strong; sh = shoulder. Modes assigned to ν(Re–Cl) are given in italics.

tallographic study. In the present work, while we have confirmed that $Re_2Cl_6(dppm)_2$ (I) can be prepared by using either acetonitrile or acetone as solvent, we find that dichloromethane is the solvent of choice since it affords I in good yield and with little contamination from other rhenium-containing species. As mentioned above, when acetone is the reaction solvent, I is contaminated with $Re_2Cl_5(dppm)_2$. When acetonitrile is used, we have been able to show that small quantities of $Re_2Cl_4(dppm)_2$ are also formed and that this complex subsequently reacts with acetonitrile to generate the same compound[15] that we now know is the source of the contamination present in our original samples of $Re_2Cl_6(dppm)_2$.[4] The spectroscopic properties of samples of $Re_2Cl_6(dppm)_2$ (IR spectra and electronic absorption spectra) as prepared from dichloromethane match exactly the corresponding data for samples isolated from acetonitrile (the latter results were reported previously in ref 4). These properties (see Table II) in turn resemble closely those for the 2-(diphenylphosphino)pyridine complex $Re_2Cl_6(Ph_2Ppy)_2$ (II),[3b] thereby implying a similarity of structure. This conclusion is supported by the electrochemical properties of these two complexes (vide infra).

One surprising feature of the electronic absorption spectra of complexes I and II is the broad, rather intense absorption in the near-IR region at ca. 1500 nm (Table II). While absorption bands in this vicinity characterize $Re_2Cl_5(dppm)_2$ (Table II) and other paramagnetic complexes containing the Re_2^{5+} core,[2,16,17] we cannot attribute the presence of such a band in the spectra of I and II to impurities of this type; indeed, other measurements (such as cyclic voltammetry and ESR spectroscopy) clearly demonstrate the absence of any significant contamination by $Re_2Cl_5(dppm)_2$ and its ilk. Accordingly, while the detailed assignment of this low-energy band in the spectra of I and II remains as yet unknown (although it is almost certainly a metal-based transition), we do believe that this is a spectral feature diagnostic of these two complexes and others of this kind.

Table III. Atomic Positional Parameters for $Re_2Cl_6(dppm)_2$[a,b]

atom	*x*	*y*	*z*	*B*, Å^2
Re	0.21319 (1)	0.20119 (3)	0.02490 (2)	2.592 (6)
Cl(1)	0.23646 (9)	0.8986 (2)	0.4407 (1)	3.19 (5)
Cl(2)	0.1608 (1)	0.0097 (2)	0.0205 (1)	3.96 (6)
Cl(3)	0.1645 (1)	0.2566 (3)	0.0971 (1)	3.99 (5)
P(1)	0.1067 (1)	0.7281 (2)	0.4264 (1)	3.08 (6)
P(2)	0.3085 (1)	0.1161 (2)	0.1305 (1)	3.10 (5)
C(1)	0.3836 (4)	0.2072 (9)	0.1529 (4)	3.3 (2)
C(11)	0.0397 (4)	0.842 (1)	0.3971 (5)	4.0 (2)
C(12)	0.0238 (5)	0.918 (1)	0.3416 (5)	5.1 (3)
C(13)	0.9727 (5)	0.003 (1)	0.3244 (6)	6.3 (3)
C(14)	0.0605 (5)	0.014 (1)	0.1400 (6)	6.6 (4)
C(15)	0.0440 (5)	0.939 (1)	0.0823 (6)	7.4 (4)
C(16)	−0.0053 (5)	0.854 (1)	0.0634 (6)	6.4 (3)
C(21)	0.3010 (4)	0.127 (1)	0.2106 (4)	3.9 (2)
C(22)	0.2654 (6)	0.035 (1)	0.2238 (6)	7.5 (4)
C(23)	0.2559 (6)	0.043 (1)	0.2823 (6)	7.8 (4)
C(24)	0.2810 (5)	0.135 (1)	0.3284 (5)	5.9 (3)
C(25)	0.1833 (6)	0.727 (1)	0.1826 (5)	5.8 (3)
C(26)	0.8265 (5)	0.7212 (9)	0.2589 (5)	4.5 (3)
C(31)	0.5655 (4)	0.088 (1)	0.4317 (5)	4.0 (2)
C(32)	0.4994 (5)	0.071 (1)	0.3787 (6)	6.9 (4)
C(33)	0.5333 (5)	0.960 (1)	0.1185 (6)	7.2 (4)
C(34)	0.4994 (5)	0.874 (1)	0.0677 (6)	6.3 (3)
C(35)	0.4350 (5)	0.894 (1)	0.0152 (5)	5.3 (3)
C(36)	0.4029 (4)	−0.005 (1)	0.5151 (5)	4.5 (3)
C(41)	0.6644 (4)	0.9585 (9)	0.3670 (5)	4.1 (3)
C(42)	0.3087 (5)	0.8827 (9)	0.0753 (5)	4.5 (3)
C(43)	0.3323 (6)	0.764 (1)	0.0821 (7)	6.0 (4)
C(44)	0.8782 (7)	0.219 (1)	0.1434 (8)	8.0 (5)
C(45)	0.5941 (9)	0.790 (1)	0.2989 (9)	11.0 (7)
C(46)	0.3849 (7)	0.916 (1)	0.1954 (8)	8.9 (5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Estimated standard deviations are given in parentheses.

Turning now to the reactions between $(n\text{-}Bu_4N)_2Re_2Cl_8$ and dppm in alcohol solvents, we find that similar products are formed in methanol, ethanol, 1-propanol, and 1-butanol, and these resemble the product described previously[4] as forming when acidified methanol was used as the reaction solvent. The crystal structure of the product isolated from ethanol (vide infra) shows that this class of complexes comprises the alkoxide derivatives $Re_2(\mu\text{-}Cl)_2Cl_3(OR)(dppm)_2$ (III). They are therefore structurally related to I, except that one of the terminal chlorine ligands has been replaced by an alkoxide ligand. These complexes form only when primary alcohols are used and, interestingly, they cannot be prepared by the direct reaction of $Re_2Cl_6(dppm)_2$ with the refluxing alcohol. The use of 2-propanol and 2-butanol produces I as the major product with no evidence for the formation of any III. We have been successful in isolating alkoxide complexes for R = Me (IIIa), Et (IIIb), *n*-Pr (IIIc), and *n*-Bu (IIId). Since the *n*-butoxide showed electrochemical and spectroscopic properties that were very similar to those of the other alkoxide derivatives, we chose not to investigate this particular derivative in any detail.

A comparison of the spectroscopic data for these alkoxide complexes with the corresponding data for I and II showed some notable differences. The IR spectra of the alkoxide complexes are quite similar to that of I in the region 4000–50 cm^{-1}, except for an intense band ca. 1050 cm^{-1} that is probably due to the presence of the OR group. The electronic absorption spectra (1900–300 nm) of the alkoxide complexes, like I, also display a band near 520 nm but, unlike I, do not exhibit a low-energy absorption near 1500 nm.

(b) Crystal Structures of $Re_2Cl_6(dppm)_2$ (I), $Re_2Cl_5(OEt)(dppm)_2$ (IIIb), and $W_2(\mu\text{-}O\text{-}i\text{-}Pr)_2(O\text{-}i\text{-}Pr)_6Cl_2$. Atomic coordinates for the three compounds are listed in Tables III–V. Table VI gives selected bond distances and angles in the three com-

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(15) We have shown from separate experiments that $Re_2Cl_4(dppm)_2$ reacts with various nitriles to produce diamagnetic complexes possessing a stoichiometry close to $[ReCl_2(dppm)(NCR)]_n$. We are currently investigating these complexes in order to establish the details of their structure and chemical reactivity.

(16) Ebner, J. R.; Walton, R. A. *Inorg. Chim. Acta* **1975**, *14*, L45.

(17) Brant, P.; Salmon, D. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 4424.

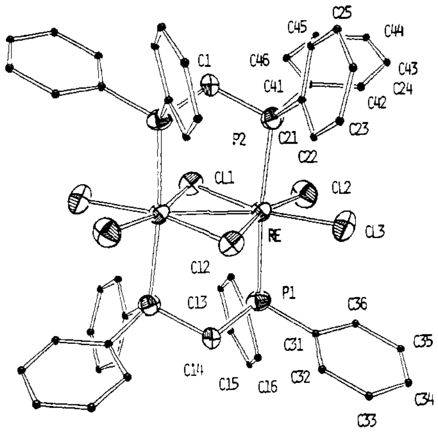

Figure 1. Molecular structure of $Re_2Cl_6(dppm)_2$ (I) showing the atomic numbering. Phenyl carbon atoms are arbitrarily small to minimize overlap. Other atoms are represented by ellipsoids of thermal vibration at the 30% probability level.

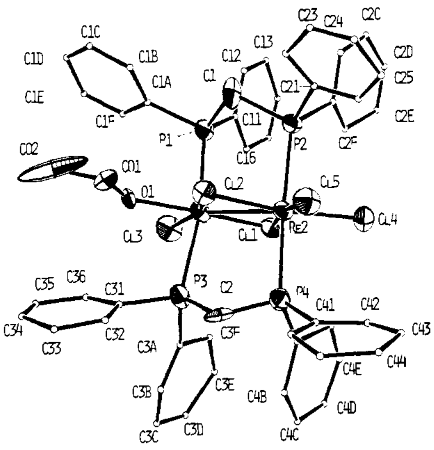

Figure 2. Molecular structure of $Re_2Cl_5(OC_2H_5)(dppm)_2$ (IIIb). The atoms are represented as in Figure 1.

Table IV. Atomic Positional Parameters for $Re_2Cl_5(OC_2H_5)(dppm)_2$ [a,b]

atom	*x*	*y*	*z*	*B*, Å^2
Re(1)	0.38708 (4)	0.080	0.07461 (8)	2.58 (2)
Re(2)	0.30970 (4)	−0.00261 (8)	−0.01822 (7)	2.50 (2)
Cl(1)	0.3999 (3)	−0.0429 (4)	0.0290 (5)	3.0 (1)
Cl(2)	0.2967 (3)	0.1276 (4)	0.0306 (5)	3.2 (1)
Cl(3)	0.4831 (3)	0.0763 (5)	0.1336 (5)	4.2 (2)
Cl(4)	0.2917 (3)	−0.1210 (4)	−0.0762 (6)	4.0 (2)
Cl(5)	0.2177 (3)	0.0268 (4)	−0.0917 (6)	4.1 (2)
P(1)	0.3582 (3)	0.0478 (4)	0.2553 (6)	2.8 (1)
P(2)	0.2647 (3)	−0.0331 (4)	0.1508 (5)	2.6 (1)
P(3)	0.4188 (3)	0.1370 (4)	−0.0973 (6)	3.2 (2)
P(4)	0.3417 (3)	0.0283 (4)	−0.1989 (6)	3.0 (1)
O(1)	0.3981 (7)	0.1850 (8)	0.136 (1)	3.2 (4)
C(O1)	0.361 (1)	0.237 (2)	0.151 (2)	4.0 (7)
C(O2)	0.392 (1)	0.305 (3)	0.221 (3)	12 (1)
C(1)	0.282 (1)	0.036 (1)	0.260 (3)	4.0 (7)
C(2)	0.638 (1)	0.622 (2)	0.200 (2)	3.2 (6)
C(11)	0.387 (1)	0.965 (1)	0.318 (2)	2.4 (5)
C(12)	0.360 (1)	0.941 (2)	0.411 (3)	6.2 (9)
C(13)	0.384 (1)	0.874 (2)	0.458 (3)	8.2 (8)
C(14)	0.432 (1)	0.839 (2)	0.407 (3)	5.8 (8)
C(15)	0.453 (1)	0.864 (2)	0.324 (2)	4.5 (7)
C(16)	0.430 (1)	0.929 (2)	0.275 (2)	3.4 (6)
C(1A)	0.373 (1)	0.118 (2)	0.355 (3)	5.0 (8)
C(1B)	0.329 (1)	0.159 (2)	0.398 (3)	6.0 (8)
C(1C)	0.340 (2)	0.209 (2)	0.475 (3)	8 (1)
C(1D)	0.605 (2)	0.718 (2)	0.482 (3)	10 (1)
C(1E)	0.441 (2)	0.179 (2)	0.470 (3)	9 (1)
C(1F)	0.427 (2)	0.129 (2)	0.391 (3)	7.6 (9)
C(21)	0.6863 (9)	0.972 (2)	0.349 (2)	3.6 (6)
C(22)	0.660 (1)	0.021 (1)	0.295 (3)	4.4 (7)
C(23)	0.601 (1)	0.018 (2)	0.309 (2)	4.8 (7)[c]
C(24)	0.576 (1)	−1.023 (1)	0.375 (3)	4.5 (7)
C(25)	0.605 (1)	0.928 (2)	0.429 (3)	6.2 (9)
C(26)	0.662 (1)	0.928 (2)	0.416 (2)	5.0 (8)
C(2A)	0.274 (1)	0.873 (2)	0.208 (2)	3.3 (6)
C(2B)	0.242 (1)	0.856 (2)	0.299 (2)	3.8 (6)[c]
C(2C)	0.749 (1)	0.791 (2)	0.150 (2)	4.3 (7)
C(2D)	0.289 (1)	0.742 (2)	0.309 (3)	5.9 (8)[c]
C(2E)	0.322 (1)	0.757 (2)	0.230 (3)	6.6 (9)
C(2F)	0.316 (1)	0.832 (2)	0.181 (2)	3.9 (6)
C(31)	0.573 (1)	0.734 (2)	0.092 (2)	3.5 (6)
C(32)	0.608 (1)	0.784 (2)	0.155 (2)	5.6 (7)
C(33)	0.592 (1)	0.860 (1)	0.146 (3)	4.1 (7)
C(34)	0.553 (1)	0.883 (1)	0.072 (3)	5.6 (8)
C(35)	0.483 (1)	0.338 (2)	0.982 (3)	7.0 (9)
C(36)	0.470 (1)	0.260 (2)	0.973 (3)	7 (1)
C(3A)	0.515 (1)	0.618 (2)	0.158 (2)	5.0 (9)
C(3B)	0.489 (1)	0.657 (2)	0.239 (2)	4.7 (7)
C(3C)	0.441 (2)	0.648 (3)	0.283 (4)	10 (1)
C(3D)	0.419 (1)	0.584 (3)	0.258 (2)	12 (1)[c]
C(3E)	0.438 (1)	0.524 (2)	0.174 (3)	4.9 (7)
C(3F)	0.491 (1)	0.549 (1)	0.129 (2)	2.8 (5)
C(41)	0.710 (1)	0.522 (2)	0.306 (2)	4.0 (7)
C(42)	0.724 (2)	0.450 (2)	0.334 (3)	6.2 (9)[c]
C(43)	0.268 (2)	0.439 (2)	0.096 (2)	8 (1)
C(44)	0.707 (1)	0.007 (3)	0.957 (3)	8 (1)
C(45)	0.275 (1)	0.584 (4)	0.070 (3)	12 (1)
C(46)	0.732 (1)	0.583 (2)	0.342 (2)	5.6 (8)
C(4A)	0.603 (1)	0.481 (2)	0.258 (2)	5.7 (8)
C(4B)	0.569 (1)	0.507 (2)	0.347 (2)	5.7 (7)
C(4C)	0.522 (1)	0.466 (2)	0.385 (2)	8.1 (9)
C(4D)	0.508 (2)	0.399 (1)	0.344 (3)	6.1 (9)
C(4E)	0.534 (2)	0.366 (2)	0.262 (3)	6.2 (9)
C(4F)	0.588 (1)	0.404 (2)	0.221 (2)	3.9 (7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.
[b] Estimated standard deviations are given in parentheses.
[c] Atoms were refined isotropically.

pounds. Complete tables of bond lengths and angles are available as supplementary material.

The common feature of the three structures is an edge-sharing bioctahedral configuration of the core atoms:

$Re_2Cl_6(dppm)_2$ (I). The molecular structure is shown in Figure 1. The dimeric unit is rigorously centrosymmetric with a Re–Re bond length of 2.616 (1) Å. The averaged Re–Cl distances for the bridging and terminal chlorides are 2.391 [2] and 2.388 [5] Å, respectively. They are thus identical in a statistical sense. The average Re–P distance is 2.475 [5] Å. The bond angles around the rhenium atoms are those of an octahedral arrangement, distorted in a familiar way[18] due to the presence of metal–metal bonding, viz., opening of the (μ-Cl)–Re–(μ-Cl) angle. The conformation of the $\overline{\text{Re–P–C–P–Re}}$ five-membered rings is that of a half chair with the two carbon atoms in anti positions with respect to the mean plane containing the rhenium and phosphorus atoms.

The structure of $Re_2Cl_5(OC_2H_5)(dppm)_2$ (IIIb), shown in Figure 2, has one of the terminal chloride ligands replaced by an ethoxide group. This affects the structure in several ways. The Re–Re bond length, 2.667 (1) Å, is significantly increased (ca. 0.05 Å) with respect to that in $Re_2Cl_6(dppm)_2$. The Re–Cl distances vary between 2.321 (6) and 2.461 (5) Å, viz., 0.14 Å as opposed to 0.07 Å in I. The $\overline{\text{Re–P–C–P–Re}}$ rings are again in half-chair conformations, but in contrast to I the two carbon atoms are syn with respect to the mean plane. Although there are no crystallographic restrictions imposed, the virtual symmetry of the molecule is C_m.

The structure of $W_2(O\text{-}i\text{-}Pr)_8Cl_2$ is represented in Figure 3. The molecules are located around inversion centers in the

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(18) Cotton, F. A.; Ucko, D. A. *Inorg. Chim. Acta* **1972**, *6*, 161.

Table V. Atomic Positional Parameters for $W_2(O\text{-}i\text{-}Pr)_8Cl_2$[a]

atom	x	y	z	B, Å^2
W(1)	0.09092 (2)	0.000	0.05263 (4)	2.981 (7)
Cl(1)	0.1727 (1)	0.000	−0.0839 (3)	4.62 (6)
O(1)	0.0310 (3)	0.000	0.1780 (6)	3.4 (1)
O(2)	0.2033 (4)	0.000	0.2648 (7)	5.0 (2)
O(3)	0.0933 (3)	0.1518 (4)	0.0357 (5)	4.2 (1)
C(1)	0.0571 (7)	0.000	0.349 (1)	4.7 (3)
C(2)	0.1031 (7)	−0.1065 (9)	0.4320 (9)	7.5 (3)
C(3)	0.2973 (6)	0.000	0.326 (1)	4.7 (3)
C(4)	0.3403 (7)	0.105 (1)	0.427 (2)	10.2 (4)
C(5)	0.1427 (5)	0.2462 (7)	0.0373 (9)	5.3 (2)
C(6)	0.1546 (6)	0.3266 (8)	0.166 (1)	7.8 (3)
C(7)	0.0929 (7)	0.296 (1)	−0.135 (1)	9.0 (3)

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

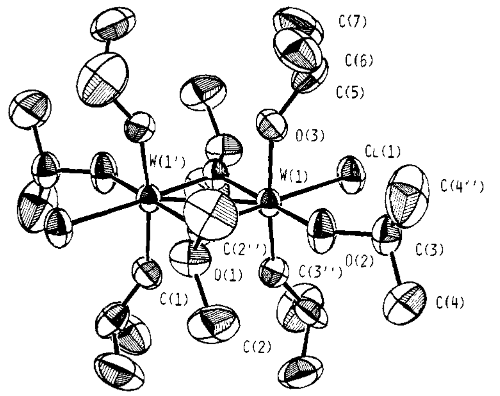

Figure 3. Molecular structure of $W_2(O\text{-}i\text{-}Pr)_8Cl_2$. All atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

monoclinic space group $C2/m$ and possess $2/m$ (C_{2h}) symmetry. The W–W bond length is 2.784 (1) Å. The W–Cl bond length is 2.449 (3) Å. The alkoxide bridges are significantly asymmetric, viz., 2.013 (7) and 2.076 (7) Å for the W–O distances trans and cis to the Cl atom, respectively. The deviations from the idealized octahedral bond angles are less severe than in I or IIIb due to the longer W–W distance.

The structure determination of $Re_2Cl_6(dppm)_2$ by single-crystal X-ray crystallography provides the satisfying finale to a series of experimental and theoretical efforts beginning with the preparation of a compound of the composition $[ReCl_3(dppm)]_n$ from the quadruply bonded dimer $[Re_2Cl_8]^{2-}$. A first assumption, based on the comparatively mild reaction conditions, was to leave the binuclear unit intact while two chloride ligands were substituted by phosphine moieties to yield a neutral species of the general type M_2L_{10}. Three possible structural models are then worthy of consideration in that there are prior examples known for each of them: (i) edge-sharing bioctahedral with a metal–metal bond; (ii) retention of the eclipsed configuration of the starting material; (iii) a dinuclear species with chloride bridges but no metal–metal bond. Possibility iii could be ruled out by determination of the magnetic properties: $Re_2Cl_6(dppm)_2$, as opposed to $Re_2Cl_6(dppe)_2$, is diamagnetic. Of the remaining two possibilities the photoelectron spectral data[4] highly favor the edge-sharing bioctahedral arrangement. An extended theoretical treatment of M_2L_{10} structures was presented.[5] It suggests that the reason for nonbonding in $Re_2Cl_6(dppe)_2$ stems from steric repulsion in the core due to a repulsive interaction of lone pairs on the axial ligands. Thus, tying them together, as with dppm, should eliminate the mutually repelling lone pairs and help to overcome this barrier. A Re–Re bond of intermediate length is predicted.

We now find both the experimental and theoretical predictions confirmed. The Re–Re distance is 2.616 (1) Å and the Re–Cl–Re bond angle is 66.33 (5)°. Following the theoretical results,[5] we expect a $\sigma^2\pi^2\delta^2\delta^{*2}$ configuration, viz., a net formal double bond and diamagnetism.

Table VI. Selected Bond Distances (Å) and Angles (deg)

	(1) $Re_2Cl_6(dppm)_2$		
	(a) Bond Lengths		
Re–Re	2.616 (1)	Re–P(1)	2.478 (2)
Re–Cl(1)	2.389 (2)	Re′–P(2)	2.471 (2)
–Cl(1)′	2.392 (2)	P(1)–C(1)	1.845 (8)
–Cl(2)	2.391 (2)	P(2)–C(1)	1.839 (8)
–Cl(3)	2.385 (2)		
	(b) Bond Angles		
Re′–Re–Cl(1)	56.89 (5)	Cl(2)–Re–Cl(3)	82.46 (8)
–Cl(1)′	56.78 (5)	–P(1)	88.29 (8)
–Cl(2)	138.41 (6)	–P(2)	84.96 (8)
–Cl(3)	139.12 (7)	Cl(3)–Re–P(1)	84.93 (8)
–P(1)	94.54 (5)	–P(2)	88.26 (8)
–P(2)	94.47 (5)	P(1)–Re–P(2)	170.99 (7)
Cl(1)–Re–Cl(1)′	113.67 (5)	Re–Cl(1)–Re	66.33 (5)
Cl(1)–Re–Cl(2)	163.77 (8)	P(1)–C(1)–P(2)	109.3 (4)
–Cl(3)	82.62 (8)	Re–P(1)–C(1)	109.7 (3)
–P(1)	96.72 (7)	–C(11)	113.8 (3)
–P(2)	88.23 (7)	–C(31)	122.2 (3)
Cl(2)–Re–Cl(3)	82.46 (8)	Re–P(2)–C(1)	110.0 (3)
–P(1)	88.29 (8)	–C(21)	114.6 (3)
–P(2)	84.96 (8)	–C(41)	121.4 (3)
	(2) $Re_2Cl_5(OC_2H_5)(dppm)_2$		
	(a) Bond Lengths		
Re(1)–Re(2)	2.667 (1)	Re(2)–Cl(1)	2.371 (5)
–Cl(1)	2.335 (6)	–Cl(2)	2.475 (6)
–Cl(2)	2.410 (6)	–Cl(4)	2.321 (6)
–Cl(3)	2.430 (5)	–Cl(5)	2.461 (6)
–P(1)	2.449 (7)	–P(2)	2.452 (6)
–P(3)	2.519 (6)	–P(4)	2.467 (7)
–O(1)	2.085 (14)		
	(b) Bond Angles		
Re(2)–Re(1)–Cl(1)	56.1 (1)	Re(1)–Re(2)–Cl(4)	142.6 (2)
–Cl(2)	58.1 (2)	–Cl(5)	132.1 (2)
–Cl(3)	141.6 (2)	–P(2)	93.3 (1)
Re(2)–Re(1)–P(1)	94.1 (1)	–P(4)	93.2 (2)
–P(3)	94.0 (2)	Cl(1)–Re(2)–Cl(2)	110.6 (2)
–O(1)	140.5 (5)	–Cl(4)	87.8 (2)
Cl(1)–Re(1)–Cl(2)	114.2 (2)	Cl(1)–Re(2)–Cl(5)	171.1 (2)
–Cl(3)	85.5 (3)	Cl(1)–Re(2)–P(2)	96.8 (2)
–P(1)	92.0 (2)	Cl(1)–Re(2)–P(4)	90.9 (2)
–P(3)	98.3 (2)	Cl(2)–Re(2)–Cl(4)	161.5 (2)
–O(1)	163.2 (5)	–Cl(5)	76.7 (2)
Cl(2)–Re(1)–Cl(3)	160.2 (3)	–P(2)	86.9 (2)
–P(1)	92.5 (2)	–P(4)	92.8 (2)
–P(3)	85.9 (2)	Cl(4)–Re(2)–Cl(5)	85.2 (2)
–O(1)	82.5 (5)	–P(2)	88.8 (2)
Cl(3)–Re(1)–P(1)	88.9 (2)	–P(4)	88.9 (2)
–P(3)	89.2 (2)	Cl(5)–Re(2)–P(2)	88.7 (2)
–O(1)	77.9 (5)	–P(4)	83.4 (2)
P(1)–Re(1)–P(3)	169.3 (2)	P(2)–Re(2)–P(4)	171.9 (2)
–O(1)	84.9 (4)	Re(1)–Cl(1)–Re(2)	69.1 (2)
P(3)–Re(1)–O(1)	84.4 (4)	–Re(2)	66.2 (2)
Re(1)–Re(2)–Cl(1)	54.8 (2)	Re(1)–O(1)–C′(01)	129 (2)
Re(1)–Re(2)–Cl(2)	55.8 (1)		
	(3) $W_2Cl_2(O\text{-}i\text{-}Pr)_8$		
	(a) Bond Lengths		
W(1)–W(1)′	2.784 (1)	O(1)–C(1)	1.461 (12)
–Cl(1)	2.449 (3)	O(2)–C(3)	1.423 (14)
–O(1)	2.013 (7)	O(3)–C(5)	1.429 (10)
–O(1)′	2.076 (7)		
–O(2)	1.913 (8)		
–O(3)	1.837 (6)		
	(b) Bond Angles		
W(1)′–W(1)–Cl(1)	135.39 (8)	O(1)–W(1)–O(3)	95.8 (2)
–O(1)	48.0 (2)	O(1)′–W(1)–O(2)	179.9 (3)
–O(2)	134.0 (3)	–O(3)	88.0 (2)
–O(3)	92.7 (2)	O(2)–W(1)–O(3)	92.0 (2)
Cl(1)–W(1)–O(1)	176.6 (2)	O(3)–W(1)–O(3)″	168.0 (3)
–O(1)′	89.2 (2)	W(1)–O(1)–W(1)′	85.8 (3)
–O(2)	90.6 (3)	–C(1)	138.7 (7)
–O(3)	84.3 (2)	W(1)–O(2)–C(3)	136.5 (7)
O(1)–W(1)–O(1)′	94.2 (3)	W(1)–O(3)–C(5)	146.5 (5)
–O(2)	85.9 (3)		

Table VII. Comparison of Important Dimensions in Two Ditungsten Compounds with a W–W Single Bond

	$W_2Cl_4(OEt)_6$	$W_2Cl_2(O\text{-}i\text{-}Pr)_8$
W–W, Å	2.715 (1)	2.784 (1)
W–Cl, Å	2.403 [9]	2.449 (3)
W–O_t, Å	1.824 [6]	1.837 (6)
W–O_{br}, Å	2.012 [2]	2.04 [4]
W–O–C, deg	144.5 [7]	142 [6]

Changes in the equatorial ligands are not expected to influence the bonding to the same dramatic extent. We do, however, notice a significant lengthening of the Re–Re bond from 2.616 (1) to 2.667 (1) Å upon substitution of one equatorial chloride by an ethoxide ligand. We cannot say with confidence what is the reason for this effect. One possibility is that it might be due to the partial donation of the oxygen lone pair electrons into the σ^* or π^* orbitals of the Re–Re bonding set, thus weakening the bond.

In an effort to see if this sort of bond-weakening effect might be general and also to see if the action of the oxygen lone pairs might be mainly through the σ^* or the π^* M–M bonding orbitals, we have compared the structure of the compound $W_2(\mu\text{-O-}i\text{-Pr})_2(O\text{-}i\text{-Pr})_6Cl_2$ with that of a homologous compound[7] containing only chlorine atoms in the group of ligands coplanar with the $W(\mu\text{-O})_2W$ unit, viz., $W_2(\mu\text{-OEt})_2(OEt)_4Cl_4$. Again, a bond-lengthening effect is found, as shown in Table VII. Since the ditungsten compounds contain only a W–W σ bond, it would seem that the postulated effect of donation into the σ^* orbital is shown here to be operative. In the rhenium compound it presumably operates also. While there could be a contribution from donation to the π^* orbital as well, the orientation of the OEt group in IIIb is certainly consistent with at least the σ^* effect.

(c) NMR Spectroscopic and Electrochemical Properties of the Dirhenium(III) Species. With the structural details of complex I (and by implication also II) and the complexes of type III firmly established, we can now consider some further properties of these complexes. Because of the low solubilities of I and II in suitable solvents we were unable to obtain satisfactory ^1H NMR spectra. However, we did observe a singlet at δ −140.6 (vs. H_3PO_4) in the $^{31}P\{^1H\}$ NMR spectrum of I (in a 1:1 (v/v) CH_2Cl_2–$CDCl_3$ solvent mixture). While one would indeed expect a singlet, since all the phosphorus atoms should be equivalent, the large shift to low frequency (high field) was quite surprising. The phosphorus resonance for free dppm was found at δ −22.7, which means that for complex I the chemical shift difference (Δ) (see Table VIII) between coordinated dppm (δ_c) and free dppm (δ_F) [i.e., $\Delta = \delta_C - \delta_F$] is −117.9. It is unlikely that this large shift is due entirely to C–P–C bond angle changes because a shift to low frequency (high field) of this magnitude would imply that these angles are "closed significantly",[19,20] and from the crystal structure this is not observed. It is also unlikely that this shift is due to any so-called ring contribution,[21] since the dppm ligand is coordinated via a five-membered ring which usually gives shifts to high frequency (low field). Indeed, the phosphorus resonance in $Re_2Cl_4(dppm)_2$ (vide infra), which also contains bridging dppm ligands in five-membered rings, exhibits a shift to high frequency (Table VIII). It is conceivable that this unusually high-field phosphorus resonance is due in part to the weak paramagnetism of I. A magnetic moment determination (by the Faraday method) did reveal that I is weakly paramagnetic ($\chi_g = (-0.179 \pm 0.05) \times 10^{-6}$ cgsu), with a μ_{eff} value of 1.13 ± 0.05 μ_B.[22] This may be a consequence of the thermal population of a low-lying paramagnetic state at room temperature. An alternative explanation in terms of a diamagnetic anisotropy effect arising from the metal–metal multiple bond,[2] while not entirely out of the question, is less likely.

A magnetic moment determination of a sample of the ethoxide complex IIIb revealed that, like I, it too is weakly paramagnetic ($\chi_g = +(0.077 \pm 0.05) \times 10^{-6}$ cgsu) with $\mu_{eff} = 1.45 \pm 0.05$ μ_B. However, quite well-defined NMR spectra were observed for these complexes (Table VIII).

The $^{31}P\{^1H\}$ NMR spectra of complexes IIIa–c consisted of two triplets (splitting = 40 Hz), but these were not of the simple type with components of equal line widths and in 1:2:1 intensity ratios. Rather, the central line was in each case much broader than the outer two lines and not twice as high. In accord with the crystal structure of the ethoxide derivative (IIIb), we believe that these have to be interpreted as a deceptively simple AA′XX′ spin system where the four central lines expected for such a spectrum are unresolved while the outer lines are below the detection level. The chemical shift differences (Δ) for these complexes, while still appreciable (−50 to −75 ppm), are less than that found for I.

The ^1H NMR spectra of CD_2Cl_2 solutions of IIIa–c exhibit two multiplets for the methylene protons (P–CH_2–P) of the dppm ligands. These protons are best described as the AA′BB′ part of an AA′BB′MM′XX′ spin system. This general pattern has been found in other A-frame types of molecules,[23,24] and no effort was made to analyze the spin system fully.

An additional noteworthy feature in the ^1H NMR spectra of the alkoxide derivatives is the unusual chemical shifts associated with the alkoxide ligand protons (Table VIII). Only in the case of the ethoxide product IIIb were we able to assign unequivocally all the alkoxide resonances. The 200-MHz NMR spectrum of IIIb exhibited a triplet at δ −0.42, but decoupling experiments did not reveal any other resonance to which this was coupled. However, in the 470-MHz NMR spectrum, a broad signal at δ +7.15 could be discerned in the phenyl region which was clearly coupled with the triplet at δ −0.42. On the basis of these decoupling experiments and integrated intensities, it was apparent that the signal at δ +7.16 was due to the $-OCH_2-$ protons and the triplet at δ −0.42 to the methyl protons of the ethoxide ligand. The *n*-propoxide complex IIIc also showed similar spectral properties; the 200-Mz NMR spectrum showed a methyl triplet at δ +0.10 and a broad β-methylene multiplet at δ −0.18. However, the resonance due to the deshielded α-methylene protons of the *n*-propoxide ligand was not located, as was the case for the $-OCH_3$ protons of the methoxide complex IIIa. It seems clear from the previous discussion that these resonances are obscured by the much more intense phenyl proton resonances.

The electrochemical properties of complexes I, II, and III have been investigated by using the cyclic voltammetry (CV) technique. These compounds exhibit well-defined redox behavior; the measured voltammetric half-wave potentials in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane are listed in Table IX. For complexes I and II, four couples are observed in the potential range +1.8 to −1.4 V vs. SCE; two correspond to one-electron oxidations (by coulometry) and two to one-electron reductions. These processes are characterized by $i_{p,c}/i_{p,a}$ ratios of unity or close to unity and constant $i_p/\nu^{1/2}$ ratios for sweep rates (ν) between 50 and 400 mV/s in accord with diffusion control. Values for the potential separations between the coupled anodic and cathodic peaks (ΔE_p) at sweep rates of 200 mV/s are given in Table IX. With our electrochemical setup,[25] these properties are consistent with the electron-transfer processes being reversible or approaching electrochemical reversibility. The fact that the electrochemical behavior of I and II is so similar lends credence to the suggestion that these two complexes are similar structurally. If these complexes do possess metal–metal double bonds as predicted theoretically,[5] with the electronic configuration $\sigma^2\pi^2\delta^2\delta^{*2}$, then these CV's indicate that the double bond can survive two one-electron oxidations, thereby generating a triply bonded Re_2^{8+} core possessing the electronic configuration $\sigma^2\pi^2\delta^2$, and two

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

(20) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(21) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(22) A previous determination of the magnetic susceptibility of $Re_2Cl_6(dppm)_2$ (by the Gouy method) gave a χ_g value of -0.30×10^{-6} cgsu.[4]

(23) Balch, A. L.; Hunt, C. T.; Lee, C. L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764.

(24) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996.

(25) Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

Table VIII. $^{31}P\{^1H\}$ and ^1H NMR Spectral Data for Dirhenium Complexes of Bis(diphenylphosphino)methane[a]

	^{31}P			^{1}H			
				P-CH$_2$-P			OR
compd	δ	J(P-P), Hz	Δ,[b] ppm	δ	J(H-H), Hz	J(P-H), Hz	δ
dppm	−22.7 s						
$Re_2Cl_6(dppm)_2$ (I)	−140.6 s		−117.9	*c*			
$Re_2Cl_5(OR)(dppm)_2$							
R = CH_3 (IIIa)	−76.8 t	40	−54.1	+4.19[d]			
	−91.6 t		−68.9	+2.71[d]			
R = CH_2CH_3 (IIIb)	−82.7 t	39	−60.0	+4.16[e]	12.5	5.1	−0.42 t
	−96.1 t		−73.4	+2.63[e]		4.1	+7.15 m, br
R = $CH_2CH_2CH_3$ (IIIc)	−81.9 t	40	−59.2	+4.18[e]	12.4	5.0	−0.18 m, br
	−95.5 t		−72.8	+2.63[e]		4.0	+0.10 t
$Re_2Cl_4(dppm)_2$	−3.3 s		+19.4	+5.21 p		4.9	

[a] $^{31}P\{^1H\}$ spectra recorded in 1:1 $CDCl_3/CH_2Cl_2$ (positive chemical shifts measured downfield from 85% H_3PO_4), while the ^1H spectra were measured for CD_2Cl_2 solutions. Abbreviations are as follows: s = singlet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad. [b] $\Delta = \delta_C - \delta_F$; δ_C = chemical shift for coordinated dppm; δ_F = chemical shift for free dppm. [c] Not observed due to the low solubility of the complex. [d] Broad and unresolved. [e] Two overlapping pentets giving rise to a 1:4:6:5:5:6:4:1 intensity ratio.

Table IX. Cyclic Voltammetric Data for Dichloromethane Solutions of Dirhenium Complexes[a]

compd	$E_{1/2}$(ox(2))	$E_{1/2}$(ox(1))	$E_{1/2}$(red(1))	$E_{1/2}$(red(2))
$Re_2Cl_6(dppm)_2\cdot{}^2/_3CH_2Cl_2$ (I)	−1.63 (120)	+0.81 (95)	−0.54 (100)	−1.41 (120)
$Re_2Cl_6(Ph_2Ppy)_2$ (II)	+1.75 (100)	+0.85 (100)	−0.49 (95)	−1.41 (120)
$Re_2Cl_5(OR)(dppm)_2$				
R = CH_3 (IIIa)	+1.38 (100)	+0.51 (90)	−0.85 (95)	
R = CH_2CH_3 (IIIb)	+1.37 (95)	+0.51 (100)	−0.85 (110)	
R = $CH_2CH_2CH_3$ (IIIc)	+1.35 (95)	+0.50 (100)	−0.86 (100)	
$Re_2Cl_6(dppa)_2$	+1.60[b]	+0.86 (80)	−0.43 (85)	−1.38 (110)
$Re_2Cl_5(dppm)_2\cdot(C_2H_5)_2O$		+0.51 (100)	−0.36[c]	
$Re_2Cl_4(dppm)_2$	+0.80 (85)	+0.27 (85)		
$Re_2Cl_4(dppa)_2\cdot 2.5C_6H_6$	+0.86 (120)	+0.37 (80)		
$Re_2Cl_4(PMe_2Ph)_2(dppa)$	+1.37[b]	+0.64 (95)		

[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] $E_{p,a}$ value. [c] $E_{p,c}$ value.

one-electron reductions to give a singly bonded Re_2^{4+} core with the $\sigma^2\pi^2\delta^2\delta^{*2}\pi^{*2}$ electronic configuration.

The alkoxide complexes IIIa–c similarly exhibit quite rich electrochemistry, the appropriate data being presented in Table IX. In each case, two one-electron oxidations and a single one-electron reduction are observed in the CV measurements. These electron-transfer processes, like those for I and II, meet the usual criteria for electrochemical reversibility that pertains to our cell configuration[25] and the 0.2 M TBAH–CH_2Cl solvent system. The fact that these alkoxide complexes show only one reduction, whereas two are seen in the CV's of I and II, can be explained by the fact that all the potentials for the complexes IIIa–c are shifted to more negative potentials by approximately 0.30 V in comparison to I, thereby implying that the second reduction for IIIa–c will be outside the solvent limits for dichloromethane. This shift of −0.30 V upon replacement of a chloride ligand in I with an alkoxide ligand may reflect the fact that the OR^- ligand is a better σ donor than Cl^-, thereby leading to an increase in electron density at the metal centers and making oxidation easier and reduction less so.

(d) Synthesis and Redox Chemistry of $Re_2Cl_5(dppm)_2$ and $Re_2Cl_4(dppm)_2$. Because the reactions of the $[Re_2Cl_8]^{2-}$ anion with dppm were found to be solvent dependent, it seemed likely that the corresponding reactions of the phosphine-substituted derivatives of $[Re_2Cl_8]^{2-}$ [i.e., $Re_2Cl_6(PR_3)_2$] with dppm might also behave in this way. In the course of examining the behavior of $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$, we found that it reacts with dppm in refluxing diethyl ether to produce $Re_2Cl_5(dppm)_2$ as an ether solvate. This complex was previously isolated from the reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with dppm in acetone along with significant quantities of I.[6] We have also discovered a new and far superior synthetic route to the complex $Re_2Cl_4(dppm)_2$ from the reaction of $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$ with dppm in refluxing methanol. The previously reported method for the preparation of this complex was by the reaction of $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ with dppm in benzene.[4] This new method requires substantially shorter reaction times and does not necessitate the use of $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$, which itself has first to be prepared from $(n\text{-}Bu_4N)_2Re_2Cl_8$.[9]

While $Re_2Cl_4(dppm)_4$ is diamagnetic, the complex $Re_2Cl_5(dppm)_2$ is ESR-active[6] and accordingly does not exhibit a well-defined ^1H NMR spectrum. The ^1H NMR spectrum of $Re_2Cl_4(dppm)_2$ exhibits a pentet (Table VIII) for the methylene protons of the dppm ligand. While we would expect these methylene protons to be inequivalent in any static structure for the five-membered Re_2P_2C ring, a mechanism apparently exists which renders these protons equivalent. This mechanism is sufficient to time average the two proton environments such that only one chemical shift is observed with the pentet splitting arising from coupling to the phosphorus spin system.

The members of the series of complexes $Re_2Cl_6(dppm)_2$ (I), $Re_2Cl_5(dppm)_2$, and $Re_2Cl_4(dppm)_2$ are related to one another by successive one-electron redox changes with a concomitant gain or loss of chloride ion. Consequently we sought to establish whether such interconversions were possible. The complex $Re_2Cl_4(dppm)_2$ shows two reversible one-electron oxidations in its CV at +0.80 and +0.27 V (Table IX), behavior that is typical of Re_2^{4+} complexes of the M_2L_8 type containing bridging bidentate ligands.[3b,26] Bulk electrolysis of solutions of $Re_2Cl_4(dppm)_2$ at +0.40 V in the presence of 1 equiv of benzyltriethylammonium chloride was shown to produce the complex $Re_2Cl_5(dppm)_2$ through a comparison of the resultant CV to the one obtained for a pure sample of this complex (Table IX). The complex $Re_2Cl_5(dppm)_2$ is characterized electrochemically as possessing a reversible oxidation at +0.51 V and an irreversible reduction at −0.36 V vs. SCE. It might be anticipated that this irreversible

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

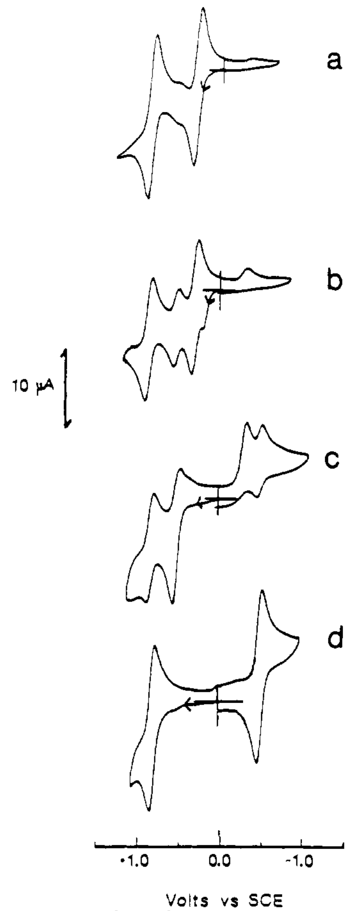

Figure 4. Sequence of cyclic voltammograms (measured in 0.2 M TBAH–CH_2Cl_2 at a Pt-bead electrode) showing the conversion of $Re_2Cl_4(dppm)_2$ to $Re_2Cl_5(dppm)_2$ and subsequently to $Re_2Cl_6(dppm)_2$, following controlled potential electrolysis at +0.6 V vs. SCE in the presence of benzyltriethylammonium chloride: (a) $Re_2Cl_4(dppm)_2$ containing a trace of $Re_2Cl_5(dppm)_2$; (b) electrolysis ca. 25% complete; (c) electrolysis ca. 75% complete; (d) electrolysis essentially complete.

reduction results from the loss of the weakly bound axial chloride ligand from $[Re_2Cl_5(dppm)_2]^-$ upon reduction of the Re_2^{5+} core to Re_2^{4+}. This was confirmed by electrolysis of a solution of $Re_2Cl_5(dppm)_2$ at −0.50 V; a CV of the resultant solution showed that $Re_2Cl_4(dppm)_2$ had been generated. These experiments demonstrate that the interconversion of $Re_2Cl_4(dppm)_2$ and $Re_2Cl_5(dppm)_2$ can be accomplished through coupled electrochemical–chemical reaction series (i.e., EC processes).

The next step was to ascertain whether $Re_2Cl_5(dppm)_2$ could in a similar fashion be converted to $Re_2Cl_6(dppm)_2$. This is indeed the case as shown in Figure 4. The experiment was conducted as follows. A solution of $Re_2Cl_4(dppm)_2$ in 0.2 M TBAH–CH_2Cl_2, to which was added slightly more than 2 equiv of benzyltriethylammonium chloride, was electrolyzed at +0.60 V. This potential is sufficient not only to oxidize $Re_2Cl_4(dppm)_2$ to $[Re_2Cl_4(dppm)_2]^+$ but also to oxidize $Re_2Cl_5(dppm)_2$ to its monocation once the former species has been formed from the reaction of $[Re_2Cl_4(dppm)_2]^+$ with Cl^-. Once $[Re_2Cl_5(dppm)_2]^+$ is produced, it in turn reacts quickly with Cl^- to give $Re_2Cl_6(dppm)_2$. This sequence of steps is shown in Figure 4, where the CV's were measured on aliquots of the electrolyzed solution as the coupled electrochemical–chemical reactions proceeded. The characteristic electrochemical processes of $Re_2Cl_5(dppm)_2$ are seen to grow in as the waves associated with $Re_2Cl_4(dppm)_2$ diminish, while in time the former disappear as the couples due to $Re_2Cl_6(dppm)_2$ increase in intensity. With the switching potentials used in these particular CV's only two of the four one-electron transfer processes that characterize $Re_2Cl_6(dppm)_2$ are seen (see Figure 4d). The two remaining redox processes are outside the range of these measurements (see Table IX). An especially noteworthy feature of the conversion of $Re_2Cl_5(dppm)_2$ to $Re_2Cl_6(dppm)_2$ is that it represents an oxidation of the Re_2^{5+} core to Re_2^{6+} with an associated decrease in the metal–metal bond order (from 3.5 to 2). Usually, such an oxidation leads to an increase in the bond order from 3.5 to 4.[17,26]

(e) Synthesis and Characterization of dppa Complexes. Several transition-metal complexes that contain the ligand dppa are known,[27-32] and like dppm, dppa can act as either a bridging[28,30,31] or chelating[27,29,31,32] ligand. Because dppa is similar sterically to dppm, it was of interest to see if the presence of the NH bridgehead group would play any significant role in the reaction chemistry of this ligand with dinuclear rhenium complexes. While we were able to isolate complexes with stoichiometries $Re_2Cl_6(dppa)_2$ and $Re_2Cl_4(dppa)_2$, which exhibit spectroscopic and electrochemical properties analogous to their dppm analogues, the course of the reactions did indeed change over those with dppm.

The reactions of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with dppa in methanol, acetone, and acetonitrile all yielded a purple complex with stoichiometry $Re_2Cl_6(dppa)_2$. Its electronic absorption and IR spectral data (Table II) properties (Table IX) indicate that this complex is structurally similar to $Re_2(\mu\text{-}Cl)_2Cl_4(dppm)_2$. What is of interest, though, is the formation of significant quantities of the mononuclear rhenium(III) complex $[ReCl_2(dppa)_2]Cl$ ($\mu_{eff} = 1.71$ μ_B) in these reactions. This implies that dppa has a pronounced tendency to cleave the dinuclear unit, a property that is also exhibited, for reasons not yet well understood, by the ligand 1,2-bis(diphenylphosphino)ethane (dppe) in its reactions with the octahalodirhenate(III) anions.[4,33,34]

The reactions of dppa with $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ and $Re_2Cl_4(PMe_2Ph)_4$ provided the most successful routes to the complexes $Re_2Cl_4(dppa)_2$ and $Re_2Cl_4(PMePh)_2(dppa)$. Both exhibit very similar spectroscopic and electrochemical properties to those of their dppm analogues (see Tables II and IX of ref 4). Our attempts to generate the complex $Re_2Cl_5(dppa)_2$ by electrolyzing solutions of $Re_2Cl_4(dppa)_2$ at +0.5 V in the presence of chloride ion were unsuccessful; only the formation of $Re_2Cl_6(dppa)_2$ was detected by the CV technique. It may be that $Re_2Cl_5(dppa)_2$ is an unexpectedly unstable derivative of the Re_2^{5+} core.

(f) Concluding Remarks. The structural identification of the complex $Re_2Cl_6(dppm)_2$ (and its Ph_2Ppy and dppa analogues) and the series of complexes $Re_2Cl_5(OR)(dppm)_2$ (R = Me, Et, *n*-Pr, and *n*-Bu) as molecules that contain metal–metal double bonds expands considerably the scope of this chemistry within the transition elements.[2] Previously, the rhenium(III) halides Re_3X_9[2] and the ditungsten(IV) alkoxides $W_2Cl_4(OR)_4(ROH)_2$[35] have constituted the most noteworthy and extensive series of non-organometallic doubly bonded dimetal complexes. The dppm complexes of dirhenium(III) introduce us to a new class of such derivatives, ones that differ electronically from the aforementioned examples.

Within the series of complexes $Re_2Cl_4(dppm)_2$, $Re_2Cl_5(dppm)_2$, and $Re_2Cl_6(dppm)_2$ we find that electrochemically induced one-electron redox changes coupled with the gain or loss of a chloride ligand provides a means of interconverting these molecules, viz.

$$\underset{\sigma^2\pi^4\delta^2\delta^{*2}}{\mathrm{Re_2Cl_4(dppm)_2}} \underset{+e^-,\,-Cl^-}{\overset{-e^-,\,+Cl^-}{\rightleftharpoons}} \underset{\sigma^2\pi^4\delta^2\delta^{*1}}{\mathrm{Re_2Cl_5(dppm)_2}} \xrightarrow{-e^-,\,+Cl^-} \underset{\sigma^2\pi^2\delta^2\delta^{*2}}{\mathrm{Re_2Cl_6(dppm)_2}}$$

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(27) Ellerman, J.; Mader, L. *Z. Naturforsch., B* **1980**, *35B*, 307.

(28) Schmidbaur, H.; Wagner, F. E.; Wohlleben-Hammer, A. *Chem. Ber.* **1979**, *112*, 496.

(29) Ellerman, J.; Gruber, W. H. *Z. Naturforsch., B* **1973**, *28B*, 310.

(30) Ellerman, J.; Geheeb, N.; Thiele, G.; Zoubek, G. *Z. Naturforsch., B* **1977**, *32B*, 1271.

(31) Ellerman, J.; Hohenberger, E. F.; Kehr, W.; Pürzer, A.; Thiele, G. *Z. Anorg. Allg. Chem.* **1980**, *464*, 45.

(32) Andrews, G. T.; Colquhoun, I. J.; McFarlane, W. *Polyhedron* **1983**, *2*, 783.

(33) Jaecker, J. A.; Robinson, W. R.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1975**, 698.

(34) Jaecker, J. A.; Murtha, D. P.; Walton, R. A. *Inorg. Chim. Acta* **1975**, *13*, 21.

(35) Cotton, F. A.; Falvello, L. R.; Fredrich, M. F.; DeMarco, D.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 3088 and references cited therein.

The conversion of $Re_2Cl_5(dppm)_2$ to $Re_2Cl_6(dppm)_2$ affords an unprecedented example of a one-electron oxidation of the Re_2^{5+} core (bond order 3.5) to Re_2^{6+} in which the metal-metal bond order is reduced rather than increased.

An important question that arises is why does $Re_2Cl_6(dppm)_2$ assume this chlorine-bridged structure rather than one in which all the Re–Cl bonds are terminal and the Re–Re bond is of order 4 (i.e., a $\sigma^2\pi^4\delta^2$ electronic configuration)? It is already known from the structure determination on $Re_2Cl_5(dppm)_2$[6] that the Re–Cl bond that occupies one of the coaxial positions on the metal atoms is a very long one and, hence, a weak one. Furthermore, ligand–ligand repulsions cause a quite dramatic contraction of the Cl–Re–Cl and P–Re–P angles (of the $ReCl_2P_2$ units) so that these coaxial sites are sterically congested. This may lead to an inherent instability of a structure in which a second axial Re–Cl bond has to be formed; consequently, the di-μ-chloro-bridged structure, in which all Re–Cl bonds are reasonably strong, results. Even though this structural change results in a decrease in the Re–Re bond order (from 4 to 2), this is more than compensated for (in a thermodynamic sense) by the formation of stronger Re–Cl bonds.

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Supplementary Material Available: Structure factor tables, tables of anisotropic thermal vibration parameters, complete lists of bond lengths and angles, and details of crystallographic work for all three structures (56 pages). Ordering information is given on any current masthead page.

Mechanism of the Ozonolysis of Ethylene–Acetaldehyde Mixtures

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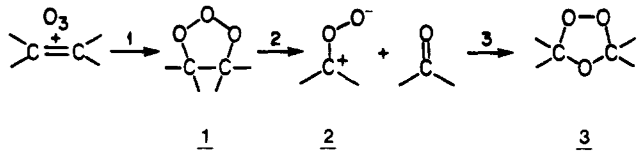
Abstract: Ethylene-$1,1\text{-}d_2$ was ozonized in the presence of acetaldehyde. The yields of ethylene ozonide-d_0, -d_2, and -d_4 and propylene ozonide-d_0 and -d_2 were determined by proton NMR, microwave spectroscopy, and manometric measurements. The ratio of propylene ozonide-d_0/propylene ozonide-d_2 decreased as the concentration of acetaldehyde increased. This indicates that an inverse kinetic secondary isotope effect is associated with the recombination reactions of the carbonyl oxide (Criegee intermediate). A kinetic model was employed to describe the Criegee reaction mechanism and to estimate the final product ratios. This model resulted in quantitative estimates of the KSIE for the carbonyl oxide, the relative dipolarophilicity of formaldehyde and acetaldehyde, and the cage effect upon primary ozonide decomposition. The inverse KSIE for the carbonyl oxide and formaldehyde in their recombination reaction is consistent with a concerted process.

The three step Criegee mechanism describes the formation of ozonides in solution.[1] This proposal (Scheme I) receives broad acceptance even though direct observation of the Criegee intermediate (**2**) is still lacking. In order to rationalize stereochemical results with substituted ethylenes, it has been postulated that the three reaction steps are a concerted cycloaddition, cycloreversion, and cycloaddition, respectively.[2] This leads to syn or anti isomerism in **2** followed by stereoselective recombination with the carbonyl compound in step 3. The evidence that step 1 is concerted is reasonably conclusive.[1,3,4] However, for steps 2 and 3, the evidence is more indirect and inferential since it is based on the observed stereochemistry in the final ozonide[2] (**3**) and on analysis of thermochemical[3] and ab initio reaction energetics.[5] Furthermore, some puzzling stereochemical results, solvent effects, and ozonide yields have resulted in suggestions that steps 2 and 3 may be nonconcerted at least for some conditions.[6]

Scheme I



One potential probe of concertedness in these steps employs deuterium kinetic secondary isotope effects (KSIE). An inverse KSIE ($k_H/k_D \approx 0.80$–0.95 at 25 °C) has been observed for a number of cycloaddition reactions where the carbons transform from sp^2 to sp^3 hybridization in the transition state.[7] Cycloaddition or reversion reactions which are nonconcerted and which

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(1) Recent reviews: (a) Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 745. (b) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978, Vol. 1; 1982, Vol. 2. (c) Kuczkowski, R. L. *Acc. Chem. Res.* **1983**, *16*, 42.

(2) (a) Bauld, N. L.; Thompson, J. A.; Hudson, C. E.; Bailey, P. S. *J. Am. Chem. Soc.* **1968**, *90*, 1822. (b) Bailey, P. S.; Ferrell, T. M. *Ibid.* **1978**, *100*, 894-898. (c) Lattimer, R. P.; Kuczkowski, R. L.; Gillies, C. W. *Ibid.* **1974**, *96*, 348.

(3) Nangia, P. S.; Benson, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 3105.

(4) Choe, J. I.; Srinivasan, M.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1983**, *105*, 4703.

(5) (a) Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7199. (b) *Ibid.* **1981**, *103*, 3619. (c) *Ibid.* **1981**, *103*, 3627. (d) *Ibid.* **1981**, *103*, 3633. (e) *Angew. Chem.* **1981**, *93*, 934.

(6) (a) Murray, R. W.; Hagen, R. *J. Org. Chem.* **1971**, *36*, 1098. (b) Su, J. S.; Murray, R. W. *Ibid.* **1980**, *45*, 678. (c) Ramachandran, V.; Murray, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2197. (d) Murray, R. W.; Su, J. S. *J. Org. Chem.* **1983**, *48*, 817. (e) Harding, L. B; Goddard, W. A., III. *J. Am. Chem. Soc.* **1978**, *100*, 7180.

(7) (a) Fong, G. A.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 3763. (b) Van Sickel, D. E.; Rhodin, J. O. *Ibid.* **1964**, *86*, 3091. (c) Seltzer, S. *Ibid.* **1965**, *87*, 1534. (d) Dai, S. H.; Dolbier, W. R. *Ibid.* **1972**, *94*, 3946. (e) Streitwieser, A.; Jagow, R. H.; Fahey, R. C.; Suzuki, S. *Ibid.* **1958**, *80*, 2326. (f) Wolfsberg, M.; Stern, M. J. *Pure Appl. Chem.* **1964**, *8*, 225, 325. (g) Denney, D. B.; Tunkel, N. *Chem. Ind.* (London) **1959**, *24*, 1383.

0002-7863/84/1506-2891$01.50/0