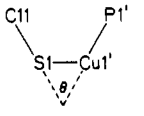
axes of I; the SPh ligands of cubanoid $(\mu_3\text{-SPh})_4Cu_4(PPh_3)_4$ would be collinear with these axes and therefore positioned within the cone of six Ph groups connected as $PhS-Cu-(-P-Ph_2)_3$. Connections of this type occur in **4**, along Ph–S1–Cu1′–P1′. Therefore the structural unit, including phenyl rings, sufficient for construction of cubanoid $(\mu_3\text{-SPh})_4Cu_4(PPh_3)_4$ is present in **4**. The critical dimensional property is the angle θ shown in **12**: in the



12

cubanoid structure this angle between threefold axes is 70.5°, while in **4** it is ca. 59° (S1–Cu1′–P1′ = 119.0°, C11–S1–Cu1′ = 119.8°). In **7**, Cl–Cu–P angles average 122°. From this we conclude that SPh- -Ph_2P contacts in the cubanoid $(\mu_3\text{-SPh})_4Cu_4(PPh_3)_4$ would be slightly shorter than in **4**, and this may be the reason for the adoption of the step structure II.

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Supplementary Material Available: A tabulation of all atomic coordinates and thermal parameters and a listing of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Structural Characterization of the Triply Bonded Dirhenium(II) Complexes $Re_2Cl_4(\mu\text{-}Ph_2PCH_2PPh_2)_2$ and $\alpha\text{-}Re_2Cl_4(Me_2P(CH_2)_2PMe_2)$

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The complexes $Re_2Cl_4(LL)_2$, where LL are the bidentate ligands $Ph_2PCH_2PPh_2$ (dppm) (**1**) and $Me_2P(CH_2)_2PMe_2$ (dmpe) (**2**), which both possess the electronic configuration $\sigma^2\pi^4\delta^2\delta^{*2}$ and thus formally a metal–metal triple bond, have been structurally characterized by X-ray crystallography. $Re_2Cl_4(dppm)_2$ (**1**): $Re_2Cl_4P_4C_{50}H_{44}$; monoclinic, $P2_1/n$; $a = 11.647$ (3) Å, $b = 12.849$ (4) Å, $c = 38.691$ (9) Å, $\beta = 85.96$ (2)°, $V = 5776$ (43) Å^3, $Z = 4$. The molecule has two dppm molecules spanning the Re–Re bond. The two fused five-membered rings assume twist-boat conformations, leading to a completely staggered arrangement of the substituents on the two rhenium atoms. The average Cl–Re–Re–Cl torsion angle is 56 [1]°, and the Re–Re bond length is 2.234 (3) Å. $Re_2Cl_4(dmpe)_2\cdot CH_3OH$ (**2**) was isolated and crystallized as the α isomer, viz., with the dmpe ligands chelating. The crystallographic parameters are as follows: $Re_2Cl_4P_4OC_{13}H_{36}$; orthorhombic, *Ccma* (nonstandard setting of *Cmca*); $a = 11.595$ (2) Å, $b = 14.475$ (2) Å, $c = 14.925$ (2) Å, $V = 2505$ (1) Å, $Z = 4$. The dimetallic unit has a Re–Re bond length of 2.264 (1) Å and an eclipsed conformation with the geminal chlorides in a cis configuration. The five-membered chelate rings have envelope conformations.

Introduction

The reaction of the dimeric rhenium(III) halo complexes $Re_2X_8^{4-}$ with bidentate phosphines (LL) affords complexes of the type $Re_2X_6(LL)_2$, $Re_2X_5(LL)_2$, and $Re_2X_4(LL)_2$, many of which have been previously described.[2–4] The extent of reduction is dependent upon the nature of the Re^{III} starting material, the diphosphine ligands, and the reaction conditions.

We describe here the preparation and structural characterization, by X-ray crystallography, of two Re(II)–Re(II) dimers, $Re_2Cl_4(dppm)_2$ (**1**) and $Re_2Cl_4(dmpe)_2$ (**2**). Both have the electronic configuration $\sigma^2\pi^4\delta^2\delta^{*2}$, viz., a formal metal–metal triple bond, and thus no electronically imposed barrier to rotation about the metal–metal bond.

$Re_2Cl_4(dppm)_2$ (**1**) was prepared several years ago, and an interesting and intensive reaction chemistry has since developed.[3,5–7] Furthermore, the complex constitutes a member of the series $Re_2Cl_4(dppm)_2$, $Re_2Cl_5(dppm)_2$, and $Re_2Cl_6(dppm)_2$, which are formally related to one another by one-electron oxidation and concomitant gain of Cl^-. With the successful growth of single crystals, after many earlier frustrations, we were now able to complete the structural investigation of this series.

When bis(phosphines) with a two-carbon linkage are involved, the reduction process is known to provide two major configurational isomers: the α (chelating) and the β (bridging) forms. Our present results corroborate previous findings that the isolation of the α or β isomer depends on whether the reaction proceeds under kinetic or thermodynamic control.[8] It appears that the α form is in all instances the primary product, which will eventually isomerize to the more stable β form.

Experimental Section

Preparation of $Re_2Cl_4(dppm)_2$ (1). Samples of $Re_2Cl_4(dppm)_2$ were obtained by a slight modification of the existing literature preparation.[3] A mixture of $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$ (0.674 g, 0.682 mmol) and dppm (1.4 g, 3.6 mmol) was added to 30 mL of *reagent grade* methanol and refluxed for 0.5 h. The resulting purple solid was filtered off and washed with copious amounts of diethyl ether to remove any unreacted dppm. The excess dppm can be recovered unchanged from the ether washings by addition of methanol and chilling to 0 °C. The purple complex was obtained in a sufficiently pure state by this process to avoid the necessity

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

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of purification by recrystallization; yield 0.76 g (87%).

The solid complex should be stored under an inert atmosphere to avoid its oxidation and decomposition to $Re_2Cl_5(dppm)_2$ and other species. This oxidation process also occurs when its solutions are exposed to the atmosphere. $Re_2Cl_4(dppm)_2$ is fairly soluble in many common solvents, i.e., acetone, benzene, chloroform, dichloromethane, and tetrahydrofuran, although it displays very poor solubility in alcohols and diethyl ether.

Single Crystals of $Re_2Cl_4(dppm)_2$. Crystals of reasonable size and well-developed faces were obtained by almost any of the established techniques such as slow cooling, solvent layering, etc. Despite their flawless macroscopic appearance they turned out to be unsuitable for single-crystal diffractometry because they were either poor scatterers of X-rays or twins. Good single crystals were eventually obtained by filtering a dilute CH_2Cl_2 solution of $Re_2Cl_4(dppm)_2$ through a thick layer of Celite. The filtrate was placed into a carefully cleaned glass tube (10 mm o.d.) inside a Schlenk flask. The tube was surrounded by dry, air-free hexane. Over a period of 4 weeks, by slow diffusion of the CH_2Cl_2 into the hexane, crystals grew on the wall of the NMR tube. Crystals of various morphologies were thereby observed: prisms, rods, and plates. Inspection under polarized light revealed that only the plates had single-crystalline regions, and the specimen used for data collections was cut out of such a plate.

Preparation of α-$Re_2Cl_4(dmpe)_2 \cdot CH_3OH$ (2). $(n\text{-}Bu_4N)_2Re_2Cl_8$ was prepared according to a previously published procedure,[9] and 0.50 g (0.55 mmol) of this blue-green material was placed in a flask equipped with a stir bar. Methanol (40 mL) containing 3 drops of concentrated HCl was then added, followed by 0.25 mL (1.65 mmol) of 1,2-bis(dimethylphosphino)ethane (dmpe). This mixture was stirred, and the color immediately changed to bright green. The mixture was stirred at room temperature for 1 h. A green precipitate quickly settled out of a green-brown solution after stirring was ceased. The solid product was filtered off on a medium glass frit and washed with 20 mL of methanol. Before it was allowed to dry completely, the product was dissolved in 20 mL of dichloromethane in order to attempt recrystallization. Layering 5 mL of this CH_2Cl_2 solution with hexane yielded large, single crystals. The remainder of the CH_2Cl_2 solution was cooled at −20 °C to give additional crystalline product; yield of $Re_2Cl_4(dmpe)_2 \cdot CH_3OH$ 0.34 g (73%).

X-ray Crystallography. $Re_2Cl_4(dppm)_2$ (1). The crystallographic measurements were performed on a Nicolet P3 four-circle diffractometer. The Enraf-Nonius crystallographic computing package, VAXSDP, was used for all calculations.[10]

A large number of crystals of **1** had to be surveyed before a single crystal was found. The latter was an irregularly shaped fragment chipped off a larger crystal. It was mounted inside a Lindemann glass capillary surrounded by mother liquor. The cell dimensions were derived from 25 reflections and, together with the Laue class, confirmed by axial photographs.

A total of 2798 reflections were collected for $5° < 2\theta < 45°$, of which 2636 were unique. After data reduction the structure was solved by the Patterson method and refined by alternating cycles of least-squares refinement and difference Fourier maps. Since the amount of measured data considered to be significant was limited (1862 reflections, with use of a 3σ cutoff on F_o^2) by the crystal size, only the atoms of the coordination sphere were refined anisotropically. The carbon atoms of the phenyl rings were treated isotropically and refined with satisfactory thermal parameters. The last cycle of refinement included the fit of 333 parameters to 1862 observations and gave residuals of $R = 0.052$, $R_w = 0.062$. The final difference Fourier map was featureless with a highest peak of 0.81 e/Å^3.

α-$Re_2Cl_4(dmpe)_2 \cdot CH_3OH$ (2). A green prismatic crystal was coated with epoxy cement and mounted on the tip of a glass fiber. Routine data collection was carried out on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo Kα radiation. A total of 1254 reflections in the range of $4° < 2\theta < 50°$ were collected without any significant change in the intensity of three standard reflections during the 9 h of X-ray exposure time.

After correction for Lorentz and polarization effects, an empirical absorption correction, based on azimuthal scans of nine reflections with Eulerian angle χ near 90°, was applied. In all, there were 854 unique data with $F_o^2 > 3\sigma(F_o^2)$.

The systematic absences (hkl, $h + k = 2n + 1$; $hk0$, $h = 2n + 1$, $k = 2n + 1$; $0kl$, $l = 2n + 1$) limited the choice of possible space groups to *Ccma* and *Cc2a*. The centrosymmetric choice was confirmed by successful refinement. After the structural model for the dimeric unit had been developed and refined withh isotropic thermal parameters, two major peaks in the difference Fourier map were indicative of a methanol solvent molecule. The presence of methanol in the lattice was later confirmed by IR spectroscopy. Crystallographically, a disordered model had to be refined with the oxygen atom at an inversion center (0, 0, $^1/_2$) with site symmetry $2/m$. Consequently, there are four equivalent positions for the carbon atom connected to this oxygen atom and a multiplicity of 0.25 was therefore assigned.

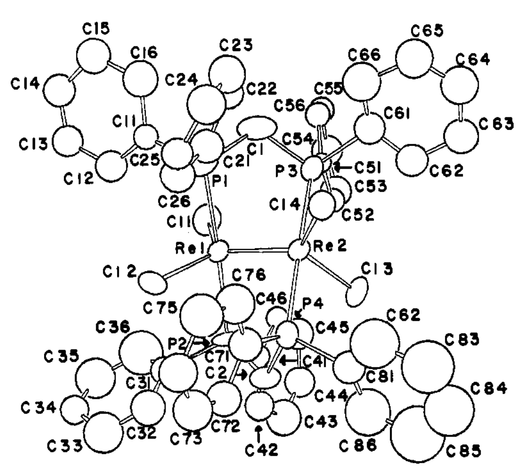

Figure 1. Computer-drawn view of the $Re_2Cl_4(dppm)_2$ molecule. Atoms are represented by their ellipsoids or spheres of thermal vibration at the 50% probability level.

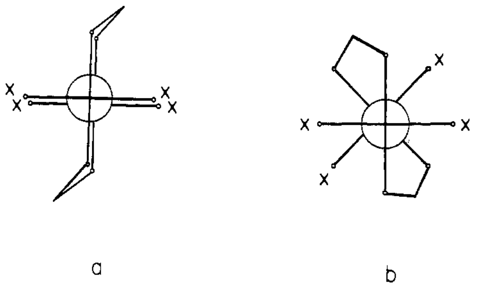

Figure 2. Diagrams showing the two conformations for β-$M_2X_4(R_2PCH_2PR_2)_2$ molecules: (a) eclipsed, with envelope-shaped heterocyclic rings; (b) staggered, with a twist conformation in the ring.

The dirhenium molecule was refined with anisotropic thermal parameters for the non-hydrogen atoms while the solvent was refined isotropically. Convergence of the refinement resulted in residuals of $R = 0.027$ and $R_w = 0.044$. The largest peak in the final difference Fourier map was 0.99/Å and was located 0.93 Å from the solvent oxygen atom.

The pertinent crystallographic parameters for both structures are summarized in Table I. Parts a and b of Table II contain the positional parameters with the isotropic equivalents of the thermal parameters for **1** and **2**, respectively.

Results and Discussion

$Re_2Cl_4(dppm)_2$ (1). The triply bonded complex $Re_2Cl_4(dppm)_2$ (**1**) was prepared several years ago.[4] At the time, it was proposed to have the same type of eclipsed M_2L_8 structure that is characteristic of many multiply bonded dimetal species. More recently, there have been several interesting and important developments in the reaction chemistry of **1**, specifically, in the development of its redox chemistry,[3] and the discovery of several novel species in its reaction with nitriles,[5] isocyanides,[6] and carbon monoxide.[7] This work has necessitated the complete structural characterization of **1** so that meaningful comparisons can be drawn with the structures of other complexes derived therefrom.

Figure 1 shows an ORTEP representation of the dimeric unit. Averaged[11] bond distances and angles are listed in Table III while a complete list has been deposited with the supplementary material. The structure possessses the broad, general features that would

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(9) Barder, T. J.; Walton, R. A. *Inorg. Chem.* **1982**, *21*, 2510.

(10) Crystallographic calculations were done with VAXSDP software on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University.

(11) Chemically equivalent bond lengths and angles were averaged. Values in parentheses connote esd's. $[X]$ is defined as $[X]^2 = \sum\Delta_i^2/n(n-1)$ for the deviations, Δ_i, of n independent values.

Table I. Crystallographic Data

	$Re_2Cl_4P_4OC_{13}H_{36}$	$Re_2Cl_4P_4C_{50}H_{44}$
fw	846.55	1283.02
space group	*Ccma* (nonstd for *Cmca*)	$P2_1/n$
systematic absences	*hkl*: $h + k = 2n + 1$ *hk*0: $h = 2n + 1$, $k = 2n + 1$ 0*kl*: $l = 2n + 1$	*h*0*l*: $h + l = 2n + 1$ 0*k*0: $k = 2n + 1$
a, Å	11.595 (2)	11.647 (3)
b, Å	11.475 (2)	12.849 (4)
c, Å	14.925 (2)	38.691 (9)
β, deg		85.96 (2)
V, Å^3	2505 (1)	5776 (4)
Z	4	4
d_{calcd}, g/cm^3	2.25	1.48
cryst size, mm	0.33 × 0.34 × 0.37	0.20 × 0.15 × 0.05
μ(Mo Kα), cm^{-1}	104.37	45.70
data collection instrument	Enraf-Nonius CAD-4	Nicolet R3
radiation (monochromated in incident beam)	Mo Kα	Mo Kα
orientation reflcns: no., range (2θ), deg	25, 14–38	25, 14–20
temp, °C	25	25
scan method	ω/2θ	ω
data collecn range, 2θ, deg	4–50	4–45
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	854	1862
no. of parameters refined	57	333
exptl trans factors: max, min, %	99.4, 76.5	99.9, 54.3
R^a	0.0274	0.052
R_w^b	0.0444	0.062
quality-of-fit indicator^c	1.438	0.999
largest shift/esd, final cycle	0.35	0.22
largest peak, e/Å^3	0.99	0.81

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

have been expected. Thus, the two dppm ligands span the Re–Re bond and the $ReCl_2P_2$ units at each end have trans stereochemistry. The Re–Re bond length, 2.234 (3) Å, is within the expected range.

The surprising feature of this structure is in the conformations of the two fused metallocyclic rings. In general, there are two preferred conformations, represented by the Newman projections along the metal–metal axis in Figure 2. The envelope configuration (Figure 2a) results in an eclipsed arrangement of the substituents at the metal center while permitting the low-energy chair conformation for the remainder of the ring. The conformation in Figure 2b is derived from the twist-boat conformation of the cyclohexane ring. The conformation of the metal–metal bond is staggered, but the remainder of the ring is strained relative to the chair conformation.

For a Re(II)–Re(II) compound in which there is a $\sigma^2\pi^4\delta^2\delta^{*2}$ triple bond that imposes no barrier to rotation, the observed staggered arrangement appears to correspond to an energy minimum for the pseudorotation of five-membered dimetallocycles of comparable configuration and metric properties. In a qualitative sense this is easy to visualize because a twist about the metal–metal axis relieves the most obvious repulsive steric interactions such as the vicinal Cl···Cl and P···P repulsions.

The situation is changed entirely when electronic restrictions are imposed. The almost isomorphous Re(II)–Re(III) dimer, $Re_2Cl_5(dppm)_2$ (**3**) has the electronic configuration $\sigma^2\pi^4\delta^2\delta^{*1}$, with a formal bond order of 3.5. Efficient overlap of δ orbitals (the resulting MO is only half-populated in **3**) is favored by an eclipsed conformation at the metal–metal bond,[12] and indeed an envelope conformation of the five-membered rings is observed in **3**. It appears that the energy corresponding to half of the δ component together with the additional steric interaction between the phenyl rings and the axial chloride atom suffices to overcome whatever energy difference there is between the envelope and the twisted conformation. Not surprising, then, is the envelope conformation observed in all quadruply bonded $M_2(dppm)_2X_4$ (M = Mo, W) species, where there is the potential strength of a full δ bond favoring the eclipsed conformation about the M–M axis.

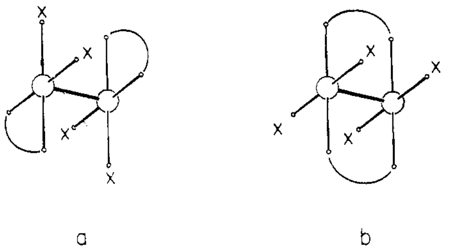

Figure 3. Diagrams of the (a) chelated (α) and (b) bridged (β) structures for $M_2X_4(P\text{-}P)_2$ type molecules. In reality β structures are often partly staggered.

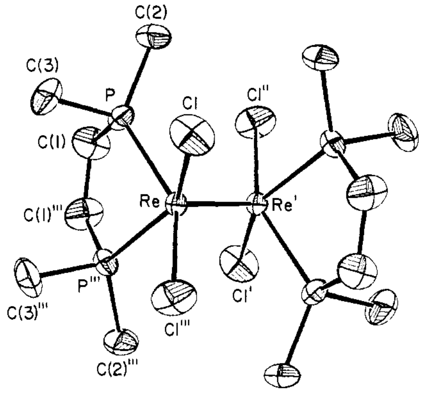

Figure 4. ORTEP view of the principal molecule of α-$Re_2Cl_4(dmpe)_2 \cdot CH_3OH$. Singly primed, doubly primed, and triply primed atoms are related to unprimed atoms by an inversion center, a twofold axis, and a mirror plane, respectively.

$Re_2Cl_4(dmpe)_2$ (2). If for the reduction of the Re_2^{6+} core to the Re_2^{4+} core a bis(phosphine) with an ethylene bridge is employed, two products can, in general, be isolated under favorable conditions: the chelated (α) structure and the bridged (β) structure (Figure 3). Much evidence has been garnered from study of the analogous quadruply bonded $Mo_2X_4(PP)_2$ compounds to show that the α form is the kinetically favored product, while the β form is obtained when the reaction proceeds to thermodynamic equilibrium.[8] This is consistent with some recent observations on $Re_2X_4(LL)_2$ systems: When $Re_2Cl_4(depe)_2$ (depe is 1,2-bis(diethylphosphino)ethane) was prepared by refluxing $(n\text{-}Bu_4N)_2[Re_2Cl_6]$ and depe in ethanol for several hours, β-$Re_2Cl_4(depe)_2$ was isolated as the only product.[13] The rate-determining step in this case appears to be the dissolving of the starting material since $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ is only slightly soluble in ethanol. On the other hand, in this study $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ was reacted in methanol, where it is highly soluble, with dmpe, and a swift reaction was observed at room temperature with simultaneous precipitation of the product, α-$Re_2Cl_4(dmpe)_2$.

The molecular structure and the atom-numbering scheme of α-$Re_2Cl_4(dmpe)_2$ are displayed in Figure 4. Important bond distances and angles are listed in Table IV. The molecule possesses crystallographic 2/*m* symmetry with both rhenium atoms located on a mirror plane and the 2-fold axis being a perpendicular bisector of the Re–Re bond. The five-membered metallacycles formed by the chelating dmpe ligands are in an envelope con-

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[12] Cotton, F. A. *Inorg. Chem.* **1965**, *4*, 334.

[13] Campbell, F. L.; Cotton, F. A.; Powell, G. L. *Inorg. Chem.*, in press.

Table II. Positional Parameters and Their Estimated Standard Deviations[a] for $Re_2Cl_4(dppm)_2$ and $Re_2Cl_4(dmpe)_2$

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
				a. $Re_2Cl_4(dppm)_2$					
Re1	0.1208 (2)	0.4760 (1)	0.13402 (5)	2.98 (5)	C41	0.294 (3)	0.244 (3)	0.093 (1)	3 (1)*
Re2	0.0565 (2)	0.3661 (1)	0.17578 (5)	2.81 (5)	C42	0.300 (4)	0.166 (3)	0.068 (1)	5 (1)*
Cl1	0.3158 (9)	0.5279 (9)	0.1354 (4)	4.9 (3)	C43	0.405 (4)	0.095 (4)	0.068 (1)	8 (1)*
Cl2	−0.009 (1)	0.5330 (9)	0.0940 (3)	5.0 (3)	C44	0.480 (4)	0.116 (4)	0.091 (1)	6 (1)*
Cl3	0.1576 (9)	0.2091 (8)	0.1797 (3)	4.2 (3)	C45	0.475 (4)	0.197 (4)	0.116 (1)	6 (1)*
Cl4	−0.1074 (8)	0.4101 (8)	0.2122 (3)	3.9 (3)	C46	0.368 (3)	0.266 (3)	0.119 (1)	2.9 (9)*
P1	0.0761 (9)	0.6252 (9)	0.1712 (3)	3.7 (3)	C51	0.325 (3)	0.441 (3)	0.2212 (9)	2.4 (8)*
P2	0.165 (1)	0.3307 (8)	0.0932 (3)	4.2 (4)	C52	0.383 (3)	0.360 (3)	0.2064 (9)	3.4 (9)*
P3	0.1653 (9)	0.4566 (9)	0.2178 (3)	3.5 (3)	C53	0.502 (4)	0.359 (4)	0.209 (1)	6 (1)*
P4	−0.057 (1)	0.2740 (9)	0.1347 (3)	4.1 (4)	C54	0.563 (4)	0.435 (4)	0.225 (1)	6 (1)*
C1	0.161 (4)	0.598 (3)	0.211 (1)	6 (2)	C55	0.505 (3)	0.511 (3)	0.245 (1)	4 (1)*
C2	0.049 (4)	0.231 (3)	0.098 (1)	5 (1)	C56	0.378 (3)	0.516 (3)	0.2426 (9)	3.5 (9)*
C11	0.131 (3)	0.747 (3)	0.155 (1)	3 (1)*	C61	0.108 (4)	0.436 (4)	0.266 (1)	5 (1)*
C12	0.170 (4)	0.755 (4)	0.122 (1)	6 (1)*	C62	0.113 (4)	0.327 (4)	0.271 (1)	6 (1)*
C13	0.206 (3)	0.857 (4)	0.112 (1)	5 (1)*	C63	0.083 (4)	0.294 (4)	0.306 (1)	6 (1)*
C14	0.203 (4)	0.942 (4)	0.132 (1)	6 (1)*	C64	0.044 (4)	0.372 (5)	0.329 (1)	7 (1)*
C15	0.159 (4)	0.938 (4)	0.167 (1)	6 (1)*	C65	0.033 (4)	0.475 (4)	0.320 (1)	7 (1)*
C16	0.124 (4)	0.836 (4)	0.180 (1)	7 (1)*	C66	0.069 (4)	0.515 (5)	0.284 (1)	8 (1)*
C21	−0.073 (4)	0.651 (4)	0.186 (1)	6 (1)*	C71	−0.180 (4)	0.331 (4)	0.117 (1)	6 (1)*
C22	−0.093 (3)	0.693 (3)	0.221 (1)	5 (1)*	C72	−0.212 (4)	0.290 (4)	0.084 (1)	6 (1)*
C23	−0.212 (4)	0.721 (4)	0.231 (1)	6 (1)*	C73	−0.313 (4)	0.328 (4)	0.072 (1)	7 (1)*
C24	−0.298 (4)	0.710 (4)	0.212 (1)	7 (1)*	C74	−0.377 (4)	0.403 (4)	0.086 (1)	7 (1)*
C25	−0.275 (3)	0.685 (3)	0.177 (1)	5 (1)*	C75	−0.357 (5)	0.445 (4)	0.120 (1)	8 (2)*
C26	−0.153 (4)	0.652 (4)	0.163 (1)	6 (1)*	C76	−0.253 (4)	0.407 (4)	0.135 (1)	7 (1)*
C31	0.171 (4)	0.377 (4)	0.046 (1)	4 (1)*	C81	−0.118 (4)	0.149 (4)	0.151 (1)	5 (1)*
C32	0.079 (4)	0.354 (4)	0.026 (1)	7 (1)*	C82	−0.197 (6)	0.158 (5)	0.176 (2)	12 (2)*
C33	0.089 (4)	0.383 (5)	−0.008 (1)	9 (2)*	C83	−0.254 (6)	0.064 (7)	0.192 (2)	13 (2)*
C34	0.175 (4)	0.452 (3)	−0.018 (1)	5 (1)*	C84	−0.222 (6)	−0.030 (6)	0.181 (2)	12 (2)*
C35	0.273 (5)	0.461 (5)	0.001 (2)	9 (2)*	C85	−0.143 (7)	−0.035 (7)	0.153 (2)	15 (3)*
C36	0.266 (6)	0.431 (5)	0.037 (2)	11 (2)*	C86	−0.079 (6)	0.054 (6)	0.137 (2)	11 (2)*
				b. $Re_2Cl_4(dmpe)_2$					
Re	0.09757 (3)	0.0000	0.00293 (3)	1.678 (9)	C(2)	0.055 (1)	0.2239 (6)	0.1178 (7)	4.2 (2)
Cl	0.1985 (2)	0.1089 (2)	−0.0911 (2)	4.49 (5)	C(3)	0.2636 (9)	0.1281 (7)	0.1442 (8)	5.0 (3)
P	0.1093 (2)	0.1053 (2)	0.1212 (2)	2.61 (4)	O	0.0000	0.0000	0.500	13 (1)*
C(1)	0.056 (1)	0.0536 (7)	0.2252 (6)	4.2 (2)	C	0.019 (5)	0.064 (5)	0.453 (5)	7 (2)*

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

Table III. Averaged[12] Bond Lengths and Angles for $Re_2Cl_4(dppm)_2$ (1)

	(a) Bond Lengths (Å)		
Re–Re	2.234 (3)	$P–C_{Ph}$	1.86 [5]
Re–Cl	2.360 [11]	$C_p–C_{ortho}$	1.39 [6]
Re–P	2.45 [3]	$C_{ortho}–C_{meta}$	1.46 [5]
$P–C_{br}$	1.88 [4]	$C_{meta}–C_{para}$	1.37 [4]
	(b) Bond Angles (deg)		
Re–Re–Cl	117 [2]	P–Re–P	117.0 [1]
–P	91.1 [6]	$Re–P–C_{br}$	107 [4]
Cl–Re–Cl	125 [2]	$–C_{Ph}$	119 [5]
Cl–Re–P	89 [4]	$P–C_{br}–P$	108.0 [2]
	(c) Torsion Angles (deg)		
Cl–Re–Re–Cl	56 [1]	Re–Re–P–C	56.9 [6], 39.3 [1]
P–Re–Re–P	47 [1]	Re–P–C–P	33.0 [4], 2.4 [4]

Table IV. Bond Distances and Angles in α-$Re_2Cl_4(dmpe)_2$

	Distances (Å)		
Re–Re	2.264 (1)	P–C(2)	1.829 (8)
–Cl	2.413 (2)	–C(3)	1.851 (9)
–P	2.337 (2)	C(1)–C(1)′	1.55 (2)
P–C(1)	1.831 (8)	O–C(methanol)	1.19 (6)
	Angles (deg)		
Re–Re–Cl	117.52 (6)	Re–P–C(1)	110.7 (3)
–P	95.02 (5)	–C(2)	124.8 (3)
Cl–Re–Cl′	81.6 (1)	–C(3)	108.2 (3)
–P	89.15 (8)	C(1)–P–C(2)	106.9 (4)
–P′	146.86 (8)	–C(3)	104.1 (5)
P–Re–P′	81.4 (1)	C(2)–P–C(3)	99.8 (5)
		P–C(1)–C(1)′	114.1 (3)

formation. The conformation about the Re–Re bond is rigorously eclipsed.

It is enlightening to compare the $Re_2Cl_4(dmpe)_2$ structure with several others of the α-$Me_2X_4(LL)_2$ type. Several years ago the preparation and structure of $Re_2Cl_4(dppp)_2$ were reported.[14] Here there are two six-membered chelate rings, each in the expected chair conformation. The Re–Re distance there, 2.266 (1) Å, is effectively identical with the one found here, 2.264 (1) Å.

It is even more interesting to compare the $Re_2Cl_4(dmpe)_2$ molecule with two other molecules containing a different metal, namely α-$W_2Cl_4(dmpe)_2$[15] and α-$W_2Cl_4(dppe)_2$.[16] The compounds $Re_2Cl_4(dmpe)_2$ and $W_2Cl_4(dmpe)_2$ did not form isotypic crystals because different solvents were used and the substances actually used for crystallography were $Re_2Cl_4(dmpe)_2{\cdot}CH_3OH$ and $W_2Cl_4(dmpe)_2{\cdot}C_6H_5CH_3$. However, the two molecules have essentially identical structures. In both cases, the chelate rings have envelope conformations and the ligand part of the ring, i.e., the planar PCCP unit, has a proximal rather than a distal tilt. In contrast, the $W_2Cl_4(dppe)_2$ molecule, while it too has an eclipsed conformation about the metal–metal bond, has its chelate rings in a twist conformation. Inspection of models, or even just the various ORTEP drawings available in the published reports, suggests that this difference is attributable to the much larger size of the phenyl groups of the dppe ligand as compared to the methyl groups of the dmpe ligand. The twist conformation does a better job of directing these groups toward the outside, although it increases

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some other, less important internal contacts.

We turn, finally, to what is the most remarkable feature of the $Re_2Cl_4(dmpe)_2$ molecule, namely, that it has an eclipsed rotational conformation, despite the fact that there is no barrier to rotation about the triple Re-Re bond. In the case of the isostructural $W_2Cl_4(dmpe)_2$, this might have been attributed solely to the rotational barrier inherent in the W-W quadruple bond, but the preference of $Re_2Cl_4(dmpe)_2$ for the same structure shows that there are other important forces at work to favor this structure. We hope to provide, in a future report, a detailed and perhaps quantitative analysis of the conformational behavior of these molecules, but we can give here a brief qualitative description of the key features, which are the following:

(i) If the chelate ring conformations are kept constant and rotation about the M-M bond is carried out, the result is an enormous increase in the repulsive contacts between atoms on the two different ends of the molecule, especially one methyl-methyl and two methyl-chlorine contacts. The methyl to methyl distance at a rotation angle of 45° would be ca. 0.9 Å (C to C), an obviously impossible situation; in the eclipsed conformation actually adopted, the closest methyl-methyl contacts are ca. 3.8 Å and all other nonbonded distances are also acceptable.

(ii) If we were to flip both five-membered rings so that the envelopes bend the opposite way, i.e., with the planar PCCP units directed distally, we generate a large number of close contacts even in the eclipsed conformation (mainly, *four* methyl-chlorine contacts of less than 2.0 Å) and in the staggered conformation there are four very short methyl-methyl contacts as well as several short methyl-chlorine contacts.

In summary, the conformational characteristics of both of the α-$M_2Cl_4(dmpe)_2$ molecules appear to be dictated primarily by the nonbonded interactions between the ligand atoms (especially the methyl groups) and, in particular, the eclipsed rotational conformation about the M-M bonds occurs whether there is (in the W_2 compound) or is not (in the Re_2 compound) a δ bond. This case is therefore similar in principle to that of the $M_2X_4(PR_3)_4$ molecules, where an eclipsed conformation about the metal-metal bond is required by the ligand-ligand repulsions, regardless of whether there is (in the Mo_2 and W_2 compounds) or is not (in the Re_2 compounds) a δ bond.

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Registry No. **1**, 58298-10-5; **2**, 96808-01-4; $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$, 38832-70-1; $(n\text{-}Bu_4N)_2Re_2Cl_8$, 14023-10-0; Re, 7440-15-5.

Supplementary Material Available: Tables of structure factors and anisotropic thermal parameters for $Re_2Cl_4(dppm)_2$ and $Re_2Cl_4(dmpe)_2$ and full lists of bond distances and angles for $Re_2Cl_4(dppm)_2$ (21 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the Novel Gold-Iridium Cluster $[IrAu_4(H)_2(PPh_3)_6]BF_4$

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The novel new dihydride iridium-gold cluster complex $[IrAu_4(H)_2(PPh_3)_6]BF_4$ (**1**) was synthesized from the reaction of an acetone solution of $[IrAu_3(PPh_3)_5NO_3]BF_4$ with 1 atm of H_2. Complex **1** was isolated in good yield and was characterized in solution by ^1H and ^{31}P NMR spectroscopy and in the solid state by single-crystal X-ray diffraction. The cluster crystallizes as a 1.5 CH_2Cl_2 solvate in the monoclinic space group $C2/c$ (a = 53.46 (2) Å, b = 14.270 (8) Å, c = 29.228 (9) Å, β = 113.12 (3)°, Z = 8; V = 20 506 Å^3 and R = 0.052 for 4367 observed reflections with $F_o^2 \geq 3\sigma(F_o^2)$]. The molecular structure of the $[IrAu_4(H)_2(PPh_3)_6]^+$ cation consists of an approximately trigonal-bipyramidal (TBP) $IrAu_4$ core with an $Ir(PPh_3)_2$ unit occupying an equatorial position. The four $AuPPh_3$ units occupy the axial positions and the two remaining equatorial sites. The major deviation from ideal TBP geometry is caused by the shorter Ir-Au distances (average 2.690 (2) Å) compared with the bonded (eq-eq and eq-ax) Au-Au separations (average 2.920 (2) Å). The two hydrides were not located by the X-ray analysis but are thought to be bridging Ir-axial Au bonds. The solution ^1H NMR data tend to support this assignment, however, with some uncertainty, and a terminal Ir-H bonding description is also possible. The complex is fluxional in solution. Variable-temperature ^{31}P NMR data show that a process that interchanges the axial and equatorial Au sites is occurring.

Introduction

During the past several years there has been considerable interest in the synthesis of mixed-metal gold cluster compounds.[1-15] Our research group has been primarily interested in iridium- and rhodium-gold clusters that contain phosphine and hydrido ligands and their potential usefulness in catalysis.[1,13-15] For example, $[IrAu_2(H)(PPh_3)_4NO_3]BF_4$ (**1**)[1] and $[IrAu_3(PPh_3)_5NO_3]BF_4$ (**2**)[13] have been synthesized and characterized by single-crystal X-ray

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