since they were not shown in ref 5, and give an intradimer exchange coupling of $J/k = -115$ (1) K and an effective interdimer coupling of $J'/k = -17$ (1) K with $g = 2.18$ and a 0.8% impurity.

Registry No. (morphH)$_2$Cu$_2$Cl$_6$, 61825-58-9; (morphH)$_2$Cu$_2$Br$_6$, 114694-36-9; (melH$_2$)Cu$_2$Br$_6$, 110132-63-3.

Supplementary Material Available: Table S1, listing anisotropic thermal parameters, Table S2, listing H atom coordinates and isotropic thermal parameters, and Table S3, listing bond distances and angles, torsion angles, least-squares planes, and interatomic contacts (7 pages); listings of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Studies on the α and β Isomers of Complexes of the Type Re$_2$X$_4$(LL)$_2$. Structural Characterization of α- and β-Re$_2$Cl$_4$(dppee)$_2$ (dppee = *cis*-Ph$_2$PCH=CHPPh$_2$)

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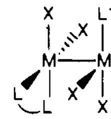
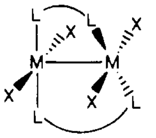
The first structural study on a pair of α and β isomers of dirhenium(II) of the type Re$_2$X$_4$(LL)$_2$ (X = Cl, Br; LL = bidentate phosphine ligand) has been carried out in the case of X = Cl and LL = *cis*-Ph$_2$PCH=CHPPh$_2$ (dppee). Crystals of α-Re$_2$Cl$_4$(dppee)$_2$·*n*-PrOH, which were grown from CH$_2$Cl$_2$/*n*-propyl alcohol, crystallize in the triclinic space group $P\bar{1}$ with the following unit cell dimensions: $a = 13.485$ (3) Å, $b = 17.556$ (5) Å, $c = 11.952$ (3) Å, $\alpha = 87.24$ (2)°, $\beta = 100.12$ (2)°, $\gamma = 110.66$ (2)°, $V = 2606$ (3) Å^3, and $Z = 4$. The structure was refined to $R = 0.037$ ($R_w = 0.048$), with quality of fit 1.403, for 5384 data with $F_o^2 > 3\sigma(F_o^2)$. There are two crystallographically independent molecules, which are essentially identical structurally with an average Re$\equiv$Re distance of 2.258 Å. The centrosymmetric molecules contain chelating dppee ligands and possess an eclipsed rotational geometry. The isomer β-Re$_2$Cl$_4$(dppee)$_2$ crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 16.917$ (2) Å, $b = 12.992$ (4) Å, $c = 22.990$ (7) Å, $\beta = 106.86$ (2)°, $V = 4836$ (4) Å^3, and $Z = 4$. The structure was refined to residuals of $R = 0.088$ and $R_w = 0.074$ and quality of fit 2.389 for 3002 data with $F_o^2 > 3\sigma(F_o^2)$. Refinement of the structure was complicated by a disorder in which a second set of rhenium atoms (20% occupancy) was found, centered at the same point as the principal pair (80% occupancy), and with the Re–Re vector roughly perpendicular to that of the primary Re$_2$ unit. The Re$\equiv$Re distance was refined to 2.242 (3) Å for the major component of the disorder. The molecules possess an overall staggered geometry in which the dppee ligands bridge the two metal centers. The resulting six-membered ring conformations in both the principal and minor molecules are of the type well-known for cyclohexene, namely, a flattened chair or half-chair. Synthetic procedures have been developed for the preparation of α-Re$_2$X$_4$(dppe)$_2$ (X = Cl, Br; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$), complexes whose β isomers have been reported previously. The first successful chemical oxidation of α isomers of dirhenium(II) has been accomplished; α-Re$_2$Cl$_4$(LL)$_2$ complexes (LL = *cis*-Ph$_2$PCH=CHPPh$_2$, Ph$_2$P(CH$_2$)$_3$PPh$_2$) have been oxidized by (Cp$_2$Fe)PF$_6$ in CH$_2$Cl$_2$ to give paramagnetic α-[Re$_2$Cl$_4$(LL)$_2$]PF$_6$.

Introduction

In a recent report we described the first instance of the isolation of dirhenium(II) complexes of the type Re$_2$X$_4$(LL)$_2$ (X = halogen; LL = bidentate phosphine ligand) in both their α and β isomeric forms (see I and II).[2] Both isomers were isolated in the case of Re$_2$Br$_4$(depe)$_2$ and Re$_2$X$_4$(dppee)$_2$ (X = Cl, Br; depe = Et$_2$PCH$_2$CH$_2$PEt$_2$; dppee = *cis*-Ph$_2$PCH=CHPPh$_2$), and details of the spectroscopic and electrochemical properties of these complexes were reported. Subsequently, we have succeeded in obtaining α- and β-Re$_2$Cl$_4$(dppee)$_2$ in a crystalline form suitable for X-ray structure determinations. The full structural details are described herein, along with details of the synthesis of α-Re$_2$X$_4$(dppe)$_2$ (X = Cl, Br; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$), complexes whose β isomers have been reported previously,[3,4] and the chemical oxidations of α-Re$_2$Cl$_4$(LL)$_2$ (LL = *cis*-Ph$_2$PCH=CHPPh$_2$, Ph$_2$P(CH$_2$)$_3$PPh$_2$) to give paramagnetic α-[Re$_2$Cl$_4$(LL)$_2$]PF$_6$. This is the first time that α isomers of dirhenium(II) have been oxidized chemically.



I (α)



II (β)

Experimental Section

Starting Materials. Samples of the complexes of α-Re$_2$Cl$_4$(dppee)$_2$,[2] β-Re$_2$Cl$_4$(dppee)$_2$,[2] and α-Re$_2$Cl$_4$(dppp)$_2$ (dppp = Ph$_2$P(CH$_2$)$_3$PPh$_2$)[5] were prepared from (n-Bu$_4$N)$_2$Re$_2$Cl$_8$[6] according to the literature methods. The oxidizing agent ferrocenium hexafluorophosphate, (Cp$_2$Fe)PF$_6$, was obtained in the usual fashion.[7] Solvents used in the preparation and characterization of the complexes were of commercial grade and were thoroughly deoxygenated prior to use.

Reaction Procedures. All reactions were performed under a nitrogen atmosphere by using standard vacuum line techniques.

A. Synthesis and Characterization of α-Re$_2$X$_4$(dppe)$_2$. (a) α-Re$_2$Cl$_4$(dppe)$_2$. A mixture of (n-Bu$_4$N)$_2$Re$_2$Cl$_8$ (0.20 g, 0.18 mmol), dppe (0.17 g, 0.44 mmol), and methanol (20 mL), to which 10 drops of concentrated HCl had been added, was refluxed for 6 h. The resulting reaction mixture was then cooled to room temperature, and the yellow-green solid was filtered off and washed with methanol until the washings were colorless. This product was recrystallized several times from CH$_2$Cl$_2$/methanol, then chromatographed on a silica gel column (CH$_2$Cl$_2$ as eluent), and finally recrystallized from CH$_2$Cl$_2$/diethyl ether. The green product was washed with hexanes and diethyl ether and dried; yield 0.03 g (13%). Anal. Calcd for C$_{52}$H$_{48}$Cl$_4$P$_4$Re$_2$: C, 47.63; H, 3.69. Found: C, 46.54; H, 3.82. It was identified as α-Re$_2$Cl$_4$(dppe)$_2$ on the basis of its electrochemical and spectroscopic properties. The cyclic voltammogram of this complex measured in 0.1 M TBAH/CH$_2$Cl$_2$ revealed the presence of two reversible one-electron oxidations at $E_{1/2} = +0.27$ V and $E_{1/2} = +1.05$ V and an irreversible reduction at $E_{p,c} = -1.57$ V vs Ag/AgCl. These electrochemical properties are similar to those of α-Re$_2$Cl$_4$(dppee)$_2$[2] and typical of other dirhenium(II) species that contain

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(1) (a) Purdue University. (b) Texas A&M University.
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the triply bonded Re_2^{4+} core.[8] The Nujol mull electronic absorption spectrum of this complex (λ_{max} in nm) exhibits bands at ~840 (w), 610 (w), 560 (w), 430 (sh), and ~370 (sh). These spectral properties match very closely those reported for α-$Re_2Cl_4(dppee)_2$.[2]

The original yellow reaction filtrate and washings from this reaction were combined and evaporated to dryness. The residue was recrystallized from CH_2Cl_2/diethyl ether and the resultant yellow product filtered off, washed with water, hexanes, and diethyl ether, and dried; yield 0.12 g (31%). This product was identified as $[ReCl_2(dppe)_2]Cl$ from its electrochemical and spectroscopic properties.[9]

(b) α-$Re_2Br_4(dppe)_2$. A mixture of $(n\text{-}Bu_4N)_2Re_2Br_8$ (0.20 g, 0.13 mmol), dppe (0.13 g, 0.33 mmol), and methanol (20 mL), to which 10 drops of concentrated HBr (48%) had been added, was refluxed for 24 h. The yellow-green reaction mixture was cooled to room temperature and filtered. The insoluble product was washed with methanol, and the remaining dark green solid was recrystallized from CH_2Cl_2/diethyl ether, chromatographed on a silica gel column (CH_2Cl_2 as eluent), and recrystallized from CH_2Cl_2/diethyl ether; yield 0.04 g (20%). Anal. Calcd for $C_{52}H_{48}Br_4P_4Re_2$: C, 41.95; H, 2.98. Found: C, 42.19; H, 2.98. This product was identified as α-$Re_2Br_4(dppe)_2$ on the basis of its electrochemical and spectroscopic properties. The cyclic voltammogram of this compound in 0.1 M TBAH/CH_2Cl_2 revealed two reversible one-electron oxidations at $E_{1/2} = +0.29$ V and $E_{1/2} = +1.03$ V and an irreversible reduction at $E_{p,c} = -1.45$ V vs Ag/AgCl. The Nujol mull electronic absorption spectrum of this complex (λ_{max} in nm) exhibits bands at ~840 (w), 610 (w), ~440 (sh), and ~400 (sh). These properties, like those for α-$Re_2Cl_4(dppe)_2$, are in accord with this product being the α isomer and differ from those expected for β-$Re_2Br_4(dppe)_2$.[2,3]

Workup of the original yellow reaction filtrate gave a crop of orange crystalline $[ReBr_2(dppe)_2]Br$; yield 0.09 g (24%). Its spectroscopic and electrochemical properties are very similar to those of $[ReBr_2(dppee)_2]Br{\cdot}H_2O$.[9]

B. Oxidation of α-$Re_2Cl_4(L\text{-}L)_2$. (i) α-$[Re_2Cl_4(dppee)_2]PF_6$. A quantity of α-$Re_2Cl_4(dppee)_2$ (0.20 g, 0.15 mmol) was suspended in CH_2Cl_2 (10 mL), and a close to stoichiometric amount of $(Cp_2Fe)PF_6$ (0.055 g, 0.17 mmol) was added. The reaction mixture was stirred at room temperature for 1 h. A brown solid was filtered off, washed with methanol, hexanes, and diethyl ether, and dried; yield 0.22 g (99%). Anal. Calcd for $C_{54}H_{48}Cl_8F_6P_5Re_2$ (i.e., $[Re_2Cl_4(dppee)_2]PF_6{\cdot}2CH_2Cl_2$): C, 39.99; H, 2.98; Cl, 17.49. Found: C, 39.07; H, 2.77, Cl, 16.84. The presence of PF_6^- was confirmed by IR spectroscopy: ν(P–F) mode of PF_6^- at 850 cm^{-1}.

(ii) α-$[Re_2Cl_4(dppp)_2]PF_6$. A quantity of α-$Re_2Cl_4(dppp)_2$ (0.20 g, 0.15 mmol) was suspended in CH_2Cl_2 (10 mL), and a slight excess of $(Cp_2Fe)PF_6$ (0.07 g, 0.21 mmol) was added. The reaction mixture was stirred at room temperature for 3 h. The brown solution that developed was reduced in volume to ~2 mL, and diethyl ether was added to precipitate the brown product. The product was filtered off, washed with THF, hexanes, and diethyl ether, and dried; yield 0.16 g (72%). Anal. Calcd for $C_{54.5}H_{53}Cl_5F_6P_5Re_2$ (i.e. $[Re_2Cl_4(dppp)_2]PF_6{\cdot}0.5CH_2Cl_2$): C, 43.04; H, 3.51; Cl, 11.65. Found: C, 42.16; H, 3.60; Cl, 11.81. The presence of PF_6^- was confirmed by IR spectroscopy (Nujol mull), which showed the ν(P–F) mode of PF_6^- at 844 cm^{-1}.

Preparation of Single Crystals of α-$Re_2Cl_4(dppee)_2$ and β-$Re_2Cl_4(dppee)_2$. Crystals of the α isomer were grown by layering a dichloromethane solution of the compound with n-propyl alcohol, while the β isomer gave X-ray-quality crystals from CH_2Cl_2/ethanol.

X-ray Data Collection, Structure Solution, and Refinement. Crystals of α- and β-$Re_2Cl_4(dppee)_2$ were mounted on glass fibers and covered with thin layers of epoxy cement. Data sets were gathered from both crystals by an automated four-circle diffractometer, using routine procedures that have been described previously.[10] In each case, the lattice dimensions and Laue group of the crystal were verified by normal-beam oscillation photography. Geometric data and important data-collection parameters are summarized in Table I.

The data sets from both crystals were reduced by routine computational procedures.[11] Absorption corrections were applied to both data sets,[12] based on azimuthal scans of several reflections with Eulerian angle χ near 90°. Neither crystal showed any sign of decomposition, as judged by the invariance of the intensities of three check reflections, which were measured at regular intervals.

Table I. Crystal Data for α-$Re_2Cl_4(dppee)_2{\cdot}n$-PrOH and β-$Re_2Cl_4(dppee)_2$

	α-$Re_2Cl_4(dppee)_2{\cdot}$ n-PrOH	β-$Re_2Cl_4(dppee)_2$
formula	$Re_2Cl_4P_4OC_{55}H_{52}$	$Re_2Cl_4P_4C_{52}H_{44}$
fw	1367.14	1307.04
space group	$P\bar{1}$	$P2_1/n$
syst absences	none	$(0k0)$, $k \neq 2n$; $(h0l)$, $h + l \neq 2n$
a, Å	13.485 (13)	16.917 (2)
b, Å	17.556 (5)	12.992 (4)
c, Å	11.952 (3)	22.990 (7)
α, deg	87.24 (2)	90
β, deg	100.12 (2)	106.86 (2)
γ, deg	110.66 (2)	90
V, Å^3	2606 (3)	4836 (4)
Z	2	4
d_{calcd}, g/cm^3	1.742	1.795
cryst size, mm	0.30 × 0.20 × 0.15	0.20 × 0.16 × 0.08
μ(Mo Kα), cm^{-1}	50.703	54.60
data collecn instrument	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation monochromated in incident beam (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
orientation rflns: no.; range (2θ), deg	25; $17.68 < 2\theta < 33.80$	25; $17.14 < 2\theta < 36.84$
temp, °C	20 ± 1	20 ± 1
scan method	ω scan	ω scan
data collecn range, 2θ, deg	$4 < 2\theta < 46$	$4 < 2\theta < 46$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	6860, 5384	6705, 3002
no. of params refined	575	442
max, min transmission factors, %	99.99, 80.04	99.79, 60.45
R^a	0.037	0.088
R_w^b	0.048	0.081
quality-of-fit indicator^c	1.403	2.389
largest shift/esd, final cycle	0.01	0.19
largest peak, e/Å^3	1.928	1.935

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

For the structure of α-$Re_2Cl_4(dppee)_2$, the positions of the metal atoms were derived by an automatic Patterson interpretation algorithm.[11c] The remainder of the structure was developed and refined in an alternating sequence of difference Fourier maps and least-squares cycles. The crystallographic asymmetric unit was found to comprise two independent half-molecules of α-$Re_2Cl_4(dppee)_2$, plus a single molecule of n-propyl alcohol. The atoms of $Re_2Cl_4(dppee)_2$ were refined with anisotropic displacement parameters, and n-propyl alcohol was refined isotropically. In the final least-squares cycle, 575 parameters were fitted to 5384 observations, for a data-to-parameter ratio of 9.4. The least-squares residuals and other relevant parameters are given in Table I.

For the structure of β-$Re_2Cl_4(dppee)_2$, the positions of the principal, unique rhenium atoms were located by a Patterson interpretation algorithm;[11c] the structure was developed and refined in an alternating sequence of difference Fourier maps and least-squares refinements. At the point of isotropic convergence, a further absorption correction was applied by the method of Walker and Stuart.[13]

The refinement of the structure of the β isomer was complicated by disorder. A second set of rhenium atoms was found, centered at the same point as the principal pair, with the Re–Re vector roughly prependicular to that of the primary dimer. There was, however, no evidence on difference maps of a distinct second ligand set. We refined the site-occupation factors of the two sets of Re atoms, with the constraint that their sum be 1.0; the values were refined quickly and without oscillation to 0.80 for the principal Re_2 unit and 0.20 for the secondary one. The disorder, which is caused by the presence of two conformers at each site, sharing nearly the same ligand atom positions, will be discussed in detail later.

One of the dppee ligands appears to be statically disordered. When it was refined freely, two phenyl groups of this ligand deviated markedly from the appropriate hexagonal shape, and several of the carbon atoms developed nonpositive definite displacement parameters. However, the disorder did not separate the atoms enough to allow them to be separately

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(11) (a) Calculations were done by a Micro VAX II computer (Micro VMS V4.5). (b) Data reduction and general manipulations were done with the commercial package SDP/V, V3.0. (c) Structure solution: SHELXS-86, Professor G. M. Sheldrick, Goettingen University. (d) Structure refinement: SHELXZ-76 and SDP/V.

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refined or seen as distinct on difference maps.

In the refinement, therefore, certain chemically reasonable constraints and restrictions were imposed. The phenyl groups were treated as rigid bodies. In order that the refinement would represent the disorder as faithfully as possible, we used anisotropic displacement parameters for the carbon atoms. Thus, the displacement parameters in this case represent the effects of static (i.e., caused by disorder) as well as dynamic (i.e., thermal) displacements. The final structural model derived from this refinement represents the "mean unit cell" as well as can be done within the usual structural parameterization.

In the final refinement, all eight phenyl groups in the molecule were refined as rigid bodies. Forty-four of the 52 carbon atoms had anisotropic displacement parameters, as did all of the Re, Cl, and P sites. The remaining carbon atoms, which had developed nonpositive definite anisotropic displacement parameters, were treated isotropically in the final refinement. In addition, the populations of the rhenium sites, which had converged in earlier cycles, were held fixed in the final refinement. In all, 441 parameters were refined to fit 3002 data in the final, convergent least-squares cycle. The residuals from this refinement are listed in Table I. We did not observe significant variation of the least-squares residuals, as functions of either $|F|$ or parity group. We did observe higher variance for low-angle data, in keeping with the presence of disorder among the lighter atoms. When refinement had been completed, a difference map showed eight peaks greater than 1e/Å^3. Six of these were ghosts of rhenium sites and can be attributed to either series termination or residual effects of absorption. The other two peaks were near the poorly behaved dppee ligand; these peaks did not have any chemical significance, although their presence is a further indication of problems with this ligand.

Physical Measurements. Infrared spectra were recorded at Nujol mulls with an IBM IR/32 Fourier transform spectrometer (4000–400 cm^{-1}). Electronic absorption spectra were recorded as CH_2Cl_2 solutions on Cary 17D and IBM 9420 spectrophotometers. Electrochemical experiments were performed by using a Bioanalytical Systems, Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x-y recorder. Dichloromethane solutions containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as a supporting electrolyte were utilized. $E_{1/2}$ values $[(E_{p,a} + E_{p,c})/2]$ were referenced against an Ag/AgCl electrode at room temperature and were uncorrected for junction potentials. Under our experimental conditions $E_{1/2} = +0.47$ V for the Cp_2Fe^+/Cp_2Fe couple. EPR spectra of CH_2Cl_2 or CH_2Cl_2/toluene glasses were recorded at 150 K with a Varian E-109 spectrometer.

Analytical Procedures. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Results

Syntheses and Spectroscopic and Electrochemical Properties. The synthesis of α-$Re_2X_4(dppe)_2$ (X = Cl, Br; dppe = $Ph_2PCH_2CH_2PPh_2$) from the reaction between $(n\text{-}Bu_4N)_2Re_2X_8$ with dppe in methanol/concentrated HX contrasts with the earlier preparations of β-$Re_2X_4(dppe)_2$ from the reactions of dppe with $Re_2X_4(PEt_3)_4$[3,14] or $Re_2(O_2CCH_3)_2X_4L_2$ (L = H_2O or 4-Mepy).[15] The isolation of α- and β-$Re_2X_4(dppe)_2$ (X = Cl, Br) constitutes the third such instance where both isomeric forms of dirhenium(II) have been obtained, the others being $Re_2Br_4(depe)_2$ and $Re_2X_4(dppee)_2$ (X = Cl, Br).[2]

In the past we have succeeded in oxidizing β-$Re_2X_4(dppe)_2$ and β-$Re_2X_4(dppee)_2$ to their corresponding paramagnetic monocations with the use of $NOPF_6$ as the oxidant in acetonitrile.[2,14] Attempts to carry out the analogous oxidation of α-$Re_2Cl_4(dppee)_2$ with $NOPF_6$ in CH_3CN led to its decomposition. However, the use of $(Cp_2Fe)PF_6$ as the oxidizing agent in a noncoordinating solvent (CH_2Cl_2) led to the formation of the brown salt α-$[Re_2Cl_4(dppee)_2]PF_6$. A similar procedure was used to oxidize α-$Re_2Cl_4(dppp)_2$ to α-$[Re_2Cl_4(dppp)_2]PF_6$. When both salts are stirred in acetonitrile at room temperture, they decompose. This behavior contrasts with the conversion of β-$[Re_2X_4(LL)_2]PF_6$ (X = Cl, Br; LL = dppe, dppee, depe) to $[Re_2X_3(LL)_2(NCMe)]^{2+}$ by acetonitrile.[2,18]

The cyclic voltammogram (CV) of a solution of α-$[Re_2Cl_4(dppp)_2]PF_6$ in 0.1 M TBAH/CH_2Cl_2 solution reveals the presence of a reversible one-electron reduction of $E_{1/2} = +0.20$ V and a reversible one-electron oxidation at $E_{1/2} = +1.11$ V vs Ag/AgCl. These electrochemical properties are those expected on the basis of the related electrochemistry of neutral α-$Re_2Cl_4(dppp)_2$. The CV of a 0.1 M TBAH/CH_2Cl_2 solution of α-$Re_2Cl_4(dppp)_2$ exhibits two reversible one-electron oxidations $E_{1/2} = +0.20$ V and $E_{1/2} = +1.11$ V vs Ag/AgCl. The CV of a solution of α-$[Re_2Cl_4(dppee)_2]PF_6$ in 0.1 M TBAH/CH_2Cl_2 shows a reversible one-electron oxidation at $E_{1/2} = +1.05$ V and one-electron reduction at $E_{1/2} = +0.30$ V vs Ag/AgCl.

The electronic absorption spectra of solutions of these two salts in CH_2Cl_2 show an intense band at ~1530 nm that is assignable to the $\delta \rightarrow \delta^*$ transition of the Re_2^{5+} core. This property is similar to that observed for complexes of the type $[Re_2X_4(PR)_4]PF_6$, all of which possess an intense absorption band in the near-IR region at ~1400 nm.[16,17] The electronic absorption spectra of α-$[Re_2Cl_4(LL)_2]PF_6$ (LL = dppee, dppp) are significantly different from those observed for dirhenium(II) species of the type β-$[Re_2Cl_4(LL)_2]PF_6$ (LL = dppe, arphos), where no electronic absorption was observed between 1000 and 2000 nm.[14] These differences reflect a much stronger δ bond associated with the salts α-$[Re_2Cl_4(LL)_2]PF_6$ compared to that for the β isomers, in which there is a staggered rotational geometry.

The X-band ESR spectrum of α-$[Re_2Cl_4(dppp)_2]PF_6$ as a CH_2Cl_2 glass (at ~160 °C) exhibits an 11-line pattern between 1500 and 5000 G with $g = 2.15$ and $A_{Re} \simeq 300$ G. The spectrum of this complex is much better resolved than that of α-$[Re_2Cl_4(dppee)_2]PF_6$, which displays a broad signal between 1000 and 4000 G that is centered at $g = 2.2$.

Structure of α-$Re_2Cl_4(dppee)_2$. ORTEP drawings of the two crystallographically independent molecules, each with a crystallographic inversion center, are shown in Figure 1. The atomic positional parameters are listed in Table II. Selected bond distances and angles are given in Table III. The two molecules are nearly identical, although there is a statistically real difference, 0.015 (1) Å, between the two Re≡Re distances, which have a mean value of 2.258 Å. The appproximate symmetry of the molecules is C_{2h}, with an effectively anti, eclipsed rotational conformation.

Structure of β-$Re_2Cl_4(dppee)_2$. The atomic positional parameters for this structure are listed in Table IV, and the principal bond distances and angles are collected in Table V. A complete drawing of the major molecule (80% occupancy) is presented in Figure 2. In Figure 3 are views down the Re–Re axes for the major and minor molecules occupying one of the crystal sites; these two have opposite chiralities (Δ and Λ, respectively), and there are two such sites. There are also two more sites in the unit cell where the major and minor molecules have Λ and Δ sites, respectively. In short, the compound is racemic. While no crystallographic symmetry is imposed, the molecules all have approximate D_2 symmetry.

Discussion

The α-$Re_2Cl_4(dppee)_2$ structure is only the second α type structure for the Re_2^{4+} unit, the first one having been that of α-$Re_2Cl_4(dppp)_2$.[5] This too had a centrosymmetric structure, and the Re–Re distance, 2.266 (1) Å, is very similar to the ones we have found here. With the elements Mo and W, several α-$M_2X_2(diphos)_2$ type molecules have been structurally characterized, namely, $W_2Cl_4(dmpe)_2$[19] and $W_2Cl_4(dppe)_2$,[20] for tungsten, and α-$Mo_2Cl_4(dppe)_2$[21] and *anti*-α-$Mo_2Cl_4(Ph_2PCH_2CH_2P$-

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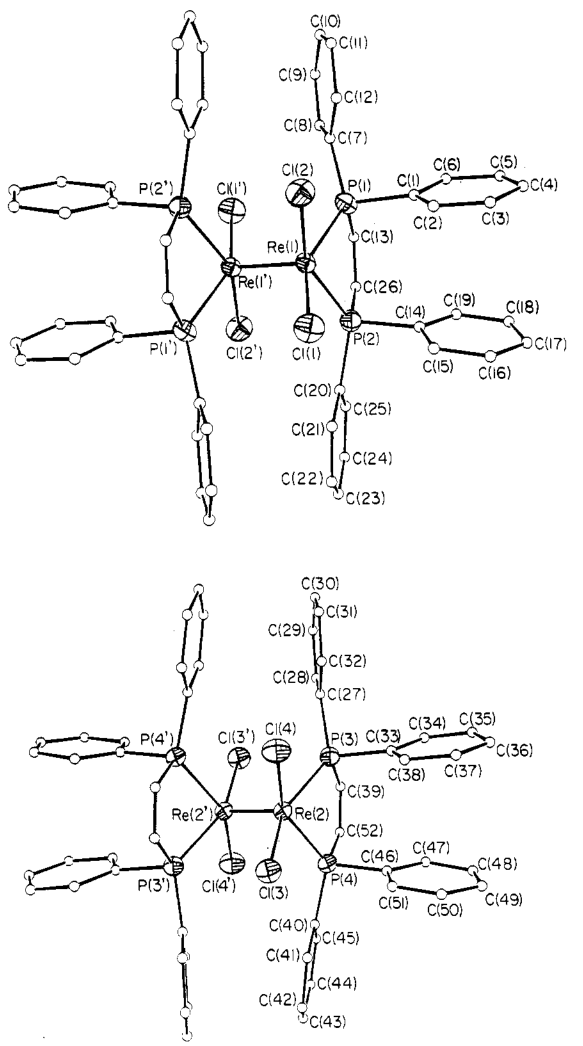


Figure 1. ORTEP drawings of the two independent molecules of α-$Re_2Cl_4(dppee)_2$. Carbon atoms are shown as circles of arbitrary radius. Re, Cl, and P atoms are represented by their 50% probability ellipsoids.

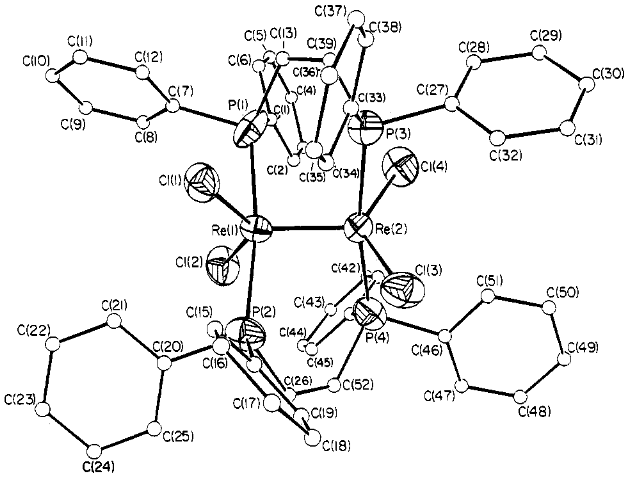


Figure 2. ORTEP drawing of the major molecule of β-$Re_2Cl_4(dppee)_2$, with the atom-labeling scheme indicated. Carbon atoms are shown as circles of arbitrary radius. Re, Cl, and P atoms are given as their 50% probability ellipsoids.

$(tol)_2)_2$.[22] All of these molecules also reside on crystallographic inversion centers.

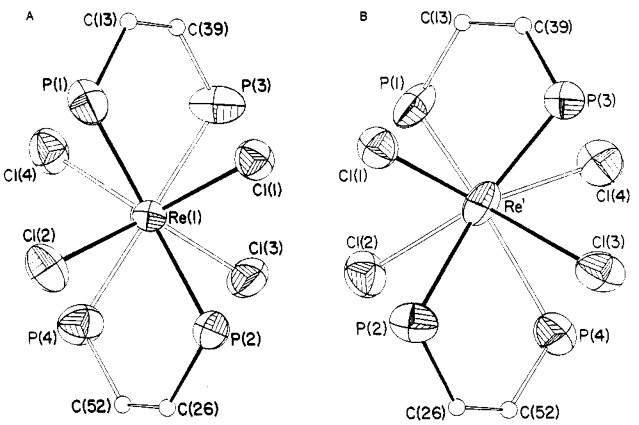
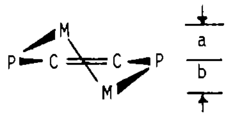


Figure 3. View along the metal–metal bond of the coordination sphere of β-$Re_2Cl_4(dppee)_2$: (a) major disordered congener, with Re(2) obscured by Re(1); (b) minor (20%) component, with Re'' obscured by Re'. In both cases, bonds to the visible Re atom are solid, while the open bonds are those to the obscured Re atom.



Ring No.	a(Å)	b(Å)
1	0.69	0.81
2	0.80	0.86
3	0.73	0.77
4	0.72	0.86

Figure 4. Distances of metal atoms from mean P—C=C—P planes, as a measure of conformity to the half-chair ring conformation.

The ring conformations found in α-$Re_2Cl_4(dppee)_2$ are similar to those in the molybdenum and tungsten compounds just mentioned. They have "envelope" type puckering with the P–C–C–P chains being essentially planar and bent in toward the center of the molecule. While this bending inward might seem disfavored sterically because it brings the CH_2CH_2 (or, in this case CH=CH) groups closer to the two Cl atoms on the other metal atom, the controlling steric factor, namely, the orientation of the phenyl groups, works the other way. The inward turn of the bridging CH_2CH_2 or CH=CH unit causes the phenyl groups to be directed outward, whereas if the ring conformations were flipped the other way, there would be serious interference between phenyl groups from the two ends of the molecule. The persistence of an "eclipsed" structure in α-$Re_2Cl_4(dppee)_2$ must, presumably, also be a consequence of the steric demands of the PPh_2 units, since there is no rotational barrier inherent in the Re≡Re bond, as is the case with the dimolybdenum and ditungsten compounds.

The structure of β-$Re_2Cl_4(dppee)_2$ displays important but understandable stereochemical differences from the β-$M_2X_4(dppe)_2$ structures, of which many have been reported and discussed.[4,23-30] The first such structure reported[4] was that of β-$Re_2Cl_4(dppe)_2$, and it showed the following leading characteristics shared by all such structures:

(1) Each crystal site is randomly occupied by one or the other of two β-$M_2X_4(dppe)_2$ molecules, one being far more prominent

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Table II. Positional Parameters and Their Estimated Standard Deviations for α-$Re_2Cl_4(dppee)_2 \cdot n$-PrOH[a]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Re(1)	0.02898 (3)	0.45210 (2)	0.04514 (3)	2.063 (8)	C(23)	0.197 (1)	0.4292 (8)	−0.418 (1)	6.3 (4)
Re(2)	0.55725 (3)	0.97730 (2)	0.06134 (3)	2.007 (8)	C(24)	0.264 (1)	0.500 (1)	−0.365 (1)	7.3 (4)
Cl(1)	−0.0613 (2)	0.3205 (1)	−0.0404 (2)	3.59 (6)	C(25)	0.2565 (9)	0.5183 (8)	−0.256 (1)	5.3 (3)
Cl(2)	−0.0728 (2)	0.3911 (2)	0.1930 (2)	3.62 (6)	C(26)	0.2725 (7)	0.5782 (6)	−0.0031 (9)	3.2 (2)
Cl(3)	0.5340 (2)	0.8398 (1)	0.0171 (2)	3.17 (6)	C(27)	0.6005 (7)	1.1539 (6)	0.2565 (8)	2.9 (2)
Cl(4)	0.4930 (2)	0.9138 (2)	0.2304 (2)	3.61 (6)	C(28)	0.5988 (8)	1.2318 (6)	0.240 (1)	3.9 (3)
P(1)	0.1681 (2)	0.5405 (2)	0.1767 (2)	2.68 (6)	C(29)	0.5674 (8)	1.2696 (6)	0.323 (1)	4.3 (3)
P(2)	0.1768 (2)	0.4775 (2)	−0.0498 (2)	2.65 (6)	C(30)	0.5418 (8)	1.2289 (7)	0.422 (1)	4.7 (3)
P(3)	0.6506 (2)	1.1031 (1)	0.1616 (2)	2.47 (5)	C(31)	0.5433 (9)	1.1496 (8)	0.438 (1)	5.0 (3)
P(4)	0.7002 (2)	1.0346 (2)	−0.0391 (2)	2.51 (5)	C(32)	0.5727 (8)	1.1124 (7)	0.3554 (9)	3.9 (3)
O	0.5041 (9)	0.7251 (7)	0.278 (1)	9.7 (3)*	C(33)	0.7710 (7)	1.1009 (6)	0.2617 (8)	2.9 (2)
C(1)	0.2436 (7)	0.4804 (6)	0.2582 (8)	3.2 (2)	C(34)	0.8537 (8)	1.1762 (7)	0.2904 (9)	4.0 (3)
C(2)	0.1981 (8)	0.3957 (6)	0.2646 (8)	3.7 (2)	C(35)	0.9467 (9)	1.1783 (8)	0.366 (1)	5.5 (3)
C(3)	0.2629 (9)	0.3537 (7)	0.321 (1)	5.0 (3)	C(36)	0.9588 (9)	1.1067 (8)	0.407 (1)	5.1 (3)
C(4)	0.3692 (9)	0.3943 (7)	0.373 (1)	5.3 (3)	C(37)	0.8759 (8)	1.0329 (7)	0.380 (1)	4.6 (3)
C(5)	0.4135 (9)	0.4793 (8)	0.367 (1)	5.6 (3)	C(38)	0.7793 (7)	1.0286 (7)	0.3055 (9)	3.9 (3)
C(6)	0.3495 (8)	0.5243 (8)	0.3105 (9)	4.6 (3)	C(39)	0.7144 (7)	1.1755 (6)	0.0585 (8)	2.7 (2)
C(7)	0.1611 (8)	0.6023 (6)	0.2905 (9)	3.7 (2)	C(40)	0.7087 (7)	1.0068 (6)	−0.1810 (8)	3.1 (2)
C(8)	0.213 (1)	0.6869 (7)	0.297 (1)	5.0 (3)	C(41)	0.6917 (8)	0.9254 (6)	−0.2002 (9)	3.8 (3)
C(9)	0.216 (1)	0.7294 (8)	0.396 (1)	6.7 (4)	C(42)	0.7081 (8)	0.9000 (7)	−0.3042 (9)	4.7 (3)
C(10)	0.166 (1)	0.6848 (8)	0.485 (1)	6.2 (3)	C(43)	0.7370 (9)	0.9602 (8)	−0.388 (1)	5.2 (3)
C(11)	0.1152 (9)	0.6014 (8)	0.480 (1)	5.9 (3)	C(44)	0.754 (1)	1.0406 (8)	−0.369 (1)	5.6 (3)
C(12)	0.1122 (9)	0.5585 (7)	0.381 (1)	5.0 (3)	C(45)	0.7402 (9)	1.0655 (7)	−0.2657 (9)	4.5 (3)
C(13)	0.2698 (7)	0.6072 (6)	0.0971 (8)	2.9 (2)	C(46)	0.8206 (7)	1.0197 (6)	0.0422 (8)	3.0 (2)
C(14)	0.2537 (7)	0.4107 (6)	0.0073 (8)	3.2 (2)	C(47)	0.9167 (7)	1.0866 (7)	0.0693 (9)	3.9 (3)
C(15)	0.2015 (8)	0.3270 (6)	−0.0003 (9)	4.0 (3)	C(48)	1.0092 (8)	1.0705 (8)	0.128 (1)	4.7 (3)
C(16)	0.2603 (9)	0.2751 (7)	0.038 (1)	5.4 (3)	C(49)	1.0026 (8)	0.9928 (8)	0.162 (1)	4.9 (3)
C(17)	0.3708 (9)	0.3098 (7)	0.081 (1)	5.4 (3)	C(50)	0.9061 (8)	0.9259 (7)	0.138 (1)	4.4 (3)
C(18)	0.4212 (8)	0.3929 (7)	0.089 (1)	4.7 (3)	C(51)	0.8129 (7)	0.9382 (6)	0.078 (1)	4.0 (3)
C(19)	0.3635 (8)	0.4449 (7)	0.0509 (9)	4.1 (3)	C(52)	0.7374 (7)	1.1455 (6)	−0.0302 (8)	2.9 (2)
C(20)	0.1768 (8)	0.4630 (6)	−0.2015 (8)	3.9 (2)	C(53)	0.584 (1)	0.694 (1)	0.247 (2)	9.8 (5)*
C(21)	0.1063 (9)	0.3920 (7)	−0.2546 (9)	4.8 (3)	C(54)	0.688 (2)	0.752 (1)	0.276 (2)	12.9 (7)*
C(22)	0.117 (1)	0.3745 (8)	−0.366 (1)	6.3 (4)	C(55)	0.729 (2)	0.781 (1)	0.398 (2)	11.3 (6)*

[a] Values marked with an asterisk denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement 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. Selected Bond Distances (Å) and Angles (deg) for α-$Re_2Cl_4(dppee)_2 \cdot n$-PrOH[a]

Distances					
Re(1)–Re(1′)	2.250 (1)	Re(2)–P(3)	2.380 (2)	P(3)–C(27)	1.824 (12)
Re(1)–Cl(1)	2.381 (2)	Re(2)–P(4)	2.345 (2)	P(3)–C(33)	1.851 (10)
Re(1)–Cl(2)	2.406 (3)	P(1)–C(1)	1.847 (11)	P(3)–C(39)	1.823 (9)
Re(1)–P(1)	2.355 (2)	P(1)–C(7)	1.814 (12)	P(4)–C(40)	1.821 (11)
Re(1)–P(2)	2.362 (3)	P(1)–C(13)	1.837 (9)	P(4)–C(46)	1.836 (10)
Re(2)–Re(2′)	2.265 (1)	P(2)–C(14)	1.857 (12)	P(4)–C(52)	1.835 (10)
Re(2)–Cl(3)	2.395 (3)	P(2)–C(20)	1.842 (11)	C(13)–C(26)	1.335 (15)
Re(2)–Cl(4)	2.407 (3)	P(2)–C(26)	1.826 (9)	C(39)–C(52)	1.335 (15)
Angles					
Re(1′)–Re(1)–Cl(1)	112.84 (7)	Cl(3)–Re(2)–P(4)	94.27 (9)	Re(2)–P(3)–C(27)	128.0 (3)
Re(1′)–Re(1)–Cl(2)	110.95 (7)	Cl(4)–Re(2)–P(3)	90.75 (8)	Re(2)–P(3)–C(33)	112.1 (3)
Re(1′)–Re(1)–P(1)	96.72 (7)	Cl(4)–Re(2)–P(4)	149.35 (9)	Re(2)–P(3)–C(39)	106.2 (3)
Re(1′)–Re(1)–P(2)	95.79 (7)	P(3)–Re(2)–P(4)	79.14 (9)	C(27)–P(3)–C(33)	97.3 (5)
Cl(1)–Re(1)–Cl(2)	82.51 (9)	Re(1)–P(1)–C(1)	107.9 (3)	C(27)–P(3)–C(39)	109.6 (5)
Cl(1)–Re(1)–P(1)	150.1 (1)	Re(1)–P(1)–C(7)	129.9 (3)	C(33)–P(3)–C(39)	100.2 (4)
Cl(1)–Re(1)–P(2)	92.67 (9)	Re(1)–P(1)–C(13)	107.8 (3)	Re(2)–P(4)–C(40)	127.5 (3)
Cl(2)–Re(1)–P(1)	91.49 (8)	C(1)–P(1)–C(7)	100.1 (5)	Re(2)–P(4)–C(46)	108.7 (3)
Cl(2)–Re(1)–P(2)	152.6 (1)	C(1)–P(1)–C(13)	100.8 (5)	Re(2)–P(4)–C(52)	107.0 (4)
P(1)–Re(1)–P(2)	79.31 (9)	C(7)–P(1)–C(13)	106.6 (4)	C(40)–P(4)–C(46)	100.0 (5)
Re(2′)–Re(2)–Cl(3)	111.22 (6)	Re(1)–P(2)–C(14)	109.7 (3)	C(40)–P(4)–C(52)	108.9 (5)
Re(2′)–Re(2)–Cl(4)	116.09 (7)	Re(1)–P(2)–C(20)	128.9 (3)	C(46)–P(4)–C(52)	101.8 (4)
Re(2′)–Re(2)–P(3)	95.88 (6)	Re(1)–P(2)–C(26)	107.0 (4)	P(1)–C(13)–C(26)	116.0 (6)
Re(2′)–Re(2)–P(4)	93.84 (6)	C(14)–P(2)–C(20)	97.1 (5)	P(2)–C(26)–C(13)	118.4 (7)
Cl(3)–Re(2)–Cl(4)	81.45 (9)	C(14)–P(2)–C(26)	101.8 (4)	P(3)–C(39)–C(52)	117.4 (7)
Cl(3)–Re(2)–P(3)	152.55 (9)	C(20)–P(2)–C(26)	109.0 (5)	P(4)–C(52)–C(39)	117.1 (7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

(≥80%) than the other (≤20%).

(2) The M_2 units of the principal and minor molecules have the same midpoint but are approximately perpendicular.

(3) The principal molecule consists of two six-membered rings with nearly ideal chair conformations, fused along the M–M bond, while the minor molecule contains two fused rings each with a twist conformation.

(4) At each site, the principal and minor isomers have opposite chiralities, viz., λΔλ (principal) and λΛλ at half of the sites, with δΛδ and δΔδ at the other half, where we use Δ and Λ to designate torsional directions about the M–M axis and δ and λ to designate torsional directions about the CH_2–CH_2 units.

Because the dppee ligand contains a CH═CH backbone, which is constrained to have a torsion angle of zero, or very nearly so (in the present case the angles are ca. ±6°), it is impossible to have true chair conformations in the six-membered rings. Instead, the ring conformations in both the principal and minor molecules are of the type well-known for cyclohexene,[31] namely a flattened

Table IV. Positional Parameters and Their Estimated Standard Deviations for β-$Re_2Cl_4(dppee)_2$[a]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Re′[b]	0.4718 (4)	0.6991 (6)	0.2405 (3)	4.2 (2)	C(21)	0.294 (2)	0.636 (3)	0.345 (2)	20 (4)
Re″[b]	0.5684 (4)	0.7585 (5)	0.3191 (4)	3.4 (2)	C(22)	0.243 (2)	0.607 (3)	0.380 (2)	13 (2)*
Re(1)[c]	0.4836 (1)	0.6966 (2)	0.30559 (8)	3.42 (6)	C(23)	0.178 (2)	0.671 (3)	0.383 (2)	17 (4)
Re(2)[c]	0.5374 (1)	0.7931 (2)	0.24555 (8)	3.57 (6)	C(24)	0.166 (2)	0.765 (3)	0.353 (2)	37 (9)
Cl(1)	0.4284 (5)	0.5374 (7)	0.2602 (4)	4.7 (3)	C(25)	0.218 (2)	0.794 (3)	0.318 (2)	15 (2)*
Cl(2)	0.4964 (6)	0.7678 (7)	0.4012 (4)	5.6 (3)	C(26)	0.343 (3)	0.913 (3)	0.276 (2)	8 (2)
Cl(3)	0.4407 (5)	0.8398 (7)	0.1553 (4)	5.3 (3)	C(27)	0.643 (2)	0.700 (2)	0.150 (1)	6 (1)
Cl(4)	0.6840 (5)	0.8228 (7)	0.2868 (5)	5.6 (3)	C(28)	0.729 (2)	0.703 (2)	0.170 (1)	6 (1)
P(1)	0.6118 (7)	0.6035 (7)	0.3520 (5)	5.1 (3)	C(29)	0.773 (2)	0.756 (2)	0.137 (1)	7 (2)
P(2)	0.3489 (6)	0.7720 (7)	0.2691 (5)	4.7 (3)	C(30)	0.731 (2)	0.805 (2)	0.083 (1)	9 (2)
P(3)	0.5779 (7)	0.6451 (8)	0.1945 (6)	5.8 (4)	C(31)	0.645 (2)	0.802 (2)	0.062 (1)	8 (2)
P(4)	0.5114 (6)	0.9541 (8)	0.2864 (5)	5.2 (4)	C(32)	0.601 (2)	0.749 (2)	0.096 (1)	7 (1)*
C(1)	0.698 (2)	0.659 (3)	0.406 (1)	7 (2)	C(33)	0.514 (2)	0.557 (2)	0.136 (1)	7 (2)
C(2)	0.704 (2)	0.761 (3)	0.425 (1)	7 (2)	C(34)	0.429 (2)	0.567 (2)	0.118 (1)	4.2 (8)*
C(3)	0.774 (2)	0.794 (3)	0.471 (1)	11 (2)	C(35)	0.380 (2)	0.503 (2)	0.072 (1)	9 (2)
C(4)	0.837 (2)	0.725 (3)	0.497 (1)	9 (2)	C(36)	0.418 (2)	0.430 (2)	0.044 (1)	8 (2)
C(5)	0.831 (2)	0.622 (3)	0.477 (1)	18 (4)	C(37)	0.504 (2)	0.420 (2)	0.062 (1)	8 (2)
C(6)	0.761 (2)	0.589 (3)	0.432 (1)	23 (5)	C(38)	0.552 (2)	0.484 (2)	0.108 (1)	9 (2)
C(7)	0.589 (1)	0.496 (2)	0.397 (1)	4.4 (8)*	C(39)	0.647 (2)	0.556 (3)	0.241 (2)	5.0 (9)*
C(8)	0.596 (1)	0.510 (2)	0.458 (1)	8 (2)	C(40)	0.562 (2)	1.003 (2)	0.366 (1)	5 (1)
C(9)	0.576 (1)	0.431 (2)	0.492 (1)	8 (2)	C(41)	0.647 (2)	1.019 (2)	0.381 (1)	7 (2)
C(10)	0.548 (1)	0.336 (2)	0.464 (1)	8 (2)	C(42)	0.690 (2)	1.055 (2)	0.439 (1)	7 (2)
C(11)	0.541 (1)	0.322 (2)	0.402 (1)	7 (2)	C(43)	0.647 (2)	1.077 (2)	0.481 (1)	9 (2)
C(12)	0.562 (1)	0.402 (2)	0.369 (1)	6 (1)	C(44)	0.562 (2)	1.062 (2)	0.465 (1)	11 (3)
C(13)	0.662 (2)	0.532 (3)	0.303 (2)	4 (1)	C(45)	0.519 (2)	1.025 (2)	0.408 (1)	17 (4)
C(14)	0.272 (2)	0.749 (3)	0.194 (1)	6 (1)	C(46)	0.536 (2)	1.062 (2)	0.246 (2)	7 (1)*
C(15)	0.253 (2)	0.646 (3)	0.178 (1)	9 (2)	C(47)	0.518 (2)	1.164 (2)	0.254 (2)	12 (2)
C(16)	0.201 (2)	0.622 (3)	0.121 (1)	8 (2)	C(48)	0.544 (2)	1.242 (2)	0.223 (2)	20 (4)
C(17)	0.168 (2)	0.700 (3)	0.079 (1)	15 (3)	C(49)	0.589 (2)	1.218 (2)	0.182 (2)	25 (5)
C(18)	0.187 (2)	0.803 (3)	0.095 (1)	14 (3)	C(50)	0.608 (2)	1.116 (2)	0.174 (2)	23 (5)
C(19)	0.239 (2)	0.827 (3)	0.152 (1)	16 (3)	C(51)	0.581 (2)	1.038 (2)	0.205 (2)	13 (3)
C(20)	0.282 (2)	0.730 (3)	0.314 (2)	8 (2)	C(52)	0.401 (2)	0.977 (3)	0.280 (2)	6 (1)*

[a] Values marked with an asterisk denote atoms refined isotropically. Anisotropically refined atoms are given in the form of equivalent isotropic displacement 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] Site modeled as 0.2 Re. [c] Site modeled as 0.8 Re.

Table V. Selected Bond Distances (Å) and Angles (deg) for β-$Re_2Cl_4(dppee)_2$[a]

		Distances			
Re′–Re″	2.196 (9)	Re(2)–P(3)	2.452 (12)	P(3)–C(27)	1.85 (3)
Re(1)–Re(2)	2.242 (3)	Re(2)–P(4)	2.385 (11)	P(3)–C(33)	1.86 (3)
Re(1)–Cl(1)	2.382 (9)	P(1)–C(1)	1.77 (3)	P(3)–C(39)	1.77 (4)
Re(1)–Cl(2)	2.337 (10)	P(1)–C(7)	1.84 (3)	P(4)–C(40)	1.89 (3)
Re(1)–P(1)	2.442 (10)	P(1)–C(13)	1.85 (4)	P(4)–C(46)	1.80 (4)
Re(1)–P(2)	2.399 (9)	P(2)–C(14)	1.86 (3)	P(4)–C(52)	1.86 (4)
Re(2)–Cl(3)	2.320 (8)	P(2)–C(20)	1.83 (4)	C(13)–C(39)	1.39 (6)
Re(2)–Cl(4)	2.417 (9)	P(2)–C(26)	1.85 (4)	C(26)–C(52)	1.27 (6)
		Angles			
Re(2)–Re(1)–Cl(1)	113.1 (3)	Cl(3)–Re(2)–P(4)	87.7 (4)	Re(2)–P(3)–C(27)	104.9 (9)
Re(2)–Re(1)–Cl(2)	114.5 (3)	Cl(4)–Re(2)–P(3)	85.1 (4)	Re(2)–P(3)–C(33)	130 (1)
Re(2)–Re(1)–P(1)	94.5 (3)	Cl(4)–Re(2)–P(4)	89.4 (3)	Re(2)–P(3)–C(39)	116 (1)
Re(2)–Re(1)–P(2)	94.0 (3)	P(3)–Re(2)–P(4)	170.1 (4)	C(27)–P(3)–C(33)	99 (1)
Cl(1)–Re(1)–Cl(2)	132.3 (4)	Re(1)–P(1)–C(1)	123 (1)	C(27)–P(3)–C(39)	101 (2)
Cl(1)–Re(1)–P(1)	87.0 (3)	Re(1)–P(1)–C(7)	108.7 (9)	C(33)–P(3)–C(39)	101 (2)
Cl(1)–Re(1)–P(2)	89.4 (3)	Re(1)–P(1)–C(13)	119 (1)	Re(2)–P(4)–C(40)	126.5 (9)
Cl(2)–Re(1)–P(1)	87.5 (3)	C(1)–P(1)–C(7)	100 (1)	Re(2)–P(4)–C(46)	112 (1)
Cl(2)–Re(1)–P(2)	89.2 (4)	C(1)–P(1)–C(13)	102 (2)	Re(2)–P(4)–C(52)	114 (1)
P(1)–Re(1)–P(2)	171.4 (4)	C(7)–P(1)–C(13)	99 (2)	C(40)–P(4)–C(46)	97 (1)
Re(1)–Re(2)–Cl(3)	113.0 (3)	Re(1)–P(2)–C(14)	127 (1)	C(40)–P(4)–C(52)	101 (2)
Re(1)–Re(2)–Cl(4)	113.6 (3)	Re(1)–P(2)–C(20)	111 (1)	C(46)–P(4)–C(52)	103 (2)
Re(1)–Re(2)–P(3)	94.4 (3)	Re(1)–P(2)–C(26)	116 (1)	P(1)–C(13)–C(39)	122 (3)
Re(1)–Re(2)–P(4)	95.4 (3)	C(14)–P(2)–C(20)	96 (2)	P(2)–C(26)–C(52)	126 (4)
Cl(3)–Re(2)–Cl(4)	133.4 (4)	C(14)–P(2)–C(26)	102 (2)	P(3)–C(39)–C(13)	131 (3)
Cl(3)–Re(2)–P(3)	89.9 (4)	C(20)–P(2)–C(26)	101 (2)	P(4)–C(52)–C(26)	130 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

chair or half-chair. This can be clearly seen in Figures 2 and 3. Another major difference between this case and the β-$M_2X_4(dppe)_2$ structures is that the principal and minor molecules at each site differ little from each other conformationally and are

Table VI. Average Torsional Angles (deg) for β-$Re_2Cl_4(dppee)_2$

	principal molecules	minor molecules
P—C═C—P (2×)[a]	5.6	5.6
P—Re—Re—P (2×)	59.4	64.6
Cl—Re—Re—Cl (2×)	61.3	55.9
Cl—Re—Re—P (4×)	29.7	29.8

[a] Numbers in parentheses are the number of values averaged for each angle (2× or 4×).

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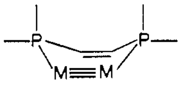
(31) Cf.: Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Wiley-Interscience: New York, 1965; pp 109–111.

essentially just enantiomorphs. A complete table of torsion angles is available as supplementary material, but in Table VI we present mean values of the most pertinent ones for the principal and minor molecules. It can be seen that differences are small. In addition, the validity of our description of these rings as half-chairs is shown by the fact that, in each case, the Re atoms lie above and below the mean P—C=C—P planes by approximately equal amounts as would be expected from the drawing in Figure 4.

It is worth mentioning that the next best conformation for cyclohexene itself is a half-boat (ca. 3 kcal mol^{-1} less stable). The analogue to that in the present case is illustrated schematically in III, where it can be seen that because of the large phenyl substituents it is understandably disfavored here.



III

In conclusion, then, the introduction of the "stiffened backbone" in dppee, as contrasted with the flexible backbone in dppe, leads to certain changes in the conformational characteristics of these molecules. These conformational changes then have consequences with respect to the way in which the molecules are assembled in the complete crystal structure.

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Registry No. α-$Re_2Cl_4(dppee)_2 \cdot n$-PrOH, 114720-22-8; β-$Re_2Cl_4(dppee)_2$, 110329-68-5; α-$Re_2Cl_4(dppe)_2$, 114720-23-9; $(n\text{-}Bu_4N)_2Re_2Cl_8$, 14023-10-0; $[ReCl_2(dppe)_2]Cl$, 15628-22-5; $(n\text{-}Bu_4N)_2Re_2Br_8$, 14049-60-6; α-$Re_2Br_4(dppe)_2$, 114720-24-0; α-$[Re_2Cl_4(dppee)_2]PF_6$, 114720-26-2; $(Cp_2Fe)PF_6$, 11077-24-0; α-$[Re_2Cl_4(dppp)_2]PF_6$, 114720-28-4; α-$Re_2Cl_4(dppp)_2$, 86436-61-5; Re, 7440-15-5; α-$Re_2Cl_4(dppee)_2$, 110329-67-4.

Supplementary Material Available: Full tables of bond distances and bond angles and tables of anisotropic displacement parameters for α-$Re_2Cl_4(dppee)_2 \cdot n$-PrOH and β-$Re_2Cl_4(dppee)_2$ and a table of torsional angles for the β isomer (14 pages); listings of observed and calculated structure factors for both compounds (45 pages). Ordering information is given on any current masthead page.

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Syntheses and Characterization of Unique Organometallic Nickel(III) Aryl Species. ESR and Electrochemical Studies and the X-ray Molecular Study of Square-Pyramidal $[Ni\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}I_2]$

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Oxidation of the Ni(II) species $[Ni(NCN')X]$ ($NCN' = C_6H_3(CH_2NMe_2)_2\text{-}o,o'$) by appropriate reagents [CuX_2 (X = Br, Cl), I_2 (X = I)] affords in high yield the unique five-coordinate Ni(III) aryl species $[Ni(NCN')X_2]$ (X: Br, **1a**; Cl, **1b**, I, **1c**) that are precursors to the NO_3 and NO_2 analogues **1d** and **1e**, respectively. ESR data for **1a–e** indicate a d^7 electronic configuration with a single unpaired electron in the d_{z^2} orbital; a low-spin configuration is also consistent with the magnetic susceptibility of 1.989 (3) μ_B found for **1c**. The iodo analogue **1c** has also been the subject of an X-ray crystallographic study that established a square-pyramidal coordination geometry for the Ni(III) center. Crystals of **1c**, $C_{12}H_{19}NiN_2I_2$, are monoclinic, space group $P2_1/c$, with $a = 13.9696$ (9) Å, $b = 7.8683$ (9) Å, $c = 15.0510$ (17) Å, $\beta = 108.769$ (7)°, $V = 1566.4$ Å^3, $Z = 4$, $d_{calcd} = 2.136$ cm^3, $F(000) = 956$ e, μ(Mo K$\bar{\alpha}$) = 48.6 cm^{-1}. On the basis of 3365 unique reflections with $F_o > 2.0\sigma F_o$, the structure has been refined to $R = 0.0499$ and $R_w = 0.0603$. Within the nickel coordination sphere one iodine atom I2, the aryl C1 atom, and the mutually trans N-donor atoms of NCN' define the square base, while the second iodine atom I1 is at the pyramid apex; the Ni atom lies ca. 0.325 Å above the plane of the basal atoms. Conductivity measurements on **1b** and **1d** show full dissociation of both X anions in aqueous solution. In acetone solution, where dissociation is not significant, $[Ni^{II}(NCN')X]$ and $[Ni^{III}(NCN')X_2]$ are electrochemically interconvertible when additional X anion is present. The $E_{1/2}$ value for the redox couple $[Ni(NCN')H_2O]^+/[Ni(NCN')(H_2O)_n]^{2+}$ in H_2O is +0.14 V (vs SCE). The importance of organometallic nickel(III) species is discussed, with particular respect being paid to their intermediacy in oxidative-addition reactions.

Introduction

Recent studies have shown that certain systems of biological interest, principally hydrogenases, may contain paramagnetic centers attributable to the less common Ni(III) state.[2,3] As would be anticipated, hard donor atoms are suitable for stabilizing the higher oxidation states of nickel, and many inorganic Ni(III) species have been reported containing nitrogen-donor macrocyclic ligands.[3]

Our studies on the coordination properties of the monoanionic terdentate ligand $C_6H_3(CH_2NMe_2)_2\text{-}o,o'$ (NCN') show that it can form square-planar Ni(II),[4] Pd(II),[5] and Pt(II)[5] complexes. These organometallic species, which contain two trans N-donor sites and a M–C σ-bond, have relatively good thermal stability, and this property has allowed an electronic structure study of certain members by ultraviolet photoelectron spectroscopy.[6] In the present report it is shown that unique air-stable square-pyramidal Ni(III) species $[Ni(NCN')X_2]$ (X: Cl, **1a**; Br, **1b**; I, **1c**) (Figure 1) result from either chemical or electrochemical oxidation of the corresponding Ni(II) halo species $[Ni(NCN')X]$ (**2a–c**). Characterization of these species, the first reported true organometallic

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