

are distinct from the carbide modes for encapsulated carbide ligands. The compounds display a strong carbide vibration in the 900-cm⁻¹ region of the infrared spectrum, indicating a butterfly carbide geometry and corresponding to vibration of the carbon atom between the two wing tips of the butterfly. This band is readily observed because it appears in a spectral region that is clear of any other cluster or PPN⁺ (PPN⁺ = bis(triphenylphosphine)nitrogen(1+)) counterion vibrational modes. The corresponding carbide modes for penta- and hexametal carbides appear at lower frequency, usually around 800 cm⁻¹.^{9,13,15}

The force constants, calculated by means of a simple bond stretching force field with neglect of CO ligands, are largest for the wing-tip iron to carbon bonds and are not sensitive to the charge on the cluster. The force constants for both the car-

bide-wing-tip metal and carbide-hinge metal interactions in these four-metal butterfly clusters are larger than the carbide-metal force constants in metal clusters having six- and eight-coordinate carbide.¹¹ Apparently, this trend reflects the more delocalized C-M bonding in the latter clusters.

Acknowledgment. Research conducted at Northwestern University was supported by NSF Grant CHE-8506011 and DOE Grant DE-AC02-83ER13104. P.L.S. acknowledges support by an MPI Grant 40% Fund.

Supplementary Material Available: Tables of IR data for the compounds reported from 1000 to ca. 500 cm⁻¹ and of determinants used in the approximate normal-coordinate analysis (4 pages). Ordering information is given on any current masthead page.

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Reactions of Small Molecules with Re₂Cl₄(PEt₃)₄. 2.¹ Products Resulting from the Reaction with Dihydrogen

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Received February 4, 1987

Treatment of Re₂Cl₄(PEt₃)₄ with H₂, carried out in dichloromethane for 24 h under a pressure of 120 atm, gave no result, but when the temperature was raised to 60 °C and maintained there for 7 days, about 44% of the Re₂Cl₄(PEt₃)₄ reacted to afford, reproducibly, three products, separable by chromatography on silica gel. These were red *trans*-ReCl₄(PEt₃)₂ (a known compound), yellow-brown [PEt₃][Re₂Cl₆(PEt₃)₂H] (1, a new compound and the major product), and yellow-green [PEt₃][ReCl₅(PEt₃)] (2, a new compound). The two new compounds were each identified and their structures determined by X-ray crystallography. In one run there were also a few pink crystals that could be only incompletely characterized crystallographically as perhaps ReCl₃(PEt₃)₂H. Crystallographic data: for 1, *P*2₁/*a* with *a* = 15.937 (9) Å, *b* = 12.101 (4) Å, *c* = 17.496 (15) Å, β = 93.41 (6)°, and *Z* = 4, refined to *R* = 0.0390 and *R*_w = 0.049; for 2, *P*2₁/*m* with *a* = 9.951 (2) Å, *b* = 10.147 (2) Å, *c* = 11.637 (2) Å, β = 91.04 (2)°, and *Z* = 2, refined to *R* = 0.0487 and *R*_w = 0.0609. Compound 1 contains a confacial bioctahedral anion, [Cl₂(Et₃P)Re(μ-H)(μ-Cl)₂ReCl₂(PEt₃)₂]⁻, which has effective C₂ symmetry. The Re-Re distance is 2.349 (1) Å, and the end-to-end symmetry of the heavy atom structure suggests that the μ-H atom is symmetrically placed, i.e., on the effective C₂ axis of symmetry. The [ReCl₅(PEt₃)]⁻ ion resides on a mirror plane and has effectively C_{4v} symmetry in the coordination sphere.

Introduction

The reaction patterns of Re(II) compounds containing the electron-rich (σ²π⁴δ²δ*²) Re-Re triple bond are varied and, in many instances, complex.³ Carbonylation of Re₂Cl₄(PR₃)₄ compounds characteristically occurs with metal-metal bond cleavage accompanied by oxidation and/or reduction.^{1,4-6} In the exceptional case involving Re₂Cl₄(μ-dppm)₂, carbonylation occurs with retention of the multiple Re-Re bond, but other bonds are rearranged to give Cl₂Re(μ-Cl)(μ-CO)(μ-dppm)₂ReCl(CO).⁷ In contrast, oxidation of Re₂⁴⁺ complexes by methanolic HCl or elemental oxygen occurs with retention of both the Re-Re multiple bond and the eclipsed conformation of the starting material. The compound Re₂Cl₄(PEt₃)₄ is oxidized to Re₂Cl₆(PEt₃)₂ by methanolic HCl, and the oxidation of Re₂Cl₄(PR₃)₄ complexes by elemental oxygen gives Re₂X₄(PR₃)₄⁺ and/or their neutral Re₂X₅(PR₃)₃ analogues.⁸⁻¹⁰

We report here the first study of the reaction of Re₂Cl₄(PEt₃)₂, a well-characterized member of a class of compounds containing an electron-rich Re₂⁴⁺ core,¹¹ with elemental hydrogen. The reaction pattern observed for hydrogenation in dichloromethane is unlike those reported for other small gaseous molecules. Because the hydrogenation reaction is relatively slow, experiments were conducted at elevated pressures with apparatus and techniques described earlier.¹²

Experimental Section

Purification of Solvents. Dichloromethane and acetonitrile were dried by refluxing for 8 h over phosphorus pentoxide under a blanket of nitrogen. The solvents were then distilled under nitrogen into another flask containing phosphorus pentoxide. After the solvents were degassed by using several freeze/thaw cycles, the solvents were refluxed under nitrogen for 17 h. Samples were fractionally distilled immediately prior to use. Hexane and tetrahydrofuran were predried over sodium for several weeks and distilled onto fresh sodium/benzophenone under nitrogen. The solvents were degassed and refluxed until the color of the benzophenone ketyl radical anion persisted.

Reagents. Hydrogen gas (Linde, ultrahigh purity) and deuterium (Matheson, CP grade, 99.5 atom % minimum) were used without further purification. Argon (Linde, prepurified) was passed through a Model 98HP purifier (Airco), to remove traces of oxygen and water.

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Synthesis of $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$. The $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ was synthesized according to the procedure of Walton and co-workers.¹³ The gray-green crystals of $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ obtained in the synthesis were washed with chilled samples of degassed methanol, ethanol, and ether and recrystallized from a dichloromethane-ether mixture. Anal. Calcd for $\text{C}_{24}\text{H}_{60}\text{Cl}_4\text{P}_4\text{Re}_2$: C, 29.21; H, 6.08; Cl, 14.38. Found: C, 28.95; H, 6.21; Cl, 14.23.

Reaction of $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ and H_2 . All solid and solution samples were manipulated by Schlenk techniques under a nitrogen atmosphere. The high-pressure reactor/infrared cell used in these experiments has been described elsewhere.¹²

A 0.7348-g (0.745-mmol) sample of $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ was dissolved in 15 mL of oxygen-free dichloromethane under an atmosphere of nitrogen. The resulting dark green solution was transferred under nitrogen with a cannula to the high-pressure reactor fitted with a stirring bar. The vigorously stirred solution was subjected to 120 atm. of dihydrogen at 25 °C for a period of 24 h. High-pressure infrared spectra gave no evidence of reaction. The temperature was increased to 60 °C and maintained there for 7 days. The color of the solution changed over this period from dark green to brown-green. The reaction mixture was cooled to 27 °C, and the solution transferred to a 50-mL round-bottomed flask (with side arm) containing 1.0 g of oxygen-free silica gel (230–400 mesh ASTM). The sample was totally adsorbed by the silica gel upon removal of the solvent under gentle vacuum. The components of the mixture adsorbed on the silica gel were then separated by flash chromatography on a 2.5 cm × 15 cm column of 230–400-mesh silica gel, which had been completely purged of atmospheric oxygen and suspended in *n*-hexane. The sample adsorbed on silica gel was placed on the top of the column under a nitrogen atmosphere. Elutions were carried out under a head pressure of 5–8 psi nitrogen.

Elution with 350 mL of a 2:1 mixture (by volume) of hexane-dichloromethane gave 21.5 mg of a red crystalline material, mp 183 °C. The mass spectrum and ¹H NMR spectrum of this compound matched those of an authentic sample of *trans*- $\text{ReCl}_4(\text{PET}_3)_2$. X-ray crystallographic data¹ confirmed the identification.

Elution with 200 mL of dichloromethane gave only trace amounts of a dark green material, which was not identified. This was followed by 200 mL of an eluant composed of a 2:1 mixture (by volume) of dichloromethane-tetrahydrofuran. Evaporation of the solvent from this fraction gave 250 mg of a dark brown oil. The oil was washed with several 10-mL portions of *n*-hexane, and washings were combined and reduced in volume under a mild vacuum, and the solution was refrigerated at –5 °C. In one run we obtained from this solution about 7 mg of a pink crystalline material, mp 138 °C. Infrared spectroscopy suggested that this might contain at least one Re–H bond. Peaks appeared at 1728 (w) and 950 cm^{–1} (m), which might be assigned to terminal Re–H stretching vibration and deformation modes, respectively.¹⁴

The yellow-brown, viscous oil, which remained after the hexane washing, was taken up in tetrahydrofuran. A small quantity of a light green material did not dissolve. This material was recrystallized from dichloromethane to give 10 mg of a light green crystalline material that decomposes at 235 °C. This compound was characterized by X-ray crystallography to be $[\text{PET}_4][\text{ReCl}_5(\text{PET}_3)]$.

Crystallization of the material from tetrahydrofuran gave 200 mg of yellow-brown, monoclinic crystals of $[\text{PET}_4][\text{Re}_2\text{Cl}_6(\text{PET}_3)_2\text{H}]$, mp 164 °C. Anal. Calcd for $\text{C}_{20}\text{H}_51\text{Cl}_6\text{P}_3\text{Re}_2$: C, 24.77; H, 5.30; Cl, 21.94; P, 9.58. Found: C, 23.87; H, 5.10; Cl, 22.88; P, 9.92. This compound was characterized by infrared spectroscopy, proton magnetic resonance spectroscopy, and X-ray crystallography.

Product yields and distribution are reproducible, except for the pink crystals, which were obtained only once. The reaction at 25 °C is very slow. When the reaction is run for 7 days at 60 °C without the pretreatment at 25 °C for 1 day, the results are essentially the same as those reported above.

We were able to separate and account for approximately 44% of the rhenium present. The component of the reaction mixture that forms an intense green stationary band on top of the column cannot be eluted. This behavior is characteristic of the starting material.

Because it had been shown earlier that $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ is oxidized to the rhenium(III) salt $[\text{Et}_3\text{PCl}_2]_2[\text{Re}_2\text{Cl}_6]$ in 85% yield by refluxing in carbon tetrachloride for 4 h,⁸ it was necessary to conduct a control experiment to test whether dichloromethane serves as a chlorinating agent under our experimental conditions. In a control experiment in which dihydrogen gas is replaced by argon, all other conditions remaining unaltered, no reaction products were obtained. Thus, unlike carbon tetrachloride, dichloromethane does not directly chlorinate $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$

Table I. Crystal Data for $[\text{PET}_4][\text{Re}_2\text{Cl}_6(\text{PET}_3)_2\text{H}]$

formula	$\text{Re}_2\text{Cl}_6\text{P}_3\text{C}_{20}\text{H}_{51}$
fw	969.68
space group	$P2_1/a$
syst absences	$(0k0) k \neq 2n; (h0l) h \neq 2n$
<i>a</i> , Å	15.937 (9)
<i>b</i> , Å	12.101 (4)
<i>c</i> , Å	17.496 (15)
β , deg	93.41 (6)
<i>V</i> , Å ³	3368 (5)
<i>Z</i>	4
<i>d</i> _{calcd} , g/cm ³	1.912
cryst size, mm	0.7 × 0.5 × 0.5
$\mu(\text{Mo K}\alpha)$, cm ^{–1}	82.2
data colln instrument	Nicolet P3/F Equivalent
radiation (monochromated in incident beam)	Mo K α (λ 0.71073 Å)
orientation reflns: no.; range (2θ), deg	22; 20–30
scan method	ω – 2θ
data colln range (2θ), deg	4.0–45.0
no. of unique data, total	4112
no. of data with $F_o^2 > 3\sigma(F_o^2)$	2300
no. of params refined	284
transmissn factors: max, min	obsd 1.00, 0.50
<i>R</i> ^a	0.0390
<i>R</i> _w ^b	0.0479
quality-of-fit indicator ^c	0.906
largest shift/esd, final cycle	0.49
largest peak, e/Å ³	0.73

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

under the experimental conditions employed in the hydrogenation reaction.

Physical Measurements. Elemental analyses were provided by Galbraith Laboratories, Knoxville, TN. Infrared spectra were obtained with a Nicolet Model 20DX FT-IR spectrophotometer. Proton magnetic resonance spectra were taken with a Nicolet 200-MHz FT-NMR spectrometer on samples in deuteriated chloroform with Me_4Si as the internal standard. Melting points were obtained on a Fischer-Johns melting point apparatus. All melting points are uncorrected. Magnetic susceptibilities were obtained on a Faraday balance at room temperature (25–28 °C).

X-ray Crystallography. The procedures used for data collection and structure solution and refinement have been described previously.¹⁵ Crystal data, data collection parameters, and least-squares residuals are given in Table I for the structure of $[\text{PET}_4][\text{Re}_2\text{Cl}_6\text{H}(\text{PET}_3)_2]$ and in Table IV for $[\text{PET}_4][\text{ReCl}_5(\text{PET}_3)]$. Both structures were solved by direct methods and developed and refined in alternating sequences of least-squares refinements and difference Fourier maps. In the structure determination of $[\text{PET}_4][\text{ReCl}_5(\text{PET}_3)]$, one terminal methyl group of the PET_4^+ ion did not appear as a discrete entity on difference maps. The C_α – C_β bond can rotate freely on a cone whose axis is the extension of the P– C_α bond, and the C_β atom was disordered to the extent that no model could be constructed for it. It was omitted from the refinement altogether. A contoured section of the final difference map in the plane in which this atom is disordered is available as supplementary material. It shows a nearly complete annulus of low electron density, indicative of the disorder.

Results

$[\text{PET}_4][\text{Re}_2\text{Cl}_6(\text{PET}_3)_2\text{H}]$ (1). The major product of the reaction of $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ with dihydrogen (120 atm) in dichloromethane at 60 °C and a reaction time of 7 days is an air-stable, yellow-brown, ionic salt of Re(III), $[\text{PET}_4][\text{Re}_2\text{Cl}_6(\text{PET}_3)_2\text{H}]$. This compound may be crystallized from tetrahydrofuran to give monoclinic crystals in space group $P2_1/a$. The structure of the anion in the crystalline compound, determined by X-ray crys-

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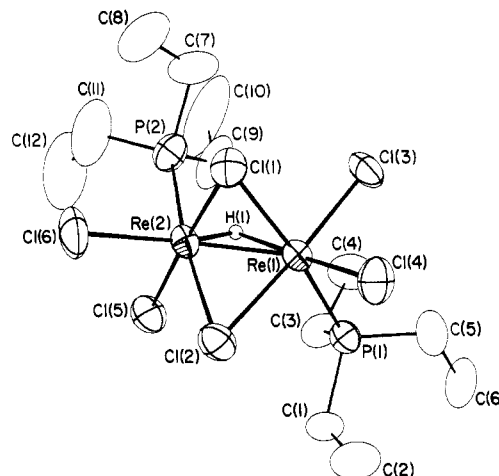
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Table II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $[\text{PEt}_4][\text{Re}_2\text{Cl}_6(\text{PEt}_3)_2\text{H}]^a$

atom	x	y	z	$B, \text{\AA}^2$
Re(1)	0.34346 (5)	0.15011 (7)	0.26155 (4)	4.20 (1)
Re(2)	0.37568 (5)	-0.03267 (6)	0.22886 (4)	4.70 (2)
Cl(1)	0.2431 (3)	-0.0004 (4)	0.2917 (3)	5.7 (1)
Cl(2)	0.4410 (3)	0.0472 (5)	0.3490 (3)	6.4 (1)
Cl(3)	0.2412 (3)	0.2384 (4)	0.1805 (3)	6.4 (1)
Cl(4)	0.3054 (3)	0.2567 (5)	0.3704 (3)	6.8 (1)
Cl(5)	0.5092 (3)	-0.0578 (5)	0.1812 (3)	7.2 (2)
Cl(6)	0.3766 (4)	-0.2160 (5)	0.2815 (4)	8.9 (2)
P(1)	0.4513 (3)	0.2762 (5)	0.2297 (3)	5.1 (1)
P(2)	0.3083 (4)	-0.0856 (5)	0.1103 (3)	6.5 (1)
P(3)	0.1879 (4)	0.6042 (6)	0.4045 (4)	8.4 (2)
C(1)	0.550 (1)	0.272 (2)	0.292 (1)	6.3 (5)
C(2)	0.542 (2)	0.315 (2)	0.371 (1)	9.6 (7)
C(3)	0.495 (1)	0.256 (2)	0.1359 (9)	6.2 (5)
C(4)	0.428 (1)	0.295 (2)	0.070 (1)	8.6 (7)
C(5)	0.415 (1)	0.417 (2)	0.233 (1)	7.4 (6)
C(6)	0.484 (2)	0.503 (2)	0.213 (2)	10.7 (9)
C(7)	0.189 (1)	-0.082 (2)	0.106 (1)	9.5 (7)
C(8)	0.153 (2)	-0.177 (2)	0.151 (2)	11.6 (9)
C(9)	0.334 (2)	0.002 (2)	0.032 (1)	10.1 (8)
C(10)	0.298 (3)	-0.027 (3)	-0.045 (2)	21 (2)
C(11)	0.321 (2)	-0.228 (2)	0.075 (2)	14.1 (9)
C(12)	0.390 (2)	-0.259 (3)	0.055 (2)	18 (1)
C(13)	0.196 (2)	0.519 (2)	0.321 (1)	10.0 (8)
C(14)	0.222 (3)	0.566 (4)	0.267 (3)	24 (2)
C(15)	0.283 (2)	0.652 (2)	0.445 (1)	10.8 (8)
C(16)	0.343 (2)	0.569 (3)	0.444 (2)	15 (1)
C(17)	0.140 (2)	0.746 (3)	0.379 (2)	26 (1)
C(18)	0.087 (2)	0.787 (3)	0.403 (2)	19 (1)
C(19)	0.126 (2)	0.536 (2)	0.463 (1)	11.3 (9)
C(20)	0.155 (2)	0.427 (2)	0.488 (1)	12.3 (9)
H(1)	0.375 (6)	0.056 (8)	0.160 (5)	1 (2) ^a

^aThe hydrogen atom was refined isotropically. ^bValues for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

tallography, is shown in Figure 1. Parameters pertinent to data collection and refinement are given in Table I. Atomic coordinates

**Figure 1.** Structure of the $[\text{Re}_2\text{Cl}_6(\text{PEt}_3)_2\text{H}]^-$ ion. The hydrogen atom is shown as a sphere of arbitrary size at a symmetrical position for reasons given in the text. Other atoms are represented by their 35% probability thermal displacement ellipsoids. The atom-labeling scheme is defined.

are given in Table II, and selected bond distances and angles are given in Table III.

The dinuclear anion has a confacial bioctahedral structure. The idealized symmetry (if the H atom is for the moment ignored) is C_2 , with the C_2 axis passing through the midpoint of the Re-Re bond and the midpoint of a line connecting the two bridging Cl atoms, Cl(1) and Cl(2). In view of this symmetrical arrangement of all of the ligand atoms other than the hydrogen atom, we believe that the μ -H atom is symmetrically placed. However, this cannot be determined directly from the structure refinement. Difference electron density maps show a weak feature in the region where the bridging hydrogen atom might be expected, but refinement led to an unsymmetrical position with large esd's and an unrealistically small thermal displacement parameter. We think the indirect evidence that it is symmetrically positioned is more reliable than the result of the refinement.

The rest of the structure of the $[\text{Re}_2\text{Cl}_6(\text{PEt}_3)_2\text{H}]^-$ anion displays a pleasing regularity and a normal degree of accuracy. The

Table III. Selected Bond Distances (\AA) and Angles (deg) and Their Estimated Standard Deviations for $[\text{PEt}_4][\text{Re}_2\text{Cl}_6(\text{PEt}_3)_2\text{H}]^a$

Distances			
Re(1)-Re(2)	2.349 (1)	Re(2)-Cl(2)	2.484 (5)
Re(1)-Cl(1)	2.500 (5)	Re(2)-Cl(5)	2.350 (6)
Re(1)-Cl(2)	2.454 (5)	Re(2)-Cl(6)	2.401 (6)
Re(1)-Cl(3)	2.353 (5)	Re(2)-P(2)	2.367 (6)
Re(1)-Cl(4)	2.408 (5)	Re(2)-H(1)	1.62 (10)
Re(1)-P(1)	2.389 (6)	P(1)-C(1)	1.86 (2)
Re(1)-H(1)	2.19 (10)	P(1)-C(3)	1.84 (2)
Re(2)-Cl(1)	2.470 (5)	P(1)-C(5)	1.80 (2)
Angles			
Re(2)-Re(1)-Cl(1)	61.1 (1)	Re(1)-Re(2)-Cl(1)	62.4 (1)
Re(2)-Re(1)-Cl(2)	62.2 (1)	Re(1)-Re(2)-Cl(2)	60.9 (1)
Re(2)-Re(1)-Cl(3)	115.7 (2)	Re(1)-Re(2)-Cl(5)	115.1 (2)
Re(2)-Re(1)-Cl(4)	140.0 (2)	Re(1)-Re(2)-Cl(6)	140.6 (2)
Re(2)-Re(1)-P(1)	112.0 (1)	Re(1)-Re(2)-P(2)	112.0 (2)
Re(2)-Re(1)-H(1)	42 (3)	Re(1)-Re(2)-H(1)	64 (4)
Cl(1)-Re(1)-Cl(2)	83.6 (2)	Cl(1)-Re(2)-Cl(2)	83.6 (2)
Cl(1)-Re(1)-Cl(3)	91.6 (2)	Cl(1)-Re(2)-Cl(5)	174.0 (2)
Cl(1)-Re(1)-Cl(4)	91.7 (2)	Cl(1)-Re(2)-Cl(6)	87.8 (2)
Cl(1)-Re(1)-P(1)	173.0 (2)	Cl(1)-Re(2)-P(2)	94.4 (2)
Cl(1)-Re(1)-H(1)	89 (3)	Cl(1)-Re(2)-H(1)	105 (4)
Cl(2)-Re(1)-Cl(3)	175.2 (2)	Cl(2)-Re(2)-Cl(5)	90.5 (2)
Cl(2)-Re(1)-Cl(4)	87.7 (2)	Cl(2)-Re(2)-Cl(6)	92.4 (2)
Cl(2)-Re(1)-P(1)	91.8 (2)	Cl(2)-Re(2)-P(2)	172.7 (2)
Cl(2)-Re(1)-H(1)	94 (3)	Cl(2)-Re(2)-H(1)	111 (4)
Cl(3)-Re(1)-Cl(4)	92.0 (2)	Cl(5)-Re(2)-Cl(6)	91.8 (2)
Cl(3)-Re(1)-P(1)	93.0 (2)	Cl(5)-Re(2)-P(2)	91.5 (2)
Cl(3)-Re(1)-H(1)	86 (3)	Cl(5)-Re(2)-H(1)	78 (4)
Cl(4)-Re(1)-P(1)	93.5 (2)	Cl(6)-Re(2)-P(2)	94.5 (3)
Cl(4)-Re(1)-H(1)	178 (3)	Cl(6)-Re(2)-H(1)	154 (4)
P(1)-Re(1)-H(1)	87 (3)	P(2)-Re(2)-H(1)	63 (4)
Re(1)-Cl(1)-Re(2)	56.4 (1)	Re(1)-Cl(2)-Re(2)	56.8 (1)
Re(1)-P(1)-C(1)	116.3 (8)	Re(1)-P(1)-C(3)	115.8 (7)
Re(1)-P(1)-C(5)	111.0 (8)	Re(1)-P(1)-C(5)	100 (1)
C(1)-P(1)-C(3)	106 (1)	C(1)-P(1)-C(5)	106 (1)
C(3)-P(1)-C(5)	107 (1)	Re(2)-P(2)-C(7)	115.2 (9)
Re(2)-P(2)-C(9)	113.1 (8)	Re(2)-P(2)-C(11)	120 (2)
C(7)-P(2)-C(9)	104 (2)	C(7)-P(2)-C(11)	98 (2)
C(9)-P(2)-C(11)	105 (1)	C(13)-P(3)-C(15)	115 (2)
C(13)-P(3)-C(17)	112 (2)	C(13)-P(3)-C(19)	106 (2)
C(15)-P(3)-C(17)	97 (3)	C(15)-P(3)-C(19)	116 (2)
C(17)-P(3)-C(19)	110 (2)	Re(1)-H(1)-Re(2)	74 (4)

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Crystal Data for $[\text{PET}_4][\text{ReCl}_5(\text{PET}_3)]$

formula	$\text{ReCl}_5\text{P}_2\text{C}_{14}\text{H}_{35}$
fw	628.85
space group	$P2_1/m$
syst absences	$(0k0): k \neq 2n$
a , Å	9.951 (2)
b , Å	10.147 (2)
c , Å	11.637 (2)
β , deg	91.04 (2)
V , Å ³	1174.8 (8)
Z	2
d_{calc} , g/cm ³	1.778
cryst size, mm	$0.3 \times 0.2 \times 0.2$
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	61.65
data colln instrument	Nicolet P3/F Equivalent
radiation (monochromated in incident beam)	Mo K α ($\lambda_x = 0.71073$ Å)
orientation reflns, no.; range (2θ), deg	15; $15 < 2\theta < 35$
temp, °C	22 ± 1
scan method	$\omega-2\theta$
data colln range (2θ), deg	5.0–45.0
no. of unique data, total	2596
no. of data with $F_o^2 > 3\sigma(F_o^2)$	1611
no. of param refined	95
transmiss factors: max, min	obsd 1.00, 0.91
R^a	0.0487
R_w^b	0.0609
quality-of-fit indicator ^c	1.137
largest shift/esd, final cycle	0.01
largest peak, e/Å ³	1.46

^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 = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{params}})]^{1/2}$.

configuration about each metal atom is only slightly distorted from octahedral, with cis bond angles ranging from 84 to 94°. The smallest angles (84°) are those subtended by the bridging chlorine atoms. Variations in the Re–Cl bond lengths are consistent with trans weakening effects by both the PET_3 and $\mu\text{-H}$ ligands but are small. Thus the Re–Cl bridge bonds trans to the phosphine ligands are ca. 0.03 Å longer than those trans to Re–Cl bonds. The Re–Cl bonds trans to $\mu\text{-H}$ are ca. 0.05 Å longer than those trans to $\mu\text{-Cl}$. In the case of $[\text{Mo}_2\text{Cl}_8\text{H}]^-$ the corresponding difference was greater,¹⁶ namely ca. 0.10 Å.

It is worth noting that the Re–P distances are about the same as the terminal Re–Cl distances. In many other cases, such as $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ ¹⁷ and $\text{Re}_2\text{Cl}_4(\text{dppe})_2$ ¹⁸ as well as the $[\text{ReCl}_5(\text{PET}_3)]^-$ ion discussed later in this paper, Re–P distances are significantly (i.e., 0.08–0.20 Å) longer than Re–Cl distances.

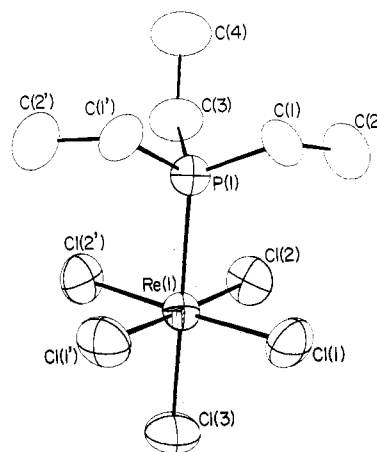
The most interesting feature of this $[\text{Re}_2\text{Cl}_6(\text{PET}_3)_2\text{H}]^-$ structure is the very short Re–Re distance, 2.349 (1) Å. This is only slightly longer than the lengths of Re–Re quadruple¹⁹ and triple bonds (typically about 2.24 Å). It is, in fact, the shortest M–M distance in any confacial bioctahedral structure²⁰ so far as we know. This is in part attributable to the presence of the bridging hydrogen atom, which has already been shown to have a marked shortening effect in the comparison of the $[\text{Mo}_2\text{Cl}_8]^{3-}$ ion ($\text{Mo–Mo} = 2.65$ Å) and the $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$ ion (2.37 Å).¹⁶

The short Re–Re distance is associated with strong Re–Re bonding. The compound is diamagnetic ($\chi_M = -749.5 \times 10^{-6}$ cgsu), and by referring to the theoretical treatment²¹ of $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$, it is possible to obtain a reasonable idea of the probable electronic structure. For $[\text{Mo}_2\text{Cl}_8\text{H}]^-$ which is a $d^3\text{-}d^3$

Table V. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $[\text{PET}_4][\text{ReCl}_5(\text{PET}_3)]$

atom	x	y	z	B^a , Å ²
Re(1)	0.71959 (7)	0.250	0.74157 (6)	3.75 (1)
Cl(1)	0.5540 (3)	0.4109 (4)	0.7182 (3)	6.26 (8)
Cl(2)	0.8850 (3)	0.4138 (3)	0.7568 (3)	6.17 (8)
Cl(3)	0.6886 (6)	0.250	0.9421 (4)	7.5 (1)
P(1)	0.7554 (4)	0.250	0.5303 (3)	3.74 (8)
C(1)	0.682 (1)	0.388 (1)	0.4518 (9)	4.6 (2)
C(2)	0.746 (1)	0.524 (1)	0.482 (1)	6.8 (4)
C(3)	0.934 (2)	0.250	0.499 (2)	5.8 (5)
C(4)	0.963 (2)	0.250	0.368 (2)	7.2 (6)
P(2)	0.2514 (5)	0.250	-0.0032 (5)	5.7 (1)
C(5)	0.073 (2)	0.250	0.044 (2)	8.4 (6)*
C(7)	0.370 (3)	0.169 (4)	0.081 (3)	10 (1)*
C(8)	0.389 (3)	0.250	0.197 (3)	11.3 (9)*
C(9)	0.314 (2)	0.416 (2)	-0.031 (2)	4.8 (5)*
C(10)	0.224 (2)	0.481 (2)	-0.134 (2)	9.4 (5)*
C(11)	0.237 (3)	0.169 (3)	-0.151 (2)	7.0 (7)*

^a Values marked with an asterisk denote isotropically refined atoms. Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

**Figure 2.** ORTEP drawing of the anion $[\text{ReCl}_5(\text{PET}_3)]^-$, with atoms represented by their 50% probability ellipsoids. The atom-labeling scheme is indicated.

system, the highest filled orbitals correspond to σ and π bonds between the metal atoms. Significantly, the LUMO is nondegenerate, lies only 0.5 eV higher, and is essentially nonbonding in a metal–metal sense. Thus, in the $d^4\text{-}d^4$ system, we are adding two more electrons to an essentially nonbonding orbital, and we can expect a diamagnetic system with a strong, short bond, as is found.

Spectroscopic data for this compound are in agreement with its structure. There is a single weak resonance at -18.0 ppm in the ¹H NMR spectrum that can be assigned to the $\mu\text{-H}$ atom. This value of the chemical shift is close to that reported for the $\mu\text{-H}$ atoms in the $[(\text{OC})_3\text{Re}(\mu\text{-H})_3\text{Re}(\text{CO})_3]^-$ ion.²² For the $[\text{P}(\text{CH}_2\text{CH}_3)_4]^+$ cation a multiplet centered at 2.47 ppm had the form (1:3:4:4:3:1) of an overlapping doublet of quartets with $^2J_{\text{P-H}} = 15.96$ Hz and $^3J_{\text{H-H}} = 7.51$ Hz; this multiplet is assigned to the α -protons. The β -protons of the PET_3^+ ion gave a doublet of triplets centered at 1.36 ppm with $^3J_{\text{P-H}} = 18.60$ Hz and $^3J_{\text{H-H}} = 7.55$ Hz. For the phosphine ligands in the $[\text{Re}_2\text{Cl}_6(\text{PET}_3)_2\text{H}]^-$ anion, the α -proton resonance was centered at 1.89 ppm with a pattern too complicated for a simple analysis, while the β -proton resonance appeared as a 1:2:2:2:1 pattern centered at 1.25 ppm with $^3J_{\text{P-H}} = 15.30$ Hz and $^3J_{\text{H-H}} = 7.65$ Hz. The measured relative intensities of the multiplets centered at 2.47, 1.36, and (1.89 + 1.25) ppm were the ratio 8:12:30 as expected.

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Table VI. Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for [PEt₄][ReCl₅(PEt₃)₂]^a

Distances					
Re(1)–Cl(1)	2.332 (3)	P(1)–C(3)	1.823 (15)	P(2)–C(9)	1.83 (2)
Re(1)–Cl(2)	2.344 (3)	C(1)–C(2)	1.55 (2)	P(2)–C(11)	1.91 (3)
Re(1)–Cl(3)	2.359 (5)	C(3)–C(4)	1.56 (3)	C(7)–C(8)	1.59 (4)
Re(1)–P(1)	2.491 (4)	P(2)–C(5)	1.86 (2)	C(9)–C(10)	1.62 (3)
P(1)–C(1)	1.822 (10)	P(2)–C(7)	1.73 (4)	C(11)–C(10')	1.54 (4)
Angles					
Cl(1)–Re(1)–Cl(1')	88.9 (2)	Cl(3)–Re(1)–P(1)	179.3 (2)	C(5)–P(2)–C(9)	112.4 (7)
Cl(1)–Re(1)–Cl(2)	90.3 (1)	Re(1)–P(1)–C(1)	115.6 (4)	C(5)–P(2)–C(11)	102 (1)
Cl(1)–Re(1)–Cl(2')	177.6 (1)	Re(1)–P(1)–C(3)	110.9 (6)	C(7)–P(2)–C(9)	108 (2)
Cl(1)–Re(1)–Cl(3)	90.6 (1)	C(1)–P(1)–C(1')	100.9 (7)	C(7)–P(2)–C(11)	110 (2)
Cl(1)–Re(1)–P(1)	89.9 (1)	C(1)–P(1)–C(3)	106.5 (5)	C(9)–P(2)–C(11)	105 (1)
Cl(2)–Re(1)–Cl(2')	90.3 (2)	P(1)–C(1)–C(2)	114.3 (8)	P(2)–C(7)–C(8)	108 (2)
Cl(2)–Re(1)–Cl(3)	91.7 (1)	P(1)–C(3)–C(4)	113 (1)	P(2)–C(9)–C(10)	109 (1)
Cl(2)–Re(1)–P(1)	87.8 (1)	C(5)–P(2)–C(7)	119 (1)	P(2)–C(11)–C(10')	109 (2)

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

An effort was made to locate and analyze the infrared spectrum due to Re–H–Re and Re–D–Re units. Unfortunately, the unambiguous identification of the four bands has not been accomplished, mainly because bands arising from the [PEt₄]⁺ ion and the PEt₃ ligands are found in some of the pertinent regions.

[PEt₄][ReCl₅(PEt₃)₂] (2). This compound was isolated in minute quantities and characterized solely by X-ray crystallography. A compound containing the analogous [ReCl₅(P-*n*-Pr₃)][−] anion has been reported previously,⁴ but we present here the first structural characterization of such a rhenium(IV) complex.

The parameters pertaining to X-ray data collection and the refinement of the structure are presented in Table IV. Atomic coordinates are given in Table V and the bond distances and angles in Table VI. A drawing of the anion is presented in Figure 2. The compound was obtained from dichloromethane solution as pale green, monoclinic crystals belonging to space group *P*2₁/*m*.

The anion resides on a crystallographic mirror plane that passes through Cl(3), Re(1), and P(1). The coordination sphere of the rhenium atom is essentially octahedral in the sense that all angles are very close to 90° or 180°. Also, the Re–Cl bond lengths are nearly equal, including the one trans to the Re–P bond. The Re–P bond is very long, 2.491 (4) Å, as is often seen in octahedral mixed halo/phosphine complexes of the early transition metals. This will presumably result in a d-level ordering (*xz*, *yz*) < *xy* < *z*² < *x*² − *y*². Whether the splitting between the (*xz*, *yz*) pair and the *xy* orbital will be large enough to lead to a doublet ground state is not known. This point and other features of the electronic structure would be worth additional study, but a preparative method giving larger yields must first be developed. It is noteworthy that the mean Re–Cl distance in *trans*-ReCl₄(PEt₃)₂,¹ 2.336 Å, is not significantly different from the mean Re–Cl distance for those Cl atoms here that are cis to the PEt₃ ligand, namely 2.338 Å. The Re–P distances in the *trans*-ReCl₄(PEt₃)₂ molecule, 2.518 (1) Å, are just slightly longer.

Discussion

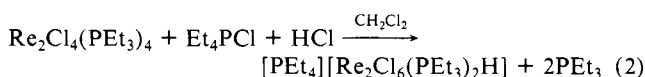
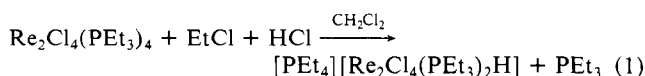
We have shown that the reaction of elemental hydrogen with Re₂Cl₄(PEt₃)₄ in dichloromethane gives as the major product the tetraethylphosphonium salt of the hydrido-bridged anion [(PEt₃)₂Cl₂Re(μ-H)(μ-Cl)₂ReCl₂(PEt₃)₂][−]. Hydrogenation is accompanied by a two-electron oxidation of the Re₂⁴⁺ core to the Re₂⁶⁺ core, and considerable bond rearrangement. An Re–Re bond is retained, however. In the only other report of a direct hydrogenation of a compound containing a metal–metal multiple bond, a hydrido-bridged product was obtained.²³ When dimolybdenum tetraacetate in the presence of excess trimethylphosphine and sodium amalgam in tetrahydrofuran is subjected to 3 atm of dihydrogen pressure, a highly distorted, edge-shared bioctahedral, hydrido-bridged complex, (Me₃P)₃HMo(μ-H)₂MoH(PMe₃)₃, is formed in high yields. The common feature of these two direct hydrogenations is that they give hydrido-bridged complexes. If we assume that the function of the sodium is to

reduce the Mo₂(O₂CCH₃)₄ to a species containing the electron-rich Mo₂²⁺ triple bond, the systems may also share a common mechanistic feature in that an electron-rich (σ²π⁴δ²δ*²) species is involved in each case.

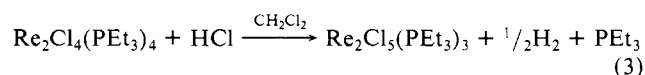
Certain mechanistic inferences may be drawn from analysis of the products and the reaction conditions. We may conclude with absolute certainty that the hydrogen atom forming the bridge in the complex anion, [Re₂Cl₆(PEt₃)₂H][−], derives from elemental hydrogen and not from the solvent. The infrared spectrum of the reaction product obtained when D₂ is substituted for H₂ shows that the bridging function is Re–D–Re and not Re–H–Re. However, as already noted, we have not been able to carry out a detailed assignment of the vibrational modes involving H and D.

We have also established in our control experiment that the solvent alone does not react with Re₂Cl₄(PEt₃)₄ under the conditions employed for hydrogenation. Furthermore, because the reaction mixture is completely shielded from visible and ultraviolet radiation, the generation of any reactive species (radical or nonradical) must occur by thermal rather than photochemical excitation.

The occurrence of the hydrido-bridged [Re₂Cl₆(PEt₃)₂H][−] anion as the major product of hydrogenation suggests, by analogy to the Mo₂Cl₈^{4−}/HCl system, that hydrogen chloride is the active hydrogenating agent. The reaction of Mo₂Cl₈^{4−} or Mo₂(O₂CCH₃)₄ with aqueous HCl gives rise to a hydrogen-bridged confacial bioctahedral anion Mo₂Cl₈H^{3−}.²⁴ On the basis of a careful kinetic study of the Mo₂Cl₈^{4−}/HCl system, Miller and Haim proposed a mechanism that involved a rapid, reversible protonation of the Mo–Mo quadruple bond followed by a rate-determining rearrangement of the protonated species to form the hydrido-bridged product.²⁵ Ebner and Walton had shown earlier that Re₂Cl₄(PEt₃)₄ reacts with hydrogen chloride in refluxing methanol to give 70% yields of Re₂Cl₆(PEt₃)₂.⁸ The presence of hydrogen chloride alone would, therefore, not lead to the hydrido-bridged species obtained in this study. We believe that the hydrido-bridged anion is stabilized in our system because, in addition to hydrogen chloride, ethyl chloride or chlorotetraethylphosphorane is also present.



Alternatively, the first reactive intermediate could be Re₂Cl₅(PEt₃)₃ obtained in the redox reaction

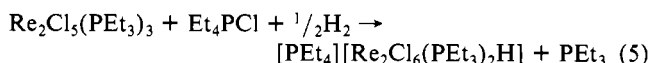
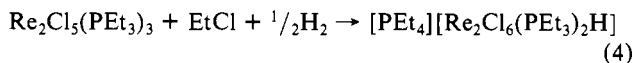


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In a very careful study of the electrochemical oxidation of $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ complexes, Walton and his co-workers showed that $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$ undergoes reversible oxidation in dichloromethane to +1 and +2 cations at $E_{1/2} = -0.42$ and $+0.80$ V, respectively.²⁶ Half-wave potentials are referenced to the saturated calomel electrode. In the presence of chloride ion the $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4^+$ cation is rapidly transformed into $\text{Re}_2\text{Cl}_5(\text{PEt}_3)_3$. In the presence of ethyl chloride or chlorotetraethylphosphorane this intermediate could react with elemental hydrogen to give $[\text{PEt}_4][\text{Re}_2\text{Cl}_6(\text{PEt}_3)_2\text{H}]$.



Crucial to our mechanistic hypothesis is the formation of hydrogen chloride and ethyl chloride. The formation of hydrogen chloride and ethyl chloride could occur by the thermodynamically favorable ($\Delta G^\circ = -66.3$ kcal), metal-catalyzed hydrogenation of dichloromethane to give ethyl chloride and hydrogen chloride, $2\text{H}_2(\text{g}) + 2\text{CH}_2\text{Cl}_2(\text{l}) \rightarrow \text{C}_2\text{H}_5\text{Cl}(\text{g}) + 3\text{HCl}(\text{g})$. With deuterium as the reducing agent, the oxidized species would be DCl, and reactions 1 and 2 would lead to the observed deuterio-bridged anion.

The formation of ethyl chloride was suggested by the occurrence of the PEt_4^+ counterion both for the hydrido-bridged anion and the minor product $[\text{PEt}_4][\text{ReCl}_5(\text{PEt}_3)]$. The chlorotetraethylphosphorane, which is required for the formation of the tetra-

ethylphosphonium salts, may form readily by the action of ethyl chloride on triethylphosphine.²⁷ The reaction of phosphines with alkyl halides to form chlorophosphoranes is a reversible reaction²⁸ that can be shifted toward the chlorophosphorane by the formation of stable phosphonium salts similar to those found in this study.

We have established that direct hydrogenation of $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$, a member of the class of compounds containing the electron-rich ($\sigma^2\pi^4\delta^2\delta^*$) Re-Re bond occurs with formation of an air-stable salt $[\text{PEt}_4]^+[\text{Re}_2\text{Cl}_6(\text{PEt}_3)_2\text{H}]^-$. While mechanistic inferences from synthetic studies are limited, our results suggest that formation of the hydrido-bridged anion in dichloromethane is a complex process involving hydrogen chloride and ethyl chloride as intermediates.

Acknowledgment. We are grateful to the SIUC Office of Research and Development and the SIUC Materials Technology Center for financial support at Southern Illinois University and to the National Science Foundation for financial support at Texas A&M University.

Registry No. 1, 109390-22-9; 2, 109390-24-1; $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$, 55400-06-9; *trans*- $\text{ReCl}_4(\text{PEt}_3)_2$, 24551-06-2; Re, 7440-15-5; H_2 , 1333-74-0.

Supplementary Material Available: Listings of bond distances and angles and anisotropic displacement parameters for **1** and anisotropic displacement parameters for **2** and a figure depicting a contoured section of the final difference Fourier map in the disordered region for **2** (5 pages); listings of calculated and observed structure factors for **1** and **2** (21 pages). Ordering information is given on any current masthead page.

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Tetrakis(dimethylamido) Complexes of Oxotungsten(VI) and (Phenylimido)tungsten(VI)

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Received August 4, 1986

The compound $\text{W}(\text{NPh})(\text{NMe}_2)_4$ (**1**) is formed in a two-step reaction by treating $\text{W}(\text{NPh})\text{Cl}_4 \cdot \text{Et}_2\text{O}$ with 1 equiv of MeOH followed by 4 equiv of LiNMe_2 . $\text{WO}(\text{NMe}_2)_4$ (**2**) can be prepared in a similar manner. An X-ray crystal structure determination shows **1** to have a geometry between square pyramidal and trigonal bipyramidal. The crystals are monoclinic ($C2/c$) with (140 K) $a = 12.383$ (7) Å, $b = 10.262$ (3) Å, $c = 14.278$ (12) Å, $\beta = 107.45$ (5)°, $V = 1731.0$ Å³, and $Z = 4$. The three-dimensional X-ray data were measured at 140 K with the ω - 2θ scan technique and a scintillation detector. The structure was resolved by Patterson and Fourier methods and refined by full-matrix least-squares calculations to give $R(F_o) = 0.019$ and $R_w(F_o) = 0.027$ for 1074 observations above 2σ . A simple bonding analysis is presented to explain the structure of **1**.

Introduction

An important property of many of the early transition metals is their ability to form multiple bonds with themselves¹ and with ligands of the first-period elements C,² N,³ and O.⁴ The major geometrical features of these complexes can be understood in terms of the strong trans influence of the multiply bonded ligands, the maximization of ligand-to-metal π bonding,⁵ and intramolecular steric interactions.⁶ Pentacoordinate complexes containing one triply bonded ligand X ($\equiv\text{O}$,⁷ $\equiv\text{NR}$,⁸ $\equiv\text{N}$,^{7b,9} $\equiv\text{ML}_3\text{L}^{10}$) typ-

ically assume a square-pyramidal geometry with the triply bonded ligand at the apex. When strongly π -donating alkoxides or amides are present, these ligands are oriented so as to π -donate into metal d orbitals not used in forming the triple bond to X. In this paper we report the synthesis of two pentacoordinate complexes of this type and the X-ray crystal structure of one where the introduction of four strongly π -donating amido groups leads to an unusual distortion toward a trigonal-bipyramidal geometry. A simple

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