$cm^2/equiv^{24}$) and (*R*)-tartrate (59.6 Ω^{-1} $cm^2/equiv^{25}$). This reduction in the equivalent conductance of the 2:2 electrolyte indicates considerable association between the ions in solution. The equivalent conductance is reported not to change with time.[1]

The observation (slow mutarotation of fresh solutions with no change in conductance) could be explained by a rapid reaction upon dissolution to give equilibrium quantities of (hydrated) $[Pt(en)_2]^{2+}$ ions, $C_4H_4O_6^{2-}$ ions, and the ion pair $\{[Pt(en)_2]^{2+}, R\text{-}C_4H_4O_6^{2-}\}$. A fraction of the $\{[Pt(en)_2]^{2+}, R\text{-}C_4H_4O_6^{2-}\}$ ion pairs would be "originals" from the crystal, still persisting (at first) in the solution. The fraction could be quite small since there is no estimate of the magnitude of the "extra" rotatory power present in the stereospecifically linked ion pairs. Mutarotation then would follow the loss of this persisting fraction of "original" ion pairs in the dynamic association–dissociation process. Newly associated ion pairs, lacking the directing effect of packing in the crystal lattice would not, even if the same sort of distortions were imposed upon their component ions, have an excess of distortions of one configurational sense, as in the original case. In this explanation, the true source of the mutarotation effect is mutual, stemming from the ion pair. Still, the "extra" rotatory power might be predominantly the consequence of the distortions in one or two other of the ions.

Acknowledgment. The generous provision of computing time by the University of Illinois at Chicago Circle Computer Center is gratefully acknowledged. The many helpful discussions with Barry G. DeBoer are also gratefully acknowledged.

Registry No. $[Pt(en)_2](C_4H_4O_6)$, 59710-52-0.

Supplementary Material Available: Listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Preparation and Structure of a Multiply Bonded Re_2^{5+} Species Bridged by Two Diphosphinomethane Ligands

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Received March 4, 1976 AIC60174Z

The compound $Re_2Cl_5[(Ph_2P)_2CH_2]_2\cdot 2PhMe$ is prepared by refluxing a mixture of $(Bu_4N)_2Re_2Cl_8$ and bis(diphenylphosphino)methane in acetone for 24 h. Toluene was used to wash the solid reaction products; from this filtrate the substance was obtained as red-brown, air-stable crystals of diffraction quality. The crystals are monoclinic with cell dimensions $a = 14.274$ (3) Å, $b = 23.380$ (7) Å, $c = 18.577$ (3) Å, $\beta = 94.58$ (2)°, and $V = 6180$ (2) Å^3, having space group $P2_1/n$ with $Z = 4$. The structure was solved and refined to $R_1 = 0.061$ and $R_2 = 0.080$ using 4305 reflections with $I > 3\sigma(I)$ in the range $0° < 2\theta < 45°$ (Mo Kα). Two trans phosphine ligands bridge the strong metal–metal bond while chlorine atoms occupy the four remaining equatorial and one of the two coaxial positions on the metal atoms. The molecule has a virtual mirror plane containing the rhenium and chlorine atoms. Important distances in the molecule are Re–Re = 2.263 (1) Å, Re–P = 2.47 (3) Å, Re–Cl$_{equat}$ = 2.35 (4) Å, and Re–Cl$_{axial}$ = 2.575 (6) Å; an ESR spectrum of the complex suggests that there is one unpaired electron coupled to two metal nuclei, each with $I = {}^5/_2$.

Introduction

Soon after the existence of the quadruple bond was recognized[1-3] in the $Re_2Cl_8^{2-}$ ion, the preparation of derivatives in which neutral ligands replace some of the anionic ligands[4-9] was reported to produce species such as $Re_2Cl_6(PR_3)_2$ and $[ReCl_3(DTH)]_x$, where DTH = $CH_3SCH_2CH_2SCH_3$. It was recognized then that reactions with neutral ligands can involve more than simple replacement, namely, reduction; the first example was $Re_2Cl_5(DTH)_2$.[5-7] Since then, Walton and co-workers have explored other reductive reactions of $Re_2Cl_8^{2-}$ and Re_3Cl_9 with phosphines and shown that there is an extensive chemistry of this kind.[10,11]

We have examined the reaction of the diphosphine $Ph_2PCH_2PPh_2$, bis(diphenylphosphino)methane, commonly abbreviated dppm, with $(Bu_4N)_2Re_2Cl_8$. Since dppm is known[12] to be sterically capable of forming approximately parallel bonds to two adjacent metal atoms which are bonded to each other, it was our hope that one or both of the products,

$Re_2Cl_6(dppm)$ and $Re_2Cl_4(dppm)_2$, stoichiometrically but not structurally analogous to $Re_2Cl_6(PEt_3)_2$[8,9] and $Re_2Cl_4(PEt_3)_4$,[11] respectively, might be isolated and then subjected to further study. Thus far, we have not been able to isolate either of the above-mentioned products but instead have obtained a purple solid with approximate composition $[ReCl_3dppm]_x$ and a brown compound with the formula $Re_2Cl_5(dppm)_2$. Since the latter is analogous in composition to $Re_2Cl_5(DTH)_2$ which was previously shown to be a mixed oxidation state compound containing a Re–Re triple bond,[5-7] we have conducted an x-ray crystallographic study of $Re_2Cl_5(dppm)_2$, and the results are reported here. It does not, as will be seen, have a structure analogous to that of $Re_2Cl_5(DTH)_2$.

Experimental Section

Reaction of $Re_2Cl_8^{2-}$ with dppm. The dppm was used as received from Pressure Chemical Co., Pittsburgh, Pa., and $(Bu_4N_2)Re_2Cl_8$ was prepared as described elsewhere.[13] Microanalysis was done by Chemanalytics, Inc., Tempe, Ariz.

$(Bu_4N)_2Re_2Cl_8$ (0.50 g) and dppm (0.40 g) were gently refluxed in reagent grade acetone (30 ml) under nitrogen for 24 h. The mixture was then filtered and the residue thoroughly extracted with a 50-ml portion of toluene, leaving a purple solid. This solid is soluble in CH_2Cl_2 and *sym*-$C_2H_2Cl_4$, and analyses of washed material are somewhat variable. They generally correspond to a formula between $ReCl_3dppm$ and $ReCl_4dppm$. The infrared spectrum is identical with that of the purple compound prepared from acetonitrile and formulated as $Re_2Cl_6(dppm)_2$, with four terminal and two bridging Cl atoms, by Ebner and Walton.[10]

The red-gold toluene solution yielded brown crystals after standing overnight in the air. One crystal with well-developed faces was glued to the end of a glass fiber and used for crystallographic study.

Collection of Crystallographic Data. The approximate dimensions of the crystal used were 0.12 × 0.18 × 0.33 mm. X-ray intensity data were collected on a Syntex $P\bar{1}$ four-circle automatic diffractometer. ω scans of several reflections had peak widths at half-height of 0.2°. Fifteen intense reflections in the 2θ range $25° < 2\theta < 30°$ were computer centered and used to calculate the following monoclinic cell constants: $a = 14.274$ (3) Å, $b = 23.380$ (7) Å, $c = 18.577$ (3) Å, $\beta = 94.58$ (2)°, and $V = 6180$ (2) Å^3. The experimental density of 1.63 g cm^{-3} is accounted for by assuming that in addition to four molecules of $Re_2Cl_5(dppm)_2$ the unit cell contains eight molecules of toluene. On this basis the calculated density is 1.61 g cm^{-3}. The systematic absences identify the space group as $P2_1/n$.

Data were collected at 23 °C with Mo Kα radiation in the range $0° < 2\theta \leq 45°$ using the θ–2θ scan method. Each reflection was scanned from 0.9° above Kα_1 to 0.9° below Kα_2. Scan rates varied from 4 to 24° min^{-1} depending upon the reflection intensity. The intensities of three reflections were periodically monitored and did not change significantly during data collection. An absorption correction was necessary since the absorption coefficient was 45.0 and the transmission factors varied from 0.453 to 0.698. A number of standard programs were used for data reduction, absorption corrections, and structure solution.[14]

Solution and Refinement of Structure. The positions of two rhenium atoms were deduced from a three-dimensional Patterson map. Their positional parameters and a scale factor were varied in one cycle of full-matrix least-squares refinement. The phosphorus and chlorine atoms were then located in a three-dimensional electron density difference map. Several iterations of this method of refinement followed by atom search were required in order to locate all 75 atoms. Isotropic refinement of all atoms converged with discrepancy indices of $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.085$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.104$. The absorption correction was now applied to the data and only those 4305 reflections for which $I > 3\sigma(I)$ were retained. All atoms were refined anisotropically to convergence, such that no parameter shifted by more than 1% of its esd. Final R_1 and R_2 values were 0.061 and 0.080. The final error in observation of unit weight was 1.66. No unusual trends were found in the values of $\sum w(|F_o - F_c|)^2$ as a function of Miller indices, $\lambda^{-1} \sin\theta$, or $|F_o|$. The Re and P atoms were treated as anomalous scatterers using f' and f'' values taken from the tabulation by Cromer and Liberman.[15] The ordinary scattering factors for all atoms were those of Cromer

Table I. Atomic Positional Parameters

	x	y	z
Re(1)	0.062 82 (6)	0.165 74 (4)	0.119 54 (4)
Re(2)	−0.092 66 (6)	0.166 11 (4)	0.135 73 (4)
Cl(1)	0.074 3 (4)	0.114 1 (3)	0.014 1 (3)
Cl(2)	0.173 6 (5)	0.211 5 (3)	0.199 9 (3)
Cl(3)	−0.151 0 (4)	0.115 8 (3)	0.031 1 (3)
Cl(4)	−0.063 8 (4)	0.219 2 (2)	0.245 2 (3)
Cl(5)	−0.263 8 (4)	0.171 7 (3)	0.169 8 (3)
P(1)	0.065 2 (4)	0.252 2 (3)	0.045 1 (3)
P(2)	0.104 0 (4)	0.076 1 (3)	0.183 0 (3)
P(3)	−0.140 4 (4)	0.248 8 (3)	0.056 2 (3)
P(4)	−0.100 6 (4)	0.068 2 (3)	0.189 7 (3)
C(1)	0.003 8 (14)	0.029 0 (8)	0.162 7 (12)
C(2)	−0.047 3 (14)	0.257 0 (9)	−0.007 4 (12)
1C(1)	0.154 (1)	0.246 (1)	−0.020 (1)
1C(2)	0.132 (2)	0.261 (1)	−0.090 (1)
1C(3)	0.204 (2)	0.251 (1)	−0.141 (1)
1C(4)	0.290 (2)	0.232 (1)	−0.117 (1)
1C(5)	0.315 (2)	0.219 (1)	−0.044 (2)
1C(6)	0.242 (2)	0.230 (1)	0.004 (2)
2C(1)	0.086 (2)	0.321 (1)	0.086 (1)
2C(2)	0.111 (2)	0.368 (1)	0.042 (1)
2C(3)	0.120 (2)	0.424 (1)	0.073 (2)
2C(4)	0.102 (2)	0.432 (1)	0.143 (2)
2C(5)	0.077 (2)	0.386 (1)	0.186 (2)
2C(6)	0.064 (2)	0.329 (1)	0.159 (1)
3C(1)	0.129 (2)	0.074 (1)	0.281 (1)
3C(2)	0.105 (2)	0.118 (1)	0.322 (1)
3C(3)	0.127 (2)	0.115 (1)	0.401 (1)
3C(4)	0.161 (2)	0.062 (1)	0.431 (1)
3C(5)	0.176 (2)	0.020 (2)	0.384 (2)
3C(6)	0.167 (2)	0.024 (1)	0.313 (1)
4C(1)	0.207 (2)	0.042 (1)	0.148 (1)
4C(2)	0.203 (2)	−0.006 (1)	0.111 (2)
4C(3)	0.290 (2)	−0.031 (1)	0.088 (2)
4C(4)	0.369 (2)	0.000 (2)	0.102 (2)
4C(5)	0.377 (2)	0.046 (2)	0.144 (2)
4C(6)	0.294 (2)	0.069 (2)	0.166 (2)
5C(1)	−0.161 (2)	0.319 (1)	0.095 (1)
5C(2)	−0.194 (2)	0.324 (2)	0.164 (2)
5C(3)	−0.213 (2)	0.376 (1)	0.194 (2)
5C(4)	−0.195 (2)	0.427 (1)	0.154 (2)
5C(5)	−0.160 (2)	0.424 (1)	0.087 (2)
5C(6)	−0.142 (2)	0.368 (1)	0.056 (1)
6C(1)	−0.251 (2)	0.241 (1)	−0.003 (1)
6C(2)	−0.244 (2)	0.228 (1)	−0.072 (1)
6C(3)	−0.331 (2)	0.222 (2)	−0.122 (2)
6C(4)	−0.414 (2)	0.228 (1)	−0.088 (2)
6C(5)	−0.420 (2)	0.245 (1)	−0.020 (2)
6C(6)	−0.336 (2)	0.250 (1)	0.028 (1)
7C(1)	−0.199 (1)	0.023 (1)	0.155 (1)
7C(2)	−0.288 (2)	0.028 (1)	0.189 (1)
7C(3)	−0.360 (2)	−0.008 (1)	0.166 (1)
7C(4)	−0.348 (2)	−0.052 (1)	0.111 (2)
7C(5)	−0.267 (2)	−0.054 (1)	0.079 (2)
7C(6)	−0.190 (2)	−0.020 (1)	0.100 (1)
8C(1)	−0.107 (2)	0.061 (1)	0.287 (1)
8C(2)	−0.149 (2)	0.105 (1)	0.324 (1)
8C(3)	−0.158 (2)	0.100 (1)	0.400 (1)
8C(4)	−0.120 (2)	0.047 (1)	0.434 (1)
8C(5)	−0.085 (2)	0.007 (1)	0.396 (1)
8C(6)	−0.070 (2)	0.012 (1)	0.326 (1)
9C(1)	−0.027 (3)	0.338 (2)	0.768 (2)
9C(2)	−0.111 (3)	0.338 (3)	0.808 (3)
9C(3)	−0.100 (3)	0.379 (2)	0.858 (2)
9C(4)	−0.034 (5)	0.420 (3)	0.881 (2)
9C(5)	0.045 (3)	0.414 (2)	0.840 (2)
9C(6)	0.048 (2)	0.368 (1)	0.788 (2)
9C(7)	−0.022 (3)	0.300 (2)	0.704 (3)
10C(1)	0.434 (4)	0.352 (1)	0.173 (3)
10C(2)	0.343 (5)	0.361 (3)	0.194 (4)
10C(3)	0.351 (4)	0.363 (2)	0.261 (5)
10C(4)	0.435 (5)	0.369 (1)	0.323 (2)
10C(5)	0.516 (3)	0.363 (2)	0.285 (3)
10C(6)	0.520 (4)	0.356 (2)	0.206 (4)
10C(7)	0.431 (6)	0.352 (3)	0.097 (2)

Table II. Anisotropic Temperature Factors[a] (×10^4)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re(1)	30.9 (5)	12.4 (2)	15.8 (3)	−0.8 (3)	2.6 (3)	0.0 (2)
Re(2)	32.0 (5)	12.4 (2)	15.6 (3)	1.2 (3)	3.8 (3)	0.4 (2)
Cl(1)	58 (4)	21 (2)	18 (2)	3 (2)	4 (2)	−4 (1)
Cl(2)	58 (4)	20 (1)	25 (2)	−8 (2)	−10 (2)	0 (1)
Cl(3)	48 (4)	18 (1)	18 (2)	−3 (2)	−5 (2)	−2 (1)
Cl(4)	56 (4)	16 (1)	19 (2)	−1 (2)	4 (2)	−2 (1)
Cl(5)	40 (3)	22 (2)	36 (2)	7 (2)	13 (2)	4 (2)
P(1)	38 (4)	13 (1)	20 (2)	−4 (2)	3 (2)	3 (1)
P(2)	34 (3)	15 (1)	20 (2)	6 (2)	0 (2)	1 (1)
P(3)	32 (3)	14 (1)	19 (2)	−3 (2)	−1 (2)	0 (1)
P(4)	34 (3)	14 (1)	18 (2)	0 (2)	2 (2)	0 (1)
C(1)	22 (11)	6 (4)	30 (8)	4 (6)	20 (8)	−3 (5)
C(2)	21 (11)	13 (5)	30 (8)	6 (6)	−5 (8)	1 (5)
1C(1)	16 (12)	16 (6)	48 (12)	1 (7)	22 (10)	11 (7)
1C(2)	96 (24)	30 (8)	30 (10)	7 (11)	20 (13)	25 (8)
1C(3)	77 (23)	41 (10)	26 (10)	16 (14)	21 (12)	11 (8)
1C(4)	113 (30)	40 (11)	28 (11)	−17 (15)	44 (15)	1 (9)
1C(5)	94 (26)	35 (10)	78 (19)	2 (13)	68 (19)	12 (11)
1C(6)	72 (22)	24 (8)	48 (13)	−7 (11)	27 (14)	−5 (8)
2C(1)	48 (16)	12 (6)	42 (11)	−6 (7)	7 (10)	3 (6)
2C(2)	41 (16)	21 (7)	46 (12)	−24 (9)	−7 (11)	2 (7)
2C(3)	69 (22)	18 (7)	61 (15)	−22 (10)	−19 (15)	−3 (9)
2C(4)	107 (28)	10 (6)	61 (16)	−8 (10)	−41 (18)	2 (9)
2C(5)	46 (18)	25 (8)	54 (14)	20 (10)	−14 (13)	−15 (9)
2C(6)	64 (17)	18 (6)	27 (9)	−5 (9)	7 (10)	−4 (7)
3C(1)	41 (14)	11 (5)	22 (8)	−9 (7)	−3 (9)	1 (6)
3C(2)	52 (16)	12 (5)	17 (7)	−7 (7)	4 (9)	−10 (5)
3C(3)	65 (18)	18 (6)	20 (8)	11 (9)	1 (10)	2 (6)
3C(4)	44 (16)	19 (6)	30 (10)	−5 (8)	−2 (10)	1 (7)
3C(5)	104 (29)	64 (15)	37 (13)	25 (17)	42 (16)	24 (12)
3C(6)	32 (14)	25 (7)	32 (10)	4 (8)	−11 (10)	15 (7)
4C(1)	41 (15)	18 (6)	24 (8)	−4 (8)	19 (9)	−3 (6)
4C(2)	73 (22)	27 (8)	40 (12)	6 (11)	13 (12)	−7 (9)
4C(3)	41 (20)	28 (9)	114 (24)	9 (11)	11 (17)	−19 (12)
4C(4)	34 (18)	61 (14)	57 (16)	31 (14)	−7 (14)	3 (13)
4C(5)	69 (24)	54 (13)	41 (13)	−14 (14)	1 (14)	−39 (11)
4C(6)	14 (14)	56 (12)	62 (15)	−2 (11)	16 (12)	−33 (11)
5C(1)	38 (14)	9 (5)	27 (9)	−1 (6)	−11 (9)	0 (5)
5C(2)	27 (14)	62 (13)	48 (12)	−2 (12)	−2 (11)	−43 (11)
5C(3)	63 (12)	26 (8)	66 (16)	1 (11)	21 (15)	−26 (10)
5C(4)	58 (20)	26 (9)	56 (15)	4 (11)	3 (14)	−7 (10)
5C(5)	45 (17)	27 (8)	44 (12)	−15 (10)	−14 (12)	−11 (8)
5C(6)	46 (16)	19 (7)	27 (9)	−1 (8)	−13 (10)	−8 (7)
6C(1)	41 (16)	18 (6)	27 (9)	6 (8)	−22 (10)	7 (6)
6C(2)	52 (17)	28 (7)	17 (8)	13 (9)	−11 (10)	−1 (6)
6C(3)	76 (25)	73 (16)	39 (13)	−42 (17)	−11 (15)	2 (12)
6C(4)	99 (28)	34 (9)	28 (11)	−21 (13)	−32 (14)	12 (9)
6C(5)	29 (16)	43 (11)	74 (18)	13 (11)	−2 (14)	30 (12)
6C(6)	46 (17)	27 (8)	43 (12)	19 (10)	−13 (12)	−2 (8)
7C(1)	13 (11)	13 (5)	32 (9)	−12 (6)	2 (8)	−5 (6)
7C(2)	33 (14)	29 (7)	11 (7)	−5 (8)	4 (8)	−6 (6)
7C(3)	54 (17)	22 (7)	30 (10)	−12 (9)	−26 (10)	2 (7)
7C(4)	36 (16)	24 (7)	52 (13)	0 (9)	11 (12)	1 (8)
7C(5)	45 (18)	30 (8)	53 (13)	−14 (10)	−5 (13)	−6 (9)
7C(6)	65 (20)	29 (8)	34 (10)	−5 (10)	1 (11)	−22 (8)
8C(1)	59 (17)	18 (6)	19 (8)	−6 (8)	12 (10)	−5 (6)
8C(2)	56 (17)	34 (8)	12 (8)	−12 (10)	7 (9)	7 (7)
8C(3)	72 (21)	30 (9)	35 (11)	−5 (11)	16 (12)	−4 (8)
8C(4)	88 (24)	28 (8)	26 (10)	−6 (12)	21 (12)	8 (8)
8C(5)	41 (16)	16 (6)	52 (13)	−7 (8)	9 (12)	16 (8)
8C(6)	28 (13)	26 (7)	25 (9)	−5 (8)	−5 (9)	10 (7)
9C(1)	124 (35)	38 (11)	42 (13)	−2 (18)	−13 (18)	−3 (11)
9C(2)	64 (24)	116 (35)	93 (26)	−8 (24)	20 (24)	77 (28)
9C(3)	103 (41)	85 (57)	52 (21)	70 (39)	26 (22)	56 (29)
9C(4)	297 (124)	77 (28)	47 (24)	86 (52)	12 (41)	32 (20)
9C(5)	148 (39)	45 (14)	62 (18)	63 (19)	35 (22)	35 (14)
9C(6)	59 (19)	18 (7)	39 (12)	−6 (10)	−1 (12)	4 (7)
9C(7)	136 (43)	40 (14)	163 (42)	−14 (19)	−34 (34)	5 (20)
10C(1)	232 (66)	6 (7)	139 (40)	27 (18)	98 (47)	23 (13)
10C(2)	194 (76)	99 (29)	179 (59)	35 (34)	−64 (55)	−86 (36)
10C(3)	160 (54)	26 (12)	259 (70)	−11(19)	−118 (61)	21 (26)
10C(4)	358 (100)	14 (9)	54 (18)	−13 (25)	47 (35)	−11 (10)
10C(5)	120 (46)	20 (9)	135 (38)	1 (16)	−33 (35)	−21 (18)
10C(6)	91 (39)	48 (18)	205 (60)	−3 (21)	32 (43)	−27 (27)
10C(7)	481 (116)	84 (25)	41 (18)	45 (41)	−56 (39)	−13 (18)

[a] These are in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

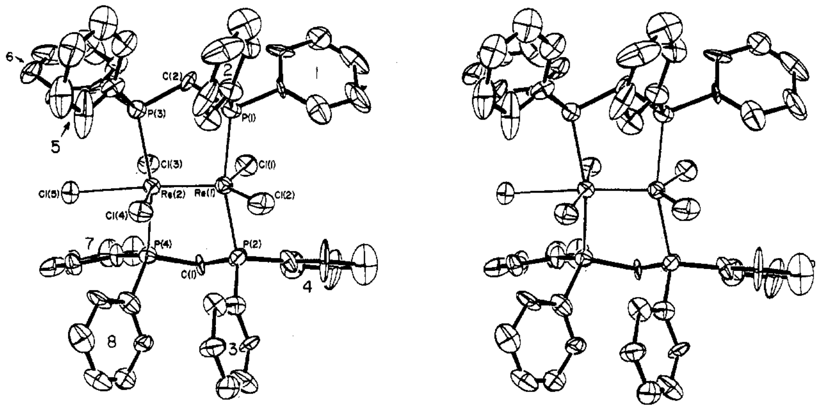

Figure 1. An ORTEP stereodrawing of the $Re_2Cl_5(dppm)_2$ molecule. Each atom is represented by a contour of its ellipsoid of thermal vibration that encloses 50% of the electron density. The numbers assigned to each phenyl ring for use in labeling ring carbon atoms are also shown.

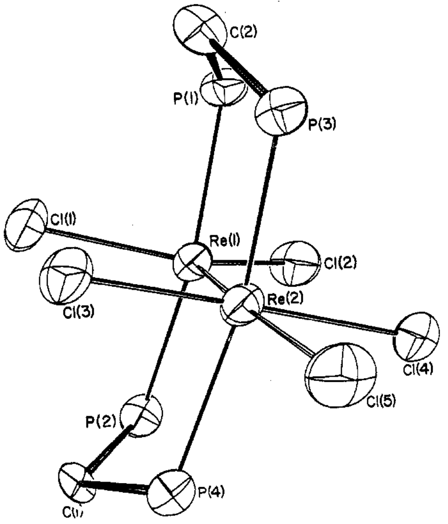

Figure 2. An ORTEP drawing of the central portion of the $Re_2Cl_5(dppm)_2$ molecule with the phenyl groups omitted. Each atom is represented by its vibration ellipsoid at the 50% level.

and Waber.[16] A list of the observed and final calculated structure factors is available.[17]

Results

The reaction of $((n\text{-}Bu)_4N_2)Re_2Cl_8$ with bis(diphenylphosphino)methane (dppm) in acetone gives as the major product a purple solid, for which analytical data suggest a composition in the range $ReCl_{3-4}$dppm. This appears to be the same compound previously reported by Walton[10] as the sole product of the reaction carried out in acetonitrile. He has proposed a binuclear structure, in which there are four terminal chlorine atoms and two bridging ones, on the basis of the x-ray photoelectron spectrum. Our attempts to determine the structure by x-ray crystallography have so far been frustrated by crystal decomposition in the x-ray beam. A principal cause of this instability appears to be that the crystals we have so far examined have contained solvent of crystallization which is driven out under irradiation, thus destroying the crystal. Efforts to overcome this problem are continuing.

The minor product of the reaction is a brown, air-stable solid. Upon crystallization from toluene, a solid with the composition $Re_2Cl_5(dppm)_2 \cdot 2C_7H_8$ is obtained. The identity and structure of this substance were ascertained by x-ray crystallography.

The atomic positional parameters and anisotropic temperature parameters are listed in Tables I and II, respectively.

Table III. Selected Bond Distances and Angles in $Re[((C_6H_5)_2P)_2CH_2]_2Cl_5 \cdot 2C_7H_8$

Distances, Å			
Re(1)–Re(2)	2.263 (1)	Re(2)–Cl(5)	2.575 (6)
Re(1)–Cl(1)	2.316 (6)	Re(2)–Cl(3)	2.364 (6)
Re(1)–Cl(2)	2.343 (6)	Re(2)–Cl(4)	2.389 (6)
Re(1)–P(1)	2.451 (6)	Re(2)–P(3)	2.494 (6)
Re(1)–P(2)	2.452 (6)	Re(2)–P(4)	2.506 (6)
P(1)–C(2)	1.81 (2)	P(3)–C(2)	1.86 (2)
P(1)–1C(1)	1.83 (2)	P(3)–5C(1)	1.83 (2)
P(1)–2C(1)	1.80 (2)	P(3)–6C(1)	1.86 (2)
P(2)–C(1)	1.82 (2)	P(4)–C(1)	1.85 (2)
P(2)–3C(1)	1.82 (2)	P(4)–7C(1)	1.83 (2)
P(2)–4C(1)	1.84 (2)	P(4)–8C(1)	1.83 (2)
Angles, Deg			
Re(2)–Re(1)–Cl(1)	104.5 (2)	Re(1)–Re(2)–Cl(3)	100.0 (2)
Re(2)–Re(1)–Cl(2)	122.2 (2)	Re(1)–Re(2)–Cl(4)	90.6 (2)
Re(2)–Re(1)–P(1)	97.4 (2)	Re(1)–Re(2)–Cl(5)	172.9 (2)
Re(2)–Re(1)–P(2)	98.0 (2)	Re(1)–Re(2)–P(3)	98.6 (1)
Cl(1)–Re(1)–Cl(2)	133.3 (2)	Re(1)–Re(2)–P(4)	97.2 (1)
Cl(1)–Re(1)–P(1)	87.0 (2)	Cl(3)–Re(2)–Cl(4)	169.3 (2)
Cl(1)–Re(1)–P(2)	86.0 (2)	Cl(3)–Re(2)–Cl(5)	87.0 (2)
Cl(2)–Re(1)–P(1)	86.7 (2)	Cl(3)–Re(2)–P(3)	80.6 (2)
Cl(2)–Re(1)–P(2)	87.7 (2)	Cl(3)–Re(2)–P(4)	81.3 (2)
P(1)–Re(1)–P(2)	164.2 (2)	Cl(4)–Re(2)–Cl(5)	82.4 (2)
Re(1)–P(1)–C(2)	107.6 (8)	Cl(4)–Re(2)–P(3)	97.0 (2)
Re(1)–P(1)–1C(1)	110.6 (8)	Cl(4)–Re(2)–P(4)	98.3 (2)
Re(1)–P(1)–2C(1)	120.6 (8)	Cl(5)–Re(2)–P(3)	83.4 (2)
Re(1)–P(2)–C(1)	105.3 (7)	Cl(5)–Re(2)–P(4)	82.8 (2)
Re(1)–P(2)–3C(1)	121.7 (8)	P(3)–Re(2)–P(4)	157.8 (2)
Re(1)–P(2)–4C(1)	111.8 (8)	Re(2)–P(3)–C(2)	106.3 (7)
P(1)–C(2)–P(3)	107.5 (11)	Re(2)–P(3)–5C(1)	120.4 (7)
P(2)–C(1)–P(4)	106.3 (10)	Re(2)–P(3)–6C(1)	117.0 (8)
		Re(2)–P(4)–C(1)	106.3 (7)
		Re(2)–P(4)–7C(1)	116.0 (8)
		Re(2)–P(4)–8C(1)	119.2 (8)

The unit cell contains eight toluene molecules and four $Re_2Cl_5(dppm)_2$ molecules. A stereoview of the latter is shown in Figure 1. This dinuclear complex has no crystallographic symmetry. However, as shown in Figure 2, in which the phenyl groups have been omitted for clarity, the molecule has a virtual mirror plane defined by the two rhenium atoms and the five chlorine atoms. Table III lists bond lengths and angles for the $Re_2Cl_5(dppm)_2$ molecule, and Table IV gives equations for mean planes and dihedral angles.

The numbering scheme for ring carbon atoms of the ligands employs a prefix number, defined in Figure 1, to designate the ring in which the atom occurs and a suffix number from 1 to 6, where 1 denotes the atom attached to the phosphorus atom. For the ring atoms of the two crystallographically independent toluene molecules an analogous scheme is followed, with the two toluene methyl carbon atoms being designated 9C(7) and 10C(7). A table of C–C distances in the ten independent

Table IV. Unweighted Least-Squares Planes

Equations of Planes[a]

Plane	Atoms of plane	*A*	*B*	*C*	*D*
1	Re(2)-Re(1)-Cl(1)	−0.0678	0.8445	−0.5312	2.038
2	Re(2)-Re(1)-Cl(2)	−0.0684	0.8416	−0.5357	2.016
3	Re(2)-Re(1)-P(1)	−0.1122	−0.5553	−0.8241	−4.050
4	Re(2)-Re(1)-P(2)	−0.1160	−0.5076	−0.8538	−3.934
5	Re(1)-Re(2)-Cl(3)	−0.0636	0.8636	−0.5002	2.183
6	Re(1)-Re(2)-Cl(4)	−0.0654	0.8553	−0.5139	2.120
7	Re(1)-Re(2)-P(3)	−0.1059	−0.6234	−0.7747	−4.199
8	Re(1)-Re(2)-P(4)	−0.1234	−0.3892	−0.9129	−3.613
9	P(1)-Re(1)-Re(2)-P(3)	−0.0654	−0.5895	−0.8051	−4.157
10	P(1)-C(2)-P(3)	0.0173	−0.9898	−0.1413	−5.922
11	P(2)-Re(1)-Re(2)-P(4)	−0.0509	−0.4470	−0.8931	−3.820
12	P(2)-C(1)-P(4)	−0.0640	0.3945	−0.9167	−2.483

Dihedral Angles

Planes	Angle, deg	Planes	Angle, deg
1–2	0.3	5–6	0.9
1–5	2.1	7–8	15.7
2–6	1.5	9–10	45.9
3–4	3.2	11–12	49.8
3–7	4.8		
4–8	7.6		

[a] The equations are of the form $AX + BY + CZ = D$.

aromatic rings is available.[17] These distances vary from 1.32 to 1.50 Å; each one has an esd of 0.03–0.07 Å and the average of all of them is 1.38 Å.

The magnetic properties of the compound were examined by E. Pedersen of the H. C. Oersted Institute, University of Copenhagen. The x-band EPR spectrum at 20 °C is broad and complex but strongly suggests the presence of one unpaired electron coupled to two Re nuclei each with spin $^5/_2$. The g values are approximately $g_\perp \approx 2.2$ and $g_\parallel < 2$. Bulk susceptibility measurements suggested that ferromagnetic impurities might be present, but μ_{eff} at 23 °C was 1.95 BM, consistent with the presence of one unpaired electron.

Discussion

In this compound the dppm ligand once again adopts the conformation which allows it to form two parallel donor bonds[12] and thus to serve as a bridge across two closely spaced metal atoms.

The bond distances and angles in this molecule seem to result from a complex interplay between steric and electronic forces. There are some structural features that might be taken to indicate that the two rhenium atoms are electronically nonequivalent to a significant extent, with Re(1) having the higher effective oxidation state. Thus the Re(1)–P distances are about 0.04 Å shorter than the Re(2)–P distances, and the Re to nonaxial chlorine atom distances are also shorter for Re(1) by about 0.05 Å. However, it might be expected that the metal atom with the higher effective oxidation number would attract the greater number of anionic ligands, whereas it is Re(2) that binds the axial Cl(5). Thus, the assignment of a higher effective charge to Re(1) on the basis of the Re–P and Re–Cl bond distances is not unexceptionable.

A purely steric argument to account for the variation in bond lengths can be constructed as follows. Given that the fifth Cl atom becomes coordinated to one Re atom, Re(2) as it happens, the other differences could be considered as necessary consequences. Thus the higher coordination number at Re(2) might cause the Re(2)–Cl and Re(2)–P bonds to increase 0.04–0.05 Å because of ligand–ligand repulsions. Furthermore, the repulsions between Cl(3) and Cl(1) and between Cl(4) and Cl(2) could then be considered the cause of the contraction of the Cl(1)–Re(1)–Cl(2) angle from a value in the 160–180° range down to the observed value of 133.3 (2)°. On this purely steric line of argument the question of how the total formal charge of 5+ is distributed over the two Re atoms is left entirely open.

The structural situation here is reminiscent of that in the amidine complexes,[18] $Re_2(Ph_3CN_2)_2Cl_4$ and $Re_2(Ph_3CN_2)_2Cl_4{\cdot}THF$. The former has virtual symmetry of D_{2h}, but when a THF molecule becomes coordinated to one rhenium atom, as in the latter, the following changes occur. At the end where the THF is coordinated the Re–Cl distances are 0.045 Å longer and the Re–N distances 0.02 Å longer than at the other end where they are essentially the same as in the unsolvated molecule. Also, the Cl–Re–Cl angle increases from 147 to 162° at the coordinated end and decreases to 143° at the other end. Finally, the Re–Re distances increases by 0.032 Å. Since there is no change of formal oxidation number here, these changes are all consequences of introducing the axial ligand at one end.

The structural differences between the two ends of $Re_2Cl_5(dppm)_2$ and the fact that the Re–Re distance here is about 0.03 Å longer than those in $Re_2Cl_6(PEt_3)_2$[9] and $Re_2Cl_4(PEt_3)_4$[11] are all very analogous to those just cited for the $Re_2Cl_4(Ph_3CN_2)_2$–$Re_2Cl_4(Ph_3CN_2)_2{\cdot}THF$ pair. Indeed the comparison is valid quantitatively as well as qualitatively. Thus, we feel that from the structural data alone it is impossible to draw any conclusion concerning the type of orbital occupied by the unpaired electron in $Re_2Cl_5(dppm)_2$.

Acknowledgment. We thank Dr. Eric Pedersen of the University of Copenhagen, who performed the ESR and magnetic susceptibility measurements described above, the Molecular Structure Corp., College Station, Tex., for help with the refinements, and Professor R. A. Walton for communicating unpublished results and for useful discussions. Financial support from the National Science Foundation (Grant No. 33142X) is gratefully acknowledged.

Registry No. $Re_2[((C_6H_5)_2P)_2CH_2]_2Cl_5{\cdot}2C_7H_8$, 59728-60-8; $(Bu_4N)_2Re_2Cl_8$, 14023-10-0.

Supplementary Material Available: Tables of structure factors and additional bond distances (20 pages). Ordering information is given on any current masthead page.

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The Tungsten–Tungsten Triple Bond. 3. Dimethyltetrakis(diethylamido)ditungsten. Structure and Dynamical Solution Behavior

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Received March 22, 1976 AIC60200T

The title compound, $(Et_2N)_2MeW{\equiv}WMe(NEt_2)_2$, has been prepared and thoroughly characterized by means of x-ray crystallography, by carbon-13 NMR over the temperature range −60 to +60 °C, and by other physical and chemical methods. In solution the molecule exists as an approximately 3:2 equilibrium mixture of anti and gauche isomers. When the compound is crystallized by lowering the temperature of a concentrated solution, the solid obtained consists entirely of the anti rotamer. The crystals belong to space group $C2/c$ with unit cell parameters a = 17.033 (5) Å, b = 8.258 (2) Å, c = 18.817 (4) Å, and β = 103.34 (2)°. The molecules are located on centers of symmetry and have the following important dimensions: W–W = 2.288 Å, W–N(mean) = 1.966 Å, W–C = 2.171 Å, W–W–C = 101.6°, W–W–N = 104.2°. The ^{13}C NMR spectra allowed us to observe the following dynamic properties. At equilibrium in toluene solution the g:a (gauche:anti) ratio is about 3:2 at all temperatures from −60 to +60 °C. Even at +60 °C the rate of $g \rightleftharpoons a$ interconversion is too small to influence line shapes. The activation energy for this process is estimated to be about 21 kcal mol^{-1}. Internal rotations about the W–N bonds allow interchange of the proximal and distal ethyl groups. The activation energies for the two types in the gauche rotamer differ by about 2.5 kcal mol^{-1} while that in the anti isomer is about halfway between. A comparison of the W–C and W–N distances supports the idea that there is significant W–N π bonding.

Introduction

In earlier communications from these laboratories[2–4] and others,[5] the existence of an extensive chemistry of dinuclear compounds containing triply bonded pairs of molybdenum and tungsten atoms has been indicated. We have prepared and characterized compounds containing only dialkylamide groups,[2,3] viz., $M_2(NR_2)_6$, as well as those containing a mixture of NR_2 groups and halogen atoms,[4] e.g., $W_2(NEt_2)_4Cl_2$. Wilkinson[5] had shown that pure alkyls (of the type incapable of β elimination, e.g., $M_2(CH_2SiMe_3)_6$) can be prepared.[6]

In this paper we describe a compound which connects the amido series with the organo series, namely, the mixed amido–alkyl species $W_2Me_2(NEt_2)_4$.

Experimental Section

Preparation. A procedure for the preparation of $W_2Me_2(NEt_2)_4$ has been given in an earlier paper.[4] However, we have since found that the following modification of that procedure gives better results. All operations are conducted in an N_2 atmosphere.

Methyllithium (9.0 mmol) in ether (6 ml) was added dropwise to a stirred solution of $W_2Cl_2(NEt_2)_4$ (2.19 g; 3.0 mmol) in ether (90 ml) at 25 °C. Stirring was continued for 60 min while a white precipitate appeared. The solvent was removed under vacuum and the residue was extracted with hexane (50 ml). The filtrate was concentrated to 20 ml and cooled slowly to −20 °C. The bright red crystals were filtered and dried under vacuum. The filtrate was warmed to 50 °C, concentrated to 10 ml, and cooled to −20 °C to give an additional crop of crystals. This filtrate was again reduced to half-volume and cooled to −20 °C to give another small crop. The total yield was 1.8 g (78%). Spectral data were reported earlier.[4]

Anal. Calcd for $C_{18}H_{46}N_4W_2$: C, 31.50; H, 6.76; N, 8.16; Cl, 0.00. Found: C, 31.4; H, 6.69; N, 8.02; Cl, 0.00.

Crystal Selection and Data Collection. Crystals potentially suitable for x-ray data collection were kept immersed in heavy mineral oil in a nitrogen-filled glovebag to prevent crystal decomposition while under examination. A rectangular-shaped crystal measuring 0.225 × 0.275 × 0.400 mm was selected for collection and sealed in a thin-walled glass capillary under mineral oil. Wedging the crystal in a capillary filled with the mineral oil has proven to be the most effective means of preventing crystal decomposition during data collection. Procedures for crystal examination and characterization have been described elsewhere.[7] The crystal appeared to be of good quality on the basis of ω scans for several intense reflections, which had peak widths at half-height of 0.18–0.22°. The crystal was found to be monoclinic, with $2/m$ Laue symmetry. A small shell of data, collected at rapid scan rates for use in space group determination, having systematically absent reflections hkl ($h + k \neq 2n$) and $h0l$ ($l \neq 2n$), showed the space group to be either Cc (acentric) or $C2/c$ (centrosymmetric). Final structure refinement showed the correct space group to be $C2/c$. The final values of the lattice constants and an orientation matrix used for the calculation of setting angles in data collection were determined by least-squares refinement of the setting angles for 15 high-angle reflections, 26.0 < 2θ(Mo Kα) < 36.5°, chosen to give a good sampling of diffractometer settings and crystal indices. The refined lattice constants ($\lambda_{MoK\bar{\alpha}}$ 0.71073 Å) are a = 17.033 (5) Å, b = 8.258 (2) Å, c = 18.817 (4) Å, β = 103.34 (2)°, and V = 2575 (1) Å^3. The observed volume was consistent with that anticipated for Z = 4, indicating that for space group $C2/c$, each molecule must lie on a crystallographic twofold axis or on an inversion center or, alternatively, that the molecules occupy general positions in space group Cc.