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Quadruply Bonded Pairs of Metal Atoms Bridged by Amidines. II. Preparation and Structures of Two Dirhenium Compounds, Including the Shortest Re–Re Bond Yet Observed

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Received December 26, 1974 AIC40846Q

The compound $Re_2(N_2CPh_3)_2Cl_4$ was prepared by fusing *N,N'*-diphenylbenzamidine (HN_2CPh_3) with $(Bu_4N)_2Re_2Cl_8$ under N_2 for 30 min. The burgundy-colored product was washed with tetrahydrofuran and recrystallized from chloroform. Two different types of crystals were formed and their structures have been determined. Crystals of the first type are ruby red platelets with cell dimensions $a = 9.231$ (3) Å, $b = 17.623$ (7) Å, $c = 11.662$ (2) Å, $\beta = 106.55$ (2)°, and $V = 1819$ (1) Å^3, having space group $P2_1/n$ with $Z = 2$. The structure was solved and refined to final R values of $R_1 = 0.084$ and $R_2 = 0.100$ using 1699 reflections with $I \geq 3\sigma(I)$ in the range of $0° \leq 2\theta \leq 115°$ (Cu Kα). The structure consists entirely of $Re_2(N_2CPh_3)_2Cl_4$ molecules, in which the Re–Re distance, 2.177 (2) Å, is the shortest yet observed, located on centers of inversion. The virtual symmetry of the molecule is D_{2h}. The $\overline{\text{Re–N–C–N–Re}'}$ rings are essentially planar with an N–C–N angle of 117 (2)°. The Re–Re–Cl angles are 106 (2)°, and the Re–N and Re–Cl distances are 2.06 (2) and 2.31 (1) Å, respectively. Crystals of the second type were dark purple with cell dimensions $a = 13.283$ (4) Å, $b = 13.850$ (3) Å, $c = 14.266$ (4) Å, $\alpha = 105.43$ (2)°, $\beta = 91.16$ (2)°, $\gamma = 119.66$ (2)°, and $V = 2162$ (1) Å^3, having space group $P\bar{1}$ with $Z = 2$. This structure was solved and refined to final R values of $R_1 = 0.067$ and $R_2 = 0.083$ using 4325 reflections with $I > 3\sigma(I)$ in the range $0° \leq 2\theta \leq 45°$ (Mo Kα). The structure consists of $Re_2(N_2CPh_3)_2Cl_4(THF)$ molecules with no crystallographically imposed symmetry. The THF molecule is coordinated (Re–O = 2.54 (2) Å) to one Re atom and the Re–Re distance, 2.209 (1) Å, is longer than that in the molecule lacking THF. Other dimensions are similar, though slight differences of significance exist. The rotational conformation here is not precisely eclipsed but deviates by about 6°.

Introduction

The metal-to-metal bond distance found in the wide variety of Re_2^{6+} derivatives prepared since the recognition of its dinuclear, quadruply bonded character[1-3] has proven to be relatively insensitive to the nature of the ligands. A complete list[3] of nine reported distances indicates that all but two are in the range 2.22–2.25 Å, the exceptions[4,5] being $Re_2I_4(O_2CPh)_2$ and $Na_2Re_2(SO_4)_4 \cdot 8H_2O$, with distances of 2.198 (1) and 2.214 (1) Å, respectively. In an effort to gain more information on the factors which affect the metal–metal bond length, even to only a small extent, we sought a compound in which the coordination of coaxial ligands would be discouraged by steric factors. In a previous investigation[6] the ligand *N,N'*-diphenylbenzamidine had been shown to serve as a replacement for bridging carboxyl groups, and it had been seen from the structure of $Mo_2(N_2CPh_3)_4$ that the *N*-phenyl groups tend to obstruct the coaxial positions. We therefore attempted to prepare derivatives of Re_2^{6+} using this ligand. This paper reports a study in which a compound of the desired type has been prepared and obtained in two crystalline forms. In one the coaxial positions are both vacant while in the other a ligand (THF) is present at one end. The structures of both substances are reported.

Experimental Section

Preparations. $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ and $C_6H_5N{=}C(C_6H_5)NH(C_6H_5)$ were prepared by literature methods.[7,8] $(Bu_4N)_2Re_2Cl_8$ (0.5 g) was fused with 0.5 g of the amidine (mp 144°) under N_2 for 30 min. After the mixture had cooled it was placed in a mortar and ground to a powder. It was then washed generously with THF. The fine powder was burgundy in color and stable to the laboratory atmosphere. Crystals were obtained by dissolving this material in $CHCl_3$ and allowing the solvent to evaporate slowly as the solution stood in a refrigerator. An optical examination of the crystals obtained showed that two types were present. Each type was examined in detail X-ray crystallographically.

Structure of the Monoclinic Crystals. A red crystal with dimensions 0.04 × 0.10 × 0.16 mm was mounted on a glass fiber. The crystal faces were $01\bar{1}$, $0\bar{1}1$, $0\bar{1}0$, 010, $1\bar{1}0$, $\bar{1}10$, 110, and $\bar{1}\bar{1}0$ with the first two being the largest. Fifteen intense reflections were computer centered on a Syntex $P\bar{1}$ four-circle automatic diffractometer. The ω scans of the brightest of these had peak widths at half-height of 0.3°. Cell constants and an orientation matrix for the monoclinic cell were determined from a least-squares refinement.

The cell constants are $a = 9.231$ (3) Å, $b = 17.623$ (7) Å, $c = 11.662$ (2) Å, $\beta = 106.55$ (2)°, and $V = 1819$ (1) Å^3. For $Z = 2$ and a formula weight (for $C_{38}H_{30}N_4Cl_4Re_2$) of 1056.4, the calculated density is 1.929 g cm^{-3}. The measured density by flotation in a 1,3-dibromopropane–heptane mixture is 1.92 [illegible] 0.03 g cm^{-3}. Systematic absences subsequently observed showed that the space group is $P2_1/n$.

Data were collected at 24 ± 1° using Cu Kα radiation and an incident-beam graphite-crystal monochromator. The θ–2θ scan technique, with the scan rate varying from 4 to 24°/min was used to collect 2765 independent reflections in the range $0° \leq 2\theta \leq 115°$. Peaks were scanned from 0.8° below the Kα_1 peak to 1.0° above the Kα_2 peak. Three intense reflections were monitored during data collection and showed no significant change. An absorption correction was made since the linear absorption coefficient is 152 cm^{-1} and the transmission factors vary from 0.266 to 0.644. The crystal was carefully measured on an optical goniometer. Programs for data reduction, absorption correction, and structure analysis were from standard sources.[9]

A three-dimensional Patterson map was used to find the position of the Re atom. Two cycles of refinement of this atom gave agreement factors of $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.25$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.33$. A difference Fourier synthesis then revealed all remaining nonhydrogen atoms. Four cycles of refinement, in which all of the atoms were treated isotropically, gave residuals of $R_1 = 0.11$ and $R_2 = 0.13$. The absorption correction was then applied, and only those 1699 reflections with $I > 3\sigma(I)$ were used to continue the refinement. Three cycles of refinement with anisotropic temperature parameters for Re, Cl, N, and one of the C atoms and the rest of the atoms isotropic involved 128 variables and converged to final R_1 and R_2 values of 0.084 and 0.100, respectively. Hydrogen atoms were entered at calculated positions in the last cycles of refinement, with B values of 5.0 Å^2; hydrogen atom parameters were not refined.

The value of the parameter p used in the expression[9] for $\sigma(I)$ was 0.060. The final error in an observation of unit weight was 2.29. A final difference Fourier map showed no peaks greater than 1.0 e Å^{-3} except for a few ghosts around Re and Cl. Re and Cl were treated as anomalous scatterers using f' and f'' values taken from the tabulations of Cromer and Liberman.[10] Ordinary scattering factors were those of Cromer and Waber.[11] The scattering factor for hydrogen was taken from Stewart, Davidson, and Simpson.[12] No unusual trends were found in the values of $\sum w(|F_o| - |F_c|)^2$ as a

Table I. Atomic Positional Parameters for the Monoclinic Structure

	x	*y*	*z*
Re	0.53417 (13)	0.54048 (6)	0.44213 (10)
Cl(1)	0.3465 (8)	0.5436 (4)	0.2619 (5)
Cl(2)	0.2342 (8)	0.4139 (4)	0.4465 (6)
N(1)	0.4273 (26)	0.6287 (11)	0.5003 (16)
N(2)	0.3575 (25)	0.5436 (12)	0.6251 (16)
C(1)	0.3580 (25)	0.6167 (12)	0.5853 (17)
C(11)	0.4246 (29)	0.7045 (14)	0.4532 (22)
C(12)	0.3075 (29)	0.7305 (15)	0.3662 (23)
C(13)	0.3017 (36)	0.8055 (17)	0.3205 (27)
C(14)	0.4249 (36)	0.8465 (18)	0.3671 (28)
C(15)	0.5453 (39)	0.8269 (21)	0.4507 (32)
C(16)	0.5448 (34)	0.7509 (18)	0.5021 (28)
C(17)	0.2684 (28)	0.6763 (14)	0.6256 (22)
C(18)	0.1173 (33)	0.6849 (17)	0.5695 (26)
C(19)	0.0358 (40)	0.7445 (21)	0.6043 (31)
C(20)	0.1098 (38)	0.7930 (18)	0.6918 (29)
C(21)	0.2568 (44)	0.7842 (21)	0.7540 (35)
C(22)	0.3372 (35)	0.7248 (18)	0.7169 (28)
C(23)	0.2949 (30)	0.5252 (14)	0.7183 (23)
C(24)	0.3704 (33)	0.5415 (17)	0.8358 (26)
C(25)	0.3119 (48)	0.5221 (22)	0.9293 (37)
C(26)	0.1756 (42)	0.4849 (21)	0.8996 (34)
C(27)	0.0911 (43)	0.4688 (20)	0.7923 (34)
C(28)	0.1500 (34)	0.4909 (18)	0.6919 (27)

function of Miller indices, classes of Miller indices, $\lambda^{-1} \sin \theta$, or $|F_o|$.

Structure of the Triclinic Crystals. A dark purple crystal with dimensions of 0.33 × 0.19 × 0.09 mm and developed faces with indices $0\bar{1}0$, 010, $1\bar{1}0$, $\bar{1}10$, $\bar{1}01$, $10\bar{1}$, $1\bar{1}1$, $\bar{1}1\bar{1}$, 101, and $\bar{1}0\bar{1}$ was mounted on a glass fiber. An orientation matrix and cell parameters were obtained in the same manner as described above. The ω scans of the most intense reflections had peak widths at half-height of 0.4°.

The cell parameters are $a = 13.283$ (4) Å, $b = 13.850$ (3) Å, $c = 14.266$ (4) Å, $\alpha = 105.43$ (2)°, $\beta = 91.16$ (2)°, $\gamma = 119.66$ (2)°, and $V = 2162$ (1) Å^3. For $z = 2$ and mol wt 1056.4 the calculated density is 1.62 g cm^{-3}. The measured density for different crystals varied from 1.83 to 1.62 g cm^{-3}, thus indicating that additional atoms are present. The volume per molecule is 170 Å^3 greater than for the monoclinic compound, indicating that there are 8–10 additional atoms in the formula unit. It was therefore anticipated that the triclinic form contained several solvent molecules per molecule of the compound with perhaps incomplete and variable occupancy of some solvent sites.

Data were collected at 24 ± 1° using Mo Kα radiation filtered by a graphite-crystal monochromator. The θ–2θ scan technique, with scan rate varying from 4 to 24°/min, was used to collect 5697 independent reflections in the range $0° \leq 2\theta \leq 45°$. Peaks were scanned from 0.8° below Kα_1 to 1.0° above Kα_2. Periodic checking of three intense reflections indicated slight decomposition of the crystal. The data required an absorption correction since the linear absorption coefficient is 62 cm^{-1} and the minimum and maximum transmission factors were 0.43 and 0.61. The crystal was measured on an optical goniometer. All programs used for data reduction, absorption correction, and structure analysis have been cited.[9]

The crystal decomposition mentioned above was found to be essentially linear with respect to X-ray exposure time and a linear correction was therefore applied to the data before any structure analysis began. The positions of two rhenium atoms were deduced from a three-dimensional Patterson map. Two cycles of least-squares refinement on these atoms gave agreement factors of $R_1 = 0.25$ and $R_2 = 0.33$. A difference Fourier synthesis then revealed all of the remaining nonhydrogen atoms of the expected $Re_2(N_2CPh_3)_2Cl_4$ molecule as well as a number of additional ones which were assigned to molecules of $CHCl_3$ and THF. All of these atomic positions except those of the $CHCl_3$ and C_4H_8O molecules were used in two cycles of isotropic refinement which led to residuals of $R_1 = 0.14$ and $R_2 = 0.17$. An absorption correction was then made to the data, and only those 4325 reflections for which $I > 3\sigma(I)$ were retained in subsequent refinement. Two least-squares cycles in which the C_4H_8O molecule was included, with two Re, four Cl, four N, one O, and two C atoms treated anisotropically and all others treated isotropically, gave $R_1 = 0.078$ and $R_2 = 0.109$. A succeeding difference Fourier synthesis contained four peaks at 4.0, 3.9, 2.6, and 2.2 e Å^{-3} which were defined as one C and three Cl atoms. Two cycles of refinement in which only these atoms—including occupancy factors—were allowed to vary gave $R_1 = 0.069$ and $R_2 = 0.086$. One final cycle of refinement on 295 variables in which two Re, four N, four Cl and one O atoms were treated anisotropically, all the rest of the atoms were refined isotropically, and the $CHCl_3$ multipliers were also refined gave final R values of 0.067 and 0.083 and an error in an observation of unit weight of 1.84. The calculated positional parameters of the phenyl hydrogen atoms were included in the last cycles of refinement but were not varied. B values of 5.0 Å^2 were used for these atoms. All peaks in a final difference Fourier map which were above 1.0 e Å^{-3} were within 1.5 Å of Re or Cl atoms. The structurally determined formula unit $Re_2(N_2CPh_3)_2Cl_4(THF)\cdot 0.63CHCl_3$ has a calculated density of 1.85 g cm^{-3} which is in good agreement with the density determined by the flotation method.

The value of the parameter p used in the expression for $\sigma(I)$ was

Table II. Temperature Factors for the Monoclinic Structure

Anisotropic Temperature Parameters ($\times 10^4$)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	107 (2)	17.3 (4)	50.6 (10)	−1.1 (8)	36.8 (9)	−1.0 (6)
Cl(1)	174 (12)	34 (2)	59 (5)	11 (5)	29 (6)	2 (3)
Cl(2)	121 (10)	29 (2)	98 (7)	−9 (4)	45 (7)	−13 (3)
N(1)	216 (43)	24 (8)	16 (14)	9 (14)	24 (21)	12 (9)
N(2)	164 (37)	32 (8)	22 (15)	20 (16)	6 (19)	−3 (10)
C(1)	100 (36)	15 (8)	23 (17)	−4 (14)	10 (20)	5 (9)

Isotropic Temperature Parameters

Atom	B, Å^2	Atom	B, Å^2	Atom	B, Å^2	Atom	B, Å^2
C(11)	3.5 (5)	C(17)	3.1 (5)	C(20)	5.1 (7)	C(23)	3.2 (5)
C(12)	3.5 (5)	C(18)	4.7 (6)	C(21)	7.0 (9)	C(24)	4.6 (6)
C(13)	5.0 (7)	C(19)	6.3 (8)	C(22)	5.2 (7)	C(25)	7.6 (10)
C(14)	4.8 (7)					C(26)	6.6 (9)
C(15)	6.3 (8)					C(27)	6.9 (9)
C(16)	4.8 (7)					C(28)	4.8 (6)

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

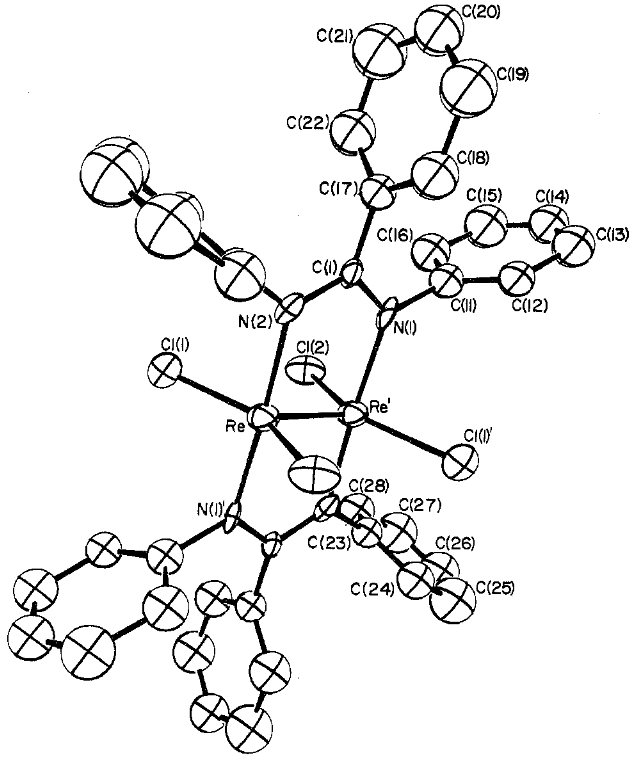

Figure 1. An ORTEP drawing of the $Re_2(N_2CPh_3)_2Cl_4$ molecule as it occurs in the monoclinic crystals. The atom-numbering scheme is shown. Unlabeled atoms are related to the labeled ones by a center of symmetry at the midpoint of the Re–Re bond, as indicated in a few cases, e.g., N(1) and N(1)', Cl(1) and Cl(1)'. Each atom is represented by its ellipsoid of thermal vibration contoured at the 50% level.

Table III. Atomic Positional Parameters for the Triclinic Structure

Atom	*x*	*y*	*z*
Re(1)	0.24501 (5)	−0.04329 (6)	0.28936 (4)
Re(2)	0.23761 (5)	−0.17711 (6)	0.15908 (4)
Cl(11)	0.4505 (4)	0.0647 (4)	0.3473 (3)
Cl(12)	0.0430 (4)	−0.1060 (4)	0.2769 (3)
Cl(21)	0.4278 (4)	−0.1279 (4)	0.1394 (3)
Cl(22)	0.0412 (4)	−0.3162 (4)	0.0916 (4)
N(1)	0.2659 (11)	0.0632 (11)	0.2032 (9)
N(2)	0.2268 (11)	−0.1476 (12)	0.3781 (10)
N(3)	0.2416 (11)	−0.0814 (12)	0.0683 (10)
N(4)	0.2374 (11)	−0.2766 (11)	0.2438 (10)
C(1)	0.2574 (13)	0.0245 (14)	0.1054 (12)
C(2)	0.2270 (14)	−0.2449 (15)	0.3412 (11)
C(11)	0.2955 (16)	0.1827 (16)	0.2506 (14)
C(12)	0.4105 (16)	0.2734 (16)	0.2737 (14)
C(13)	0.4367 (20)	0.3867 (21)	0.3284 (18)
C(14)	0.3509 (21)	0.4068 (21)	0.3529 (18)
C(15)	0.2353 (19)	0.3160 (20)	0.3290 (17)
C(16)	0.2042 (18)	0.2059 (18)	0.2730 (16)
C(17)	0.2631 (14)	0.0939 (15)	0.0407 (12)
C(18)	0.1600 (18)	0.0941 (18)	0.0143 (16)
C(19)	0.1617 (19)	0.1512 (19)	−0.0543 (16)
C(20)	0.2577 (21)	0.2056 (20)	−0.0896 (18)
C(21)	0.3589 (19)	0.2139 (20)	−0.0621 (17)
C(22)	0.3613 (16)	0.1553 (17)	0.0045 (14)
C(23)	0.2258 (14)	−0.1325 (14)	−0.0372 (12)
C(24)	0.1127 (17)	−0.2010 (17)	−0.0942 (15)
C(25)	0.0973 (18)	−0.2539 (19)	−0.1947 (16)
C(26)	0.1915 (20)	−0.2391 (20)	−0.2398 (17)
C(27)	0.3052 (19)	−0.1693 (19)	−0.1860 (17)
C(28)	0.3208 (16)	−0.1186 (16)	−0.0848 (14)
C(29)	0.2095 (14)	−0.1143 (15)	0.4776 (13)
C(30)	0.0955 (17)	−0.1646 (17)	0.4973 (15)
C(31)	0.0739 (20)	−0.1319 (20)	0.5914 (17)
C(32)	0.1698 (21)	−0.0491 (21)	0.6664 (18)
C(33)	0.2826 (20)	−0.0025 (20)	0.6484 (18)
C(34)	0.3016 (16)	−0.0354 (16)	0.5551 (14)
C(35)	0.2156 (14)	−0.3229 (14)	0.4010 (13)
C(36)	0.3028 (16)	−0.2874 (16)	0.4773 (14)
C(37)	0.2917 (18)	−0.3597 (18)	0.5322 (15)
C(38)	0.1922 (18)	−0.4673 (18)	0.5080 (16)
C(39)	0.0993 (16)	−0.5034 (17)	0.4341 (14)
C(40)	0.1131 (15)	−0.4317 (15)	0.3806 (13)
C(41)	0.2639 (15)	−0.3680 (15)	0.2060 (13)
C(42)	0.1822 (16)	−0.4705 (16)	0.1409 (14)
C(43)	0.2114 (20)	−0.5552 (20)	0.1001 (17)
C(44)	0.3235 (20)	−0.5340 (20)	0.1305 (18)
C(45)	0.4090 (18)	−0.4257 (19)	0.2015 (16)
C(46)	0.3785 (17)	−0.3424 (17)	0.2370 (15)
C(47)	0.3304 (18)	0.2655 (18)	0.5703 (16)
C(48)	0.2200 (23)	0.2063 (23)	0.5653 (20)
C(49)	0.3520 (21)	0.2042 (22)	0.4892 (18)
C(50)	0.1650 (22)	0.1000 (22)	0.4850 (19)
C(51)	−0.237 (4)	−0.490 (4)	0.151 (4)
O(1)	0.2578 (14)	0.1103 (14)	0.4421 (12)
Cl(1)	−0.201 (2)	−0.456 (2)	0.265 (2)
Cl(2)	−0.232 (2)	−0.600 (2)	0.087 (2)
Cl(3)	−0.371 (3)	−0.512 (3)	0.129 (2)

0.060. Scattering tables used for the atoms were those listed for the monoclinic structure.[8-10] No unusual trends were found in the values of $\sum w(|F_o| - |F_c|)^2$ as a function of Miller indices, classes of Miller indices, $\lambda^{-1} \sin \theta$, or $|F_o|$.

Results

The observed and calculated structure factor amplitudes, expressed as $10|F_o|$ and $10|F_c|$, for both structures are available.[13] Atomic positional parameters and anisotropic and isotropic thermal parameters for the monoclinic structure are listed in Tables I and II. Those for the triclinic structure are in Tables III and IV.

Both crystal forms of the product are stable in laboratory air and moderately soluble in chloroform. They are only slightly soluble in THF.

Table IV. Temperature Parameters for the Triclinic Structure[a]

Anisotropic Temperature Factors ($\times 10^4$)[b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re(1)	51.7 (6)	66.9 (7)	23.8 (4)	27.6 (5)	9.4 (4)	5.7 (4)
Re(2)	53.8 (6)	62.9 (7)	23.3 (4)	22.6 (5)	6.9 (4)	5.2 (4)
Cl(11)	53 (3)	87 (4)	46 (3)	23 (3)	4 (2)	2 (3)
Cl(12)	59 (4)	123 (5)	47 (3)	45 (4)	16 (2)	23 (3)
Cl(21)	77 (4)	107 (5)	49 (3)	50 (4)	28 (3)	26 (3)
Cl(22)	69 (4)	92 (5)	56 (3)	9 (4)	−9 (3)	15 (3)
N(1)	76 (13)	63 (12)	28 (8)	40 (11)	16 (8)	20 (8)
N(2)	47 (11)	70 (13)	40 (8)	25 (10)	21 (8)	16 (8)
N(3)	49 (11)	76 (14)	31 (8)	19 (10)	7 (8)	12 (9)
N(4)	54 (12)	58 (12)	50 (10)	30 (10)	12 (8)	7 (8)
C(1)	41 (13)	56 (15)	39 (11)	14 (11)	5 (9)	0 (10)
C(2)	63 (14)	76 (16)	28 (10)	42 (13)	18 (9)	15 (10)
O(1)	123 (16)	122 (17)	100 (13)	76 (15)	32 (12)	45 (12)

Isotropic Temperature Factors

Atom	*B*, Å^2	Atom	*B*, Å^2	Atom	*B*, Å^2
C(11)	3.8 (4)	C(26)	5.7 (5)	C(41)	3.6 (3)
C(12)	4.1 (4)	C(27)	5.6 (5)	C(42)	4.0 (4)
C(13)	6.0 (5)	C(28)	4.0 (4)	C(43)	5.9 (5)
C(14)	6.3 (5)	C(29)	3.5 (3)	C(44)	5.9 (5)
C(15)	5.7 (5)	C(30)	4.5 (4)	C(45)	5.3 (4)
C(16)	4.9 (4)	C(31)	5.7 (5)	C(46)	4.4 (4)
C(17)	3.3 (3)	C(32)	6.3 (5)	C(47)	5.1 (4)
C(18)	5.1 (4)	C(33)	5.9 (5)	C(48)	6.9 (6)
C(19)	5.5 (5)	C(34)	3.9 (4)	C(49)	6.0 (5)
C(20)	6.1 (5)	C(35)	3.4 (3)	C(50)	6.6 (6)
C(21)	5.7 (5)	C(36)	4.0 (4)	C(51)	7.8 (11)
C(22)	4.4 (4)	C(37)	4.8 (4)	Cl(1)	19 (1)
C(23)	3.2 (3)	C(38)	5.0 (4)	Cl(2)	16 (1)
C(24)	4.7 (4)	C(39)	4.3 (4)	Cl(3)	24 (1)
C(25)	5.3 (4)	C(40)	3.8 (3)		

[a] Value for the multiplier of $CHCl_3$ 0.634 (17). [b] In the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

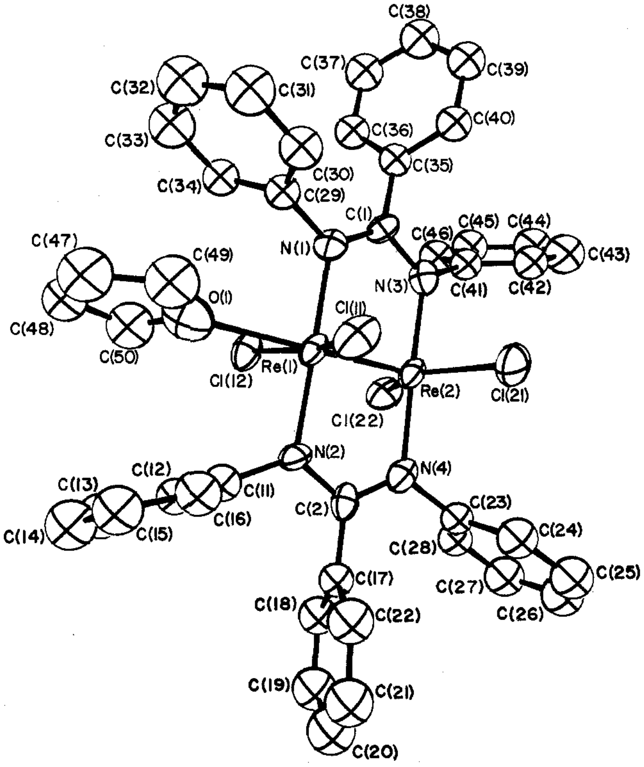

Figure 2. An ORTEP drawing of the $Re_2(N_2CPh_3)_2Cl_4(THF)$ molecule as it occurs in the triclinic crystals. Atoms are represented by 50% thermal ellipsoids.

The two crystal types differ in their unit cell contents. The monoclinic crystals contain only $Re_2(N_2CPh_3)_2Cl_4$ molecules, whereas the triclinic ones contain $Re_2(N_2CPh_3)_2Cl_4(THF)$ molecules, where the THF is coaxially coordinated, and also a fractional amount of clathrated $CHCl_3$ (0.63 (2) molecule per asymmetric unit). Figures 1 and 2 show the molecular

Table V. Bond Distances and Angles in the Monoclinic Structure

A. Bond Distances, Å

Re-Re′	2.177 (2)	C(15)-C(14)	1.30 (4)
Re-N(1)′	2.06 (2)	C(15)-C(16)	1.47 (4)
Re-N(2)	2.06 (2)	C(17)-C(18)	1.37 (4)
Re-Cl(1)	2.312 (6)	C(17)-C(22)	1.37 (4)
Re-Cl(2)′	2.308 (7)	C(19)-C(18)	1.42 (4)
N(1)-C(1)	1.34 (3)	C(19)-C(20)	1.36 (4)
N(2)-C(1)	1.37 (3)	C(21)-C(20)	1.35 (4)
N(1)-C(11)	1.44 (3)	C(21)-C(22)	1.42 (4)
N(2)-C(23)′	1.41 (3)	C(23)-C(24)	1.38 (4)
C(1)-C(17)	1.49 (3)	C(23)-C(28)	1.42 (4)
C(11)-C(12)	1.34 (3)	C(25)-C(24)	1.39 (5)
C(11)-C(16)	1.37 (4)	C(25)-C(26)	1.37 (5)
C(13)-C(12)	1.42 (4)	C(27)-C(26)	1.30 (5)
C(13)-C(14)	1.33 (4)	C(27)-C(28)	1.48 (4)

B. Bond Angles, Deg

Re′-Re-Cl(1)	107.7 (2)	Re′-N(1)-C(1)	120 (2)
Re-Re′-Cl(2)	105.4 (2)	Re′-N(1)-C(11)	122 (2)
Re-Re′-N(1)	92.3 (5)	C(1)-N(1)-C(11)	118 (2)
Re′-Re-N(2)	91.3 (6)	N(1)-C(1)-N(2)	116 (2)
Cl(1)-Re-Cl(2)′	146.9 (2)	N(1)-C(1)-C(17)	123 (2)
Cl(1)-Re-N(1)′	88.7 (6)	N(2)-C(1)-C(17)	120 (2)
Cl(1)-Re-N(2)	89.4 (5)	Re-N(2)-C(1)	120 (2)
Cl(2)-Re′-N(1)	90.3 (6)	Re-N(2)-C(23)′	119 (2)
Cl(2)′-Re-N(2)	89.6 (6)	C(1)-N(2)-C(23)′	121 (2)
N(1)′-Re-N(2)	176.3 (7)		

Table VI. Bond Lengths and Angles in the Triclinic Structure

Bond Lengths, Å

Re(1)-Re(2)	2.209 (1)	Re(2)-Cl(21)	2.313 (4)
Re(1)-Cl(11)	2.363 (4)	Re(2)-Cl(22)	2.320 (4)
Re(1)-Cl(12)	2.361 (4)	Re(2)-N(3)	2.07 (1)
Re(1)-N(1)	2.08 (1)	Re(2)-N(4)	2.06 (1)
Re(1)-N(2)	2.09 (1)	N(2)-C(2)	1.31 (2)
Re(1)-O(1)	2.54 (2)	N(2)-C(29)	1.43 (2)
N(1)-C(1)	1.34 (2)	N(4)-C(2)	1.37 (2)
N(1)-C(11)	1.45 (2)	N(4)-C(41)	1.45 (2)
N(3)-C(1)	1.32 (2)	C(2)-C(35)	1.50 (2)
N(3)-C(23)	1.44 (2)	C(29)-C(30)	1.39 (2)
C(1)-C(17)	1.48 (2)	C(29)-C(34)	1.38 (2)
C(11)-C(12)	1.37 (2)	C(31)-C(30)	1.38 (3)
C(11)-C(16)	1.42 (3)	C(31)-C(32)	1.39 (3)
C(13)-C(12)	1.41 (3)	C(33)-C(32)	1.37 (3)
C(13)-C(14)	1.33 (3)	C(33)-C(34)	1.36 (3)
C(15)-C(14)	1.38 (3)	C(35)-C(36)	1.37 (2)
C(15)-C(16)	1.36 (3)	C(35)-C(40)	1.39 (2)
C(17)-C(18)	1.42 (2)	C(37)-C(36)	1.38 (2)
C(17)-C(22)	1.36 (2)	C(37)-C(38)	1.36 (3)
C(19)-C(18)	1.31 (3)	C(39)-C(38)	1.39 (3)
C(19)-C(20)	1.40 (3)	C(39)-C(40)	1.35 (2)
C(21)-C(20)	1.33 (3)	C(41)-C(42)	1.34 (2)
C(21)-C(22)	1.41 (3)	C(41)-C(46)	1.41 (2)
C(23)-C(24)	1.40 (2)	C(43)-C(42)	1.40 (3)
C(23)-C(28)	1.40 (2)	C(43)-C(44)	1.40 (3)
C(25)-C(24)	1.38 (3)	C(45)-C(44)	1.42 (3)
C(25)-C(26)	1.37 (3)	C(45)-C(46)	1.38 (3)
C(27)-C(26)	1.38 (3)	C(51)-Cl(1)	1.56 (5)
C(27)-C(28)	1.39 (3)	C(51)-Cl(2)	1.60 (5)
C(47)-C(48)	1.26 (3)	C(51)-Cl(3)	1.66 (5)
C(47)-C(49)	1.37 (3)		
C(48)-C(50)	1.42 (3)		
O(1)-C(49)	1.26 (3)		
O(1)-C(50)	1.35 (3)		

Bond Angles, Deg

Re(2)-Re(1)-Cl(11)	98.2 (1)	Re(1)-Re(2)-Cl(21)	108.9 (1)
-Cl(12)	100.1 (1)	-Cl(22)	108.2 (1)
-N(1)	90.2 (3)	-N(3)	90.9 (4)
-N(2)	90.5 (4)	-N(4)	91.9 (4)
-O(1)	178.4 (3)	Cl(21)-Re(2)-Cl(22)	142.9 (2)
Cl(11)-Re(1)-Cl(12)	161.6 (2)	-N(3)	88.5 (4)
-N(1)	90.3 (4)	-N(4)	89.4 (4)
-N(2)	88.8 (4)	N(3)-Re(2)-N(4)	176.8 (5)
-O(1)	80.5 (4)	-Cl(22)	90.9 (4)
N(1)-Re(1)-N(2)	178.9 (5)	Cl(22)-Re(2)-N(4)	89.4 (4)
-Cl(12)	90.1 (4)	C(1)-N(3)-Re(2)	121 (1)
-O(1)	90.8 (5)	C(1)-N(3)-C(23)	120 (1)
Cl(12)-Re(1)-N(2)	90.6 (4)	C(23)-N(3)-Re(2)	119 (1)
-O(1)	81.1 (4)	C(2)-N(4)-Re(2)	119 (1)
N(2)-Re(1)-O(1)	88.4 (5)	C(2)-N(4)-C(41)	120 (1)
C(1)-N(1)-Re(1)	121 (1)	C(41)-N(4)-Re(2)	121 (1)
C(1)-N(1)-C(11)	120 (1)	N(2)-C(2)-N(4)	118 (1)
C(11)-N(1)-Re(1)	120 (1)	N(2)-C(2)-C(35)	123 (1)
C(2)-N(2)-Re(1)	120 (1)	N(4)-C(2)-C(35)	119 (1)
C(2)-N(2)-C(29)	120 (1)		
C(29)-N(2)-Re(1)	120 (1)		
N(1)-C(1)-N(3)	116 (2)		
N(1)-C(1)-C(17)	123 (1)		
N(3)-C(1)-C(17)	121 (1)		

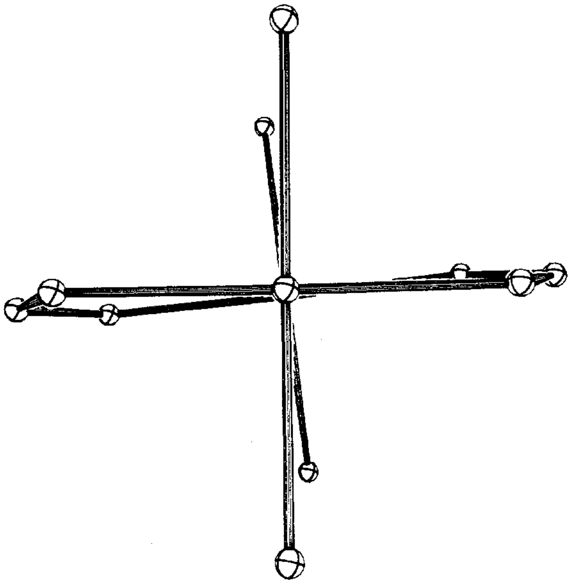

Figure 3. ORTEP drawing of the $Re_2(N_2CPh_3)_2$(THF) molecule viewed down the Re(1)-Re(2) axis. Re(2) is hidden by Re(1) and the C_4H_8O molecule and benzene rings have been omitted.

unit present in each compound. Tables V and VI give bond distances and angles for these two crystal types. Figure 3 shows the triclinic molecule viewed down the Re(1)-Re(2) axis.

Discussion

The results reported here afford the first opportunities to examine several important structural questions pertinent to molecules with quadruple bonds. The molecule found in the monoclinic crystals, $Re_2(N_2CPh_3)_2Cl_4$, will be referred to as the *parent* and the molecule found in the triclinic crystals, $Re_2(N_2CPh_3)_2Cl_4$(THF), will be called the *solvate*.

The parent has a structure essentially similar to that of the analogous iodide benzoate, $Re_2(O_2CPh)_2I_4$. The bridging groups, here the amidino anions, are trans to each other, whereas in $Re_2(O_2CCH_3)_2Cl_4$ the bridging groups are cis to each other.[14] In the present case steric considerations alone would strongly favor the trans arrangement.

Until now the Re-Re distance in $Re_2(O_2CPh)_2I_4$, 2.198 (1) Å, was the shortest one on record, but the parent compound in the present study supersedes this with a distance of 2.177 (2) Å. Possibly the main factor in accounting for this difference is the smaller van der Waals radius of Cl, which causes less opposition to closer approach of the Re atoms. The parent molecule, like every other complex of Re_2^{6+} so far described, occupies a position of crystallographic symmetry that imposes an eclipsed rotational configuration.

The structure of the solvate, both in itself and in comparison with that of the parent, exhibits three important features.

(1) The Re-Re bond is longer, by 0.032 (6) Å, than that in the parent. Whether this is a direct or an indirect result of binding a THF ligand to Re(1) is impossible to say. It is known in the case of $Mo_2(O_2CCF_3)_4$ vs. $Mo_2(O_2CCF_3)_4(py)_2$[15] that a similar lengthening, 0.039 (6) Å, occurs. In this case, there is a coaxial ligand added at each end but more weakly (Mo-N = 2.55 Å) and the rest of the structure is

Table VII. Unweighted Least-Squares Planes

Plane	Atoms defining plane	Equation of mean plane[a]
I	Re(2)-Re(1)-Cl(11)	$2.465X - 10.28Y + 10.427Z = 4.066$
II	Re(1)-Re(2)-Cl(21)	$3.751X - 10.341Y + 10.410Z = 4.379$
III	Re(2)-Re(1)-Cl(12)	$2.552X - 10.294Y + 10.430Z = 4.089$
IV	Re(1)-Re(2)-Cl(22)	$3.750X - 10.341Y + 10.410Z = 4.379$
V	Re(2)-Re(1)-N(1)	$11.890X - 1.560Y + 0.932Z = 3.231$
VI	Re(1)-Re(2)-N(3)	$11.570X - 0.563Y - 0.079Z = 2.836$
VII	Re(2)-Re(1)-N(2)	$11.779X - 1.403Y + 0.772Z = 3.170$
VIII	Re(1)-Re(2)-N(4)	$11.493X - 0.312Y - 0.332Z = 2.733$

Planes	Angle, deg	Planes		Planes	Angle, deg	Planes	Angle, deg
I–II	6.8	III–II	6.4	V–VI	5.2	VII–VI	4.4
I–IV	6.8	III–IV	6.4	V–VIII	6.5	VII–VIII	5.7

[a] Equations have the form $AX + BY + CZ = D$ where X, Y, and Z are fractional coordinates.

essentially unaltered. Hence, the effect of the coaxial ligands can be regarded as direct and the order of magnitude to be expected for a direct effect is established. In the present case, the magnitude of the change is similar, but there are also changes in the Re(2)–Re(1)–Cl angles in such a direction as to increase internal repulsion. Thus, it could be argued that perhaps the presence of THF in the coaxial site lengthens the Re–Re bond at least partly by an indirect mechanism: to make room for itself it pushes the Cl atoms on Re(1) closer to those on Re(2) thus causing increased Cl···Cl repulsions which might stretch the Re–Re bond.

(2) The coordination about the two nonequivalent rhenium atoms differs. Around Re(1), to which the THF is bound, the Re–Cl distances are longer by about 0.045 (6) Å than those at Re(2). There also appears to be a slight lengthening of the Re(1)–N bonds compared to the Re(2)–N bonds, but it is too small to be unequivocal in view of the uncertainties. Also, as already noted under point (1), the Re(2)–Re(1)–Cl angles are considerably reduced, to an average of 99°, while the Re(1)–Re(2)–Cl angles remain at values (108.2, 108.9°) similar to all of those in the parent compound. It thus appears that the coordination of THF to Re(1) causes rearrangement toward a more nearly octahedral geometry and effectively increases the bond radius of Re(1).

(3) The solvate has a rotational conformation which is twisted approximately 6° (Table VII) from the precisely eclipsed configuration found in the parent. It has been pointed out long ago,[1] as one of the principal indications of the importance of the δ bond, that this bond has its maximum strength in the eclipsed configuration and vanishes in a completely staggered conformation. It should be stressed that the presence of the δ bond does not require that the conformation of any given molecule be rigorously eclipsed; since there are forces of repulsion tending to oppose eclipsing, the energy minimum might only be near but not exactly at the eclipsed conformation. In most previous crystal structures, the crystallographic inversion center produced a strictly eclipsed structure; in short, intermolecular forces combined with the rotational dependence inherent in the δ–δ overlap to favor the fully eclipsed structure. In the solvate studied here, the molecule lies in an environment which lacks any element of symmetry, and the net balance of all forces results in a slight deviation from the perfectly eclipsed conformation.

Acknowledgment. We are grateful to the National Science Foundation for support under Grant No. 33142X and to Drs. T. R. Webb and B. A. Frenz for many helpful discussions.

Registry No. $Re_2(N_2CPh_3)_2Cl_4$, 55043-73-7; $Re_2(N_2CPh_3)_2Cl_4(THF)\cdot 0.63CHCl_3$, 55043-72-6; $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$, 14023-10-0.

Supplementary Material Available. Tables of observed and calculated structure factors for both structures will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40846Q-9-75.

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