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Some Reactions of the Octahalodirhenate(III) Ions. 11. Two New Quadruply Bonded Dirhenium Amidinato-Bridged Complexes[†]

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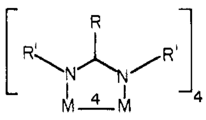
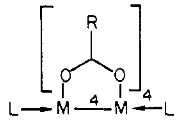
The preparation, mass spectra, and structures of the compounds $Re_2[(PhN)_2CCH_3]_2Cl_4$, **1**, and $Re_2[(CH_3N)_2CPh]_4Cl_2{\cdot}CCl_4$, **2**, are reported. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions of a = 14.774 (4) Å, b = 12.008 (4) Å, c = 16.990 (5) Å, β = 92.78°, V = 3002 (3) Å^3, and Z = 4. The molecules occupy general positions within the cell and have a rotational conformation that is twisted ~3.8° from the perfectly eclipsed conformation. The Re–Re bond length is 2.178 (1) Å, and the Re–Cl and Re–N distances are 2.314 (7) (average) and 2.06 (2) Å (average), respectively. Compound **2** crystallizes in the tetragonal space group $I4/mmm$ with unit cell parameters of $a = b$ = 14.235 (2) Å, c = 12.199 (2) Å, V = 2472 (1) Å^3, and Z = 4. The Re–Re and Re–Cl bond lengths are 2.208 (2) and 2.654 (6) Å, respectively. The structure of **1** is very similar to that previously found for $Re_2[(PhN)_2CPh]_2Cl_4$, as would be expected. Compound **2** is of interest because the methyl groups keep the axial Cl^- ligands at a greater distance than for the $Re_2(O_2CR)_4Cl_2$ compounds (R = Ph, CMe_3) which have Re–Cl ≈ 2.48 Å. The Re–Re distance in **2** is significantly shorter (by 0.027 Å) than in the carboxylato compounds, thus showing again the influence of axial ligands in weakening M–M quadruple bonds as well as the ability of the N and N′ substituents in amidinato, triazinato, and amidato ligands to restrict access to the axial positions.

Introduction

In the course of recent investigations[1,2] on the role of axial interactions in quadruply bonded dimetal compounds we have become increasingly aware of their influence on metal–metal bond lengths. We have, therefore, renewed our efforts to prepare amidinato-bridged compounds, a, because they stand in marked contrast to the corresponding carboxylato species, b, in that bulky substituents, R′, at the amidine nitrogen atoms can prevent axial coordination under certain circumstances. Whereas amidine complexes of dimolybdenum[3] and dirhenium[4] have been prepared and characterized structurally several years ago, only recently have investigations led to the crystallographic study of a dichromium species[2] and a partially substituted ditungsten compound.[5]

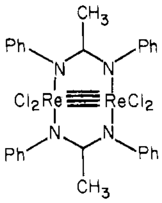


a



b

Since tetrachlorobis(N,N'-diphenylbenzamidinato)dirhenium[4] was found to contain the shortest known Re–Re bond, 2.177 (2) Å, and because recent studies[6,7] on $Re_2Cl_n(piv)_{6-n}$ [n = 2, 3, 4; piv = $(CH_3)_3CCO_2^-$] have exhibited a distinct rearrangement and substitution sequence, we have examined the reaction of $Re_2Cl_8^{2-}$ with two different amidines, N,N'-diphenylacetamidine and N,N'-dimethylbenzamidine. The former ligand reacts to give compound **1**, the structure of which is reported here. N,N'-Dimethylbenzamidine also forms a Re_2Cl_4(amidinato)$_2$ compound, as established by mass spectroscopy. However, the only crystals obtained from the reaction mixture were recognized by structure determination to be those of dichlorotetrakis(N,N'-dimethylbenzamidinato)dirhenium, **2**.



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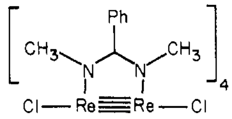

2

Experimental Section

The preparations of the starting materials $(n\text{-}Bu_4N)_2Re_2Cl_8$,[8] N,N'-diphenylacetamidine, $PhNC(CH_3)NHPh$,[5] and N,N'-dimethylbenzamidine, $CH_3NC(Ph)NHCH_3$,[2] have been reported earlier.

The mass spectra were taken on a CEC 21-110B high-resolution instrument at the Center for Trace Characterization, Texas A&M University; the measurements were performed by Dr. R. D. Grigsby and Mr. G. M. Gable. Dr M. W. Extine kindly supplied the computer program used to calculate isotope distribution patterns.

Tetrachlorobis(N,N'-diphenylacetamidinato)dirhenium, 1. A finely ground mixture of 0.11 g (0.1 mmol) of tetrabutylammonium octachlorodirhenate and 0.13 g (0.6 mmol) of N,N'-diphenylacetamidine, mp 131 °C, was heated to 140 °C in an atmosphere of dry argon. After 1 h the melt was allowed to cool, and the dark red solid was ground and extracted with CCl_4 to remove excess amidine. The residue was then dissolved in chloroform to give a red solution with a blue surface shine. Slow evaporation of this solution in air yielded red crystals of sufficient quality for X-ray diffraction.

A mass spectrum (324 °C, 10^{-6} torr) showed multiplets, having the appropriate isotope patterns of Re_2Cl_n species, at the following values of m/e (relative intensity): 932 (100, M^+), 897 (4.7), 466 (11.4, M^{2+}), 448.5 (6.7). Under high resolution the most intense parent ion peak gave an m/e value of 931.993 168; the mass calculated for the principal isotopic species of $C_{28}H_{26}N_4Cl_4Re_2$ is 931.997 148.

Tetrachlorobis(N,N'-dimethylbenzamidinato)dirhenium and Dichlorotetrakis(N,N'-dimethylbenzamidinato)dirhenium, 2. A similar procedure was employed in the reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with $CH_3NC(C_6H_5)NHCH_3$, but because of the lower melting point (81 °C) and the higher volatility of this amidine, the reaction temperature was kept at or below 110 °C. This time a brown residue remained after extraction with CCl_4, a preliminary mass spectrum (280 °C, 10^{-6} torr) showed the presence of the Re_2Cl_4(amidinato)$_2$ species at

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[†] For part 10, see ref 7.

(1) Bino, A.; Cotton, F. A.; Kaim, W. *J. Am. Chem. Soc.* **1979**, *101*, 2506.
(2) Bino, A.; Cotton, F. A.; Kaim, W. *Inorg. Chem.* **1979**, *18*, 3566.
(3) Cotton, F. A.; Inglis, T.; Kilner, M.; Webb, T. R. *Inorg. Chem.* **1975**, *14*, 2023.
(4) Cotton, F. A.; Shive, L. W. *Inorg. Chem.* **1975**, *14*, 2027.
(5) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *Inorg. Chem.* **1979**, *18*, 3569.
(6) Cotton, F. A.; Gage, L. D.; Rice, C. E. *Inorg. Chem.* **1979**, *18*, 1138.
(7) Collins, D. M.; Cotton, F. A.; Gage, L. D. *Inorg. Chem.* **1979**, *18*, 1712
(8) Cotton, F. A.; Curtis, N. F.; Robinson, W. R. *Inorg. Chem.* **1965**, *4*, 1696.

0020-1669/80/1319-2360$01.00/0

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Re_2[(PhN)_2CCH_3]_2Cl_4$ (1)[a]

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re(1)	0.26574 (5)	0.20951 (8)	0.08213 (4)	1.90 (3)	3.41 (4)	1.77 (3)	−0.29 (4)	0.40 (3)	−0.13 (4)
Re(2)	0.39594 (5)	0.22200 (8)	0.14755 (4)	1.76 (3)	3.78 (4)	1.87 (3)	0.03 (4)	0.41 (3)	0.06 (4)
Cl(1)	0.2110 (4)	0.3894 (5)	0.0724 (3)	3.4 (2)	3.9 (3)	3.3 (2)	0.4 (2)	0.9 (2)	0.6 (2)
Cl(2)	0.2438 (5)	0.0228 (5)	0.0529 (4)	6.8 (3)	3.9 (3)	4.9 (3)	−1.5 (3)	2.8 (2)	−1.4 (3)
Cl(3)	0.4150 (4)	0.4059 (5)	0.1839 (3)	4.3 (3)	4.8 (3)	3.5 (2)	−1.7 (3)	0.8 (2)	−0.6 (2)
Cl(4)	0.4582 (4)	0.0443 (5)	0.1500 (4)	5.2 (3)	5.1 (3)	4.3 (3)	1.8 (3)	2.0 (2)	1.3 (3)
N(1)	0.327 (1)	0.227 (1)	−0.0250 (9)	2.1 (6)	4.3 (8)	1.5 (6)	0.2 (7)	0.3 (5)	−0.5 (7)
N(2)	0.462 (1)	0.254 (1)	0.0441 (9)	3.3 (8)	3.1 (9)	1.9 (7)	−0.1 (7)	0.4 (6)	0.8 (6)
N(3)	0.198 (1)	0.192 (1)	0.1823 (8)	1.9 (6)	2.4 (8)	1.7 (6)	−0.7 (6)	0.7 (5)	0.2 (6)
N(4)	0.335 (1)	0.196 (1)	0.2537 (9)	1.8 (6)	2.5 (8)	2.9 (7)	0.6 (6)	0.3 (6)	−0.1 (6)
C(2)	0.462 (1)	0.275 (2)	−0.102 (1)	4 (1)	7 (1)	1.4 (7)	0 (1)	1.2 (7)	1 (1)
C(3)	0.276 (1)	0.205 (2)	−0.098 (1)	2.9 (9)	8 (2)	1.8 (8)	−1 (1)	0.7 (7)	1 (1)
C(4)	0.209 (1)	0.282 (3)	−0.123 (1)	2.0 (8)	10 (2)	4 (1)	0 (1)	−0.6 (8)	−2 (1)
C(5)	0.157 (2)	0.257 (4)	−0.196 (1)	4 (1)	21 (4)	3 (1)	2 (2)	−0 (1)	−3 (2)
C(6)	0.178 (2)	0.159 (3)	−0.235 (1)	5 (1)	11 (2)	1.1 (9)	−2 (1)	−0.2 (9)	−0 (1)
C(7)	0.244 (2)	0.085 (3)	−0.210 (1)	8 (2)	12 (2)	2 (1)	−5 (2)	1 (1)	−2 (1)
C(8)	0.295 (2)	0.105 (2)	−0.136 (1)	6 (1)	5 (1)	3 (1)	−3 (1)	2.0 (9)	0.4 (9)
C(9)	0.556 (1)	0.283 (2)	0.047 (1)	0.7 (7)	2.9 (9)	3.4 (8)	−0.4 (8)	0.6 (6)	0.0 (9)
C(10)	0.581 (1)	0.394 (2)	0.054 (1)	2.5 (9)	8 (1)	2.1 (9)	−2 (1)	−0.7 (8)	1 (1)
C(11)	0.672 (1)	0.431 (2)	0.054 (1)	2.8 (9)	4 (1)	4 (1)	1 (1)	−0.3 (8)	−0 (1)
C(12)	0.736 (1)	0.348 (2)	0.048 (1)	4 (1)	6 (1)	1.5 (8)	−3 (1)	−0.4 (8)	0.6 (9)
C(13)	0.711 (1)	0.234 (2)	0.043 (1)	2.5 (8)	7 (1)	2.9 (9)	3 (1)	0.2 (8)	1 (1)
C(14)	0.621 (1)	0.201 (2)	0.043 (1)	1.7 (8)	6 (1)	2.5 (8)	0.3 (9)	−0.2 (7)	−1 (1)
C(15)	0.243 (1)	0.192 (1)	0.255 (1)	2.3 (8)	1.6 (9)	2.5 (8)	−0.4 (7)	−0.4 (7)	0.6 (7)
C(16)	0.198 (1)	0.176 (2)	0.333 (1)	2.8 (9)	6 (1)	3 (1)	−1 (1)	0.7 (8)	−0 (1)
C(17)	0.097 (1)	0.194 (2)	0.182 (1)	2.9 (8)	3 (1)	1.8 (7)	1.4 (8)	1.7 (6)	0.4 (8)
C(18)	0.061 (1)	0.298 (2)	0.205 (1)	2.5 (8)	4 (1)	2.1 (8)	1.7 (9)	0.9 (7)	−0.3 (9)
C(19)	−0.036 (1)	0.303 (2)	0.201 (1)	3.2 (9)	7 (1)	1.6 (8)	1 (1)	0.1 (8)	1 (1)
C(20)	−0.090 (2)	0.211 (3)	0.178 (1)	4 (1)	11 (2)	3 (1)	1 (1)	−1.6 (9)	1 (1)
C(21)	−0.047 (1)	0.109 (2)	0.156 (1)	2.6 (9)	7 (2)	4 (1)	−1 (1)	−0.5 (8)	1 (1)
C(22)	0.051 (2)	0.103 (2)	0.155 (1)	5 (1)	5 (1)	2.2 (9)	−1 (1)	−1.2 (9)	−1 (1)
C(24)	0.389 (1)	0.298 (2)	0.369 (1)	4 (1)	5 (1)	1.8 (8)	−1 (1)	0.0 (8)	−0.9 (9)
C(25)	0.442 (2)	0.299 (3)	0.445 (1)	4 (1)	9 (2)	2.4 (9)	−1 (1)	0.5 (9)	0 (1)
C(26)	0.495 (1)	0.208 (2)	0.469 (1)	2.1 (9)	9 (2)	2.6 (9)	−0 (1)	−0.4 (8)	−0 (1)
C(27)	0.490 (2)	0.112 (2)	0.423 (2)	3 (1)	9 (2)	6 (1)	−0 (1)	−0 (1)	5 (1)
C(28)	0.440 (1)	0.105 (2)	0.350 (1)	4 (1)	4 (1)	5 (1)	1 (1)	−1 (1)	3 (1)

atom	*x*	*y*	*z*	*B*, Å	atom	*x*	*y*	*z*	*B*, Å
C(1)	0.413 (1)	0.249 (2)	−0.026 (1)	2.7 (4)	C(23)	0.390 (1)	0.196 (2)	0.326 (1)	2.2 (4)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

m/e ~808 with its characteristic isotope pattern (Figure 3). This mass spectrum also displayed some small multiplets at higher mass, up to m/e ~1040.

Slow evaporation of a solution of this brown material in CCl_4/$CHCl_3$ (2:1) gave air-stable orange crystals, which were recognized as the dichlorotetrakis(amidinato) species by X-ray structure determination. These crystals were found to contain CCl_4 molecules, also.

A mass spectral study of these crystals gave the following results. At lower temperatures the loss of solvent molecules was observed; the dominating peak at m/e 117 (CCl_3^+) proved that it is CCl_4, and not $CHCl_3$. Higher masses were not observed until a probe temperature of 360 °C had been reached. The final spectrum displayed the following multiplets: m/e (relative intensity) 1032 (6.0, M^+), 995 (100), 979 (25), 885 (32), 867 (6.4), 849 (12), 703 (8.8), 516 (13, M^{2+}), 487.5 (2.8), 481 (3.6), 425 (4.8).

X-ray Crystallographic Study. Suitable crystals of each compound were secured to the ends of thin glass fibers and mounted on a Syntex P$\bar{1}$ automatic diffractometer. Lattice constants were obtained by carefully centering 15 reflections in the range 20° < 2θ < 32° selected to give varied crystal orientations. The procedures preliminary to data collection have been described previously.[9]

Intensity data were collected by using Mo Kα (λ = 0.710 73 Å) radiation monochromatized in the incident beam with a graphite crystal. Data were collected in the range 0° < 2θ ≤ 45° at 22 ± 4 °C by using the θ–2θ scan technique. Variable scan rates, 4–24°/min, were used with a scan range of Kα_1 − 1.0° to Kα_2 + 1.0° and a scan to background time ratio of 2. The intensities of three standard reflections, measured after every 97 reflections as a check on crystal and electronic stability, remained constant within experimental error. The usual Lorentz and polarization corrections were applied as well as standard empirical absorption corrections, based on ψ scans at χ = 90°. The positions of the Re atoms were found by solution of the three-dimensional Patterson functions.[10] The remaining nonhydrogen atoms were found from successive Fourier and difference syntheses. Full-matrix least-squares refinement yielded the crystallographic parameters shown in Tables I and II. The final discrepancy indices are defined by the expressions

$$R_1 = (\sum||F_o| - |F_c||)/\sum w|F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$$

The function $\sum w(|F_o| - |F_c|)^2$ was minimized with the weighting factor, w, equal to $4F_o^2/\sigma(F_o^2)^2$. Atomic scattering factors were those of Cromer and Waber.[11] Anomalous dispersion effects were also included for the rhenium atoms.[12]

Results and Discussion

Preparation and Mass Spectroscopic Analysis. Under the conditions employed (140 °C) $Re_2C_8^{2-}$ reacts with PhNC(CH$_3$)NHPh to yield only one detectable species, compound **1**, which crystallizes readily from $CHCl_3$. This compound exhibits the type of mass spectrum that is typical for quadruply

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(9) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

(10) Calculations were performed by using the Molecular Structure Corp. PDP-11/45 computer and the Enraf-Nonius structure determination package with programs written chiefly by Frenz and Okaya.

(11) Cromer, D. T.; Waber, J. T. "International Tables of X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(12) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Re_2[(CH_3N)_2CPh]_4Cl{\cdot}CCl_4$ (**2**)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re(1)	0.5000 (0)	0.5000 (0)	0.0905 (1)	3.56 (6)	3	2.22 (4)	0	0	0
Cl(1)	0.5000 (0)	0.5000 (0)	0.3081 (6)	4.8 (6)	7	2.9 (3)	0	0	0
Cl(2)	0.419 (1)	0.060 (1)	0.174 (1)	16.9 (6)					
N(1)	0.398 (1)	0.3979 (0)	0.0924 (9)	3.9 (7)	5	2.7 (5)	−1.0 (6)	0.1 (7)	0

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	0.364 (2)	0.364 (0)	0.000 (0)	4.0 (5)	C(5)	0.150 (3)	0.150 (0)	0.000 (0)	6.3 (7)
C(2)	0.287 (3)	0.287 (0)	0.000 (0)	4.3 (5)	C(6)	0.358 (3)	0.358 (0)	0.201 (2)	9.6 (8)
C(3)	0.196 (2)	0.309 (2)	0.039 (2)	5.5 (6)	C(7)	0.500 (0)	0.000 (0)	0.250 (0)	8.6 (13)
C(4)	0.131 (0)	0.236 (0)	0.030 (2)	8.5 (9)					

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Bond Distances (Å) for $Re_2[(PhN)_2CCH_3]_2Cl_4$ (**1**)

Re(1)–Re(2)	2.178 (1)	C(6)–C(7)	1.38 (4)
–Cl(1)	2.310 (6)	C(7)–C(8)	1.45 (4)
–Cl(2)	2.316 (7)	C(9)–C(10)	1.39 (3)
–N(1)	2.08 (2)	–C(14)	1.38 (3)
–N(3)	2.02 (1)	C(10)–C(11)	1.42 (3)
Re(2)–Cl(3)	2.306 (7)	C(11)–C(12)	1.38 (3)
–Cl(4)	2.324 (6)	C(12)–C(13)	1.42 (4)
–N(2)	2.08 (2)	C(13)–C(14)	1.39 (3)
–N(4)	2.07 (2)	C(15)–C(16)	1.51 (3)
N(1)–C(1)	1.31 (1)	C(17)–C(18)	1.42 (3)
–C(3)	1.43 (3)	–C(22)	1.35 (3)
N(2)–C(1)	1.36 (3)	C(18)–C(19)	1.43 (3)
–C(9)	1.43 (2)	C(19)–C(20)	1.41 (4)
N(3)–C(15)	1.37 (2)	C(20)–C(21)	1.43 (4)
–C(17)	1.50 (2)	C(21)–C(22)	1.45 (3)
N(4)–C(15)	1.36 (2)	C(23)–C(24)	1.43 (3)
–C(23)	1.43 (2)	–C(28)	1.37 (3)
C(1)–C(2)	1.53 (3)	C(24)–C(25)	1.48 (3)
C(3)–C(4)	1.40 (4)	C(25)–C(26)	1.39 (4)
–C(8)	1.41 (4)	C(26)–C(27)	1.39 (4)
C(4)–C(5)	1.46 (4)	C(27)–C(28)	1.42 (4)
C(5)–C(6)	1.39 (5)		

Table IV. Bond Angles (Deg) for $Re_2[(PhN)_2CCH_3]_2Cl_4$ (**1**)

Re(2)–Re(1)–Cl(1)	105.6 (2)	C(2)–C(1)–N(2)	118.5 (20)
–Cl(2)	106.7 (2)	N(1)–C(3)–C(4)	118.2 (25)
–N(1)	91.6 (4)	–C(8)	116.8 (24)
–N(3)	92.3 (4)	C(4)–C(3)–C(8)	124.9 (25)
Cl(1)–Re(1)–Cl(2)	147.7 (2)	C(3)–C(4)–C(5)	117.9 (29)
–N(1)	90.4 (5)	C(4)–C(5)–C(6)	116.4 (30)
–N(3)	88.4 (5)	C(5)–C(6)–C(7)	125.8 (26)
Cl(2)–Re(1)–N(1)	88.6 (5)	C(6)–C(7)–C(8)	119 (3)
–N(3)	90.5 (5)	N(2)–C(9)–C(10)	119 (2)
N(1)–Re(1)–N(3)	176.1 (6)	–C(14)	120 (2)
Re(1)–Re(2)–Cl(3)	107.2 (2)	C(10)–C(9)–C(14)	121 (2)
–Cl(4)	106.6 (2)	C(9)–C(10)–C(11)	122.7 (24)
–N(2)	91.3 (5)	C(10)–C(11)–C(12)	115.9 (23)
–N(4)	91.2 (4)	C(11)–C(12)–C(13)	121.2 (21)
Cl(3)–Re(2)–Cl(4)	146.2 (2)	C(12)–C(13)–C(14)	121.7 (22)
–N(2)	89.6 (5)	N(3)–C(15)–C(16)	124.7 (19)
–N(4)	88.1 (5)	–N(4)	115.2 (18)
Cl(4)–Re(2)–N(2)	89.0 (5)	C(16)–C(15)–N(4)	120 (2)
–N(4)	91.8 (5)	N(3)–C(17)–C(18)	113.3 (20)
N(2)–Re(2)–N(4)	177.0 (7)	–C(22)	118.2 (19)
Re(1)–N(1)–C(1)	119.8 (14)	C(18)–C(17)–C(22)	128.3 (22)
–C(3)	119.9 (13)	C(17)–C(18)–C(19)	114.2 (23)
C(1)–N(1)–C(3)	120.0 (17)	C(18)–C(19)–C(20)	122.1 (25)
Re(2)–N(2)–C(1)	118.6 (14)	C(19)–C(20)–C(21)	119.5 (24)
–C(9)	120.4 (13)	C(20)–C(21)–C(22)	119.8 (26)
C(1)–N(2)–C(9)	120.9 (17)	N(4)–C(23)–C(24)	114.9 (18)
R(1)–N(3)–C(15)	121.1 (13)	–C(28)	121.4 (20)
–C(17)	122.4 (12)	C(24)–C(23)–C(28)	123.8 (21)
C(15)–N(3)–C(17)	116.1 (16)	C(23)–C(24)–C(25)	115.6 (24)
Re(2)–N(4)–C(15)	119.7 (14)	C(24)–C(25)–C(26)	121.0 (25)
–C(23)	119.4 (13)	C(25)–C(26)–C(27)	118.6 (22)
C(15)–N(4)–C(23)	120.4 (17)	C(26)–C(27)–C(28)	123.0 (26)
N(1)–C(1)–C(2)	123 (2)		
–N(2)	118.5 (20)		

bonded metal–metal dimers. It consists of an intense parent ion 1+ peak and also a molecular dication peak but only a few, weak fragment ions.

The reaction between $Re_2Cl_8^{2-}$ and $CH_3NC(Ph)NHCH_3$ had to be carried out at lower temperature (~110 °C) because of the volatility of the amidine, and, as a result, a mixture of products was obtained. The presence of the disubstituted species $Re_2Cl_4[CH_3NC(Ph)NCH_3]_2$ was established by a mass spectrum of the reaction mixture at a medium temperature (280 °C). This species *does not* appear in the mass spectrometer by way of decomposition from $Re_2Cl_2[CH_3NC(Ph)NCH_3]_4$, **2**, as might be suspected by analogy with the decomposition of $Re_2(piv)_4Cl_2$,[6] since compound **2** does not exhibit any signals at m/e ~808 in its mass spectrum.

Dichlorotetrakis(*N,N′*-dimethylbenzamidinato)dirhenium, **2**, crystallizes from the reaction mixture with CCl_4 molecules included in the crystal lattice. The complex is much less soluble than the $Re_2Cl_4L_2$ species; after evaporation of the CCl_4 molecules a probe temperature of 360 °C is necessary to obtain the mass spectrum. The spectrum itself is quite unusual. The parent ion multiplet is small, and there is extensive fragmentation; the major peaks correspond to the loss of Cl or an amidinato ligand. This observation may be taken as an indication that there is some strain in the molecule, and the structure analysis makes it evident that this strain is a result of steric repulsions between the Cl atoms and the methyl groups.

Structures. The observed and calculated structure factor amplitudes for both compounds, expressed as $10|F_o|$ and $10|F_c|$, are available as supplementary material. Atomic positional and thermal parameters for $Re_2[(PhN)_2CCH_3]_2Cl_4$, **1**, and $Re_2[(CH_3N)_2CPh]_4Cl_2$, **2**, are listed in Tables I and II, respectively. Figures 1 and 2 show the molecular structures and

Table V. Bond Distances (Å) for $Re_2[(CH_3N)_2CPh]_4Cl_2{\cdot}CCl_4$ (**2**)

Re(1)–Re(1)′	2.208 (2)	C(3)–C(3)′	0.94 (3)
–Cl(1)	2.654 (6)	–C(3)″	2.27 (3)
–N(1)	2.055 (9)	–C(4)	1.40 (2)
N(1)–C(1)	1.32 (1)	C(4)–C(4)′	0.74 (5)
–C(6)	1.54 (2)	–C(4)″	2.10 (1)
C(1)–C(2)	1.56 (2)	–C(4)‴	2.23 (2)
C(2)–C(3)	1.41 (3)	–C(5)	1.30 (1)
–C(3)′	1.41 (3)		
–C(3)″	1.41 (2)		
–C(3)‴	1.41 (2)		

Table VI. Bond Angles (Deg) for $Re_2[(CH_3N)_2CPh]_4Cl_2{\cdot}CCl_4$ (**2**)

Re(1)′–Re(1)–Cl(1)	180.00 (0)[a]	C(3)–C(2)–C(3)′	39 (1)
–N(1)	90.7 (2)	–C(3)″	107 (2)
Re(1)–N(1)–C(1)	120.4 (9)	–C(3)‴	121 (2)
–C(6)	118 (1)	C(2)–C(3)–C(4)	114 (1)
N(1)–C(1)–C(2)	121.0 (8)	C(3)–C(4)–C(5)	125 (2)
C(1)–C(2)–C(3)	119 (1)	C(4)–C(5)–C(4)′	33 (2)
–C(3)′	119 (1)	–C(4)″	108 (2)
–C(3)″	119 (2)	–C(4)‴	118 (2)
–C(3)‴	119 (2)		

[a] Required by crystallographic symmetry.

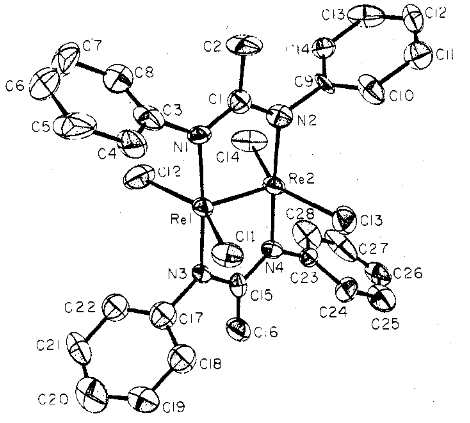

Figure 1. Molecular structure of $Re_2Cl_4[(PhN)_2CCH_3]_2$ (**1**). Each atom is represented by its ellipsoid or sphere of thermal vibration, scaled to enclose 40% of its electron density. The numbering scheme used in Tables I, III, IV, and VIII is defined.

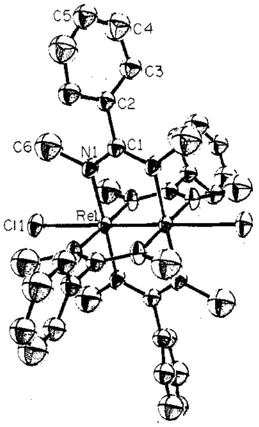

Figure 2. Molecular structure of the Re_2 complex in $Re_2[(MeN)_2CPh]_4Cl_2{\cdot}CCl_4$ (**2**). Each atom is represented by its ellipsoid or sphere of thermal vibration, scaled to enclose 40% of its electron density. The numbering scheme used in Tables II, V, and VI is defined.

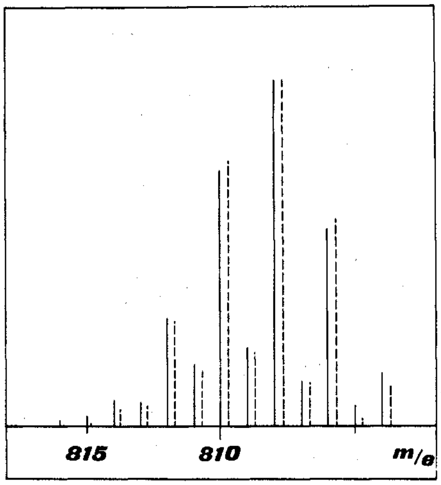

Figure 3. Parent ion multiplet in the mass spectrum of $Re_2Cl_4[(CH_3N)_2CPh]_2$. Full lines represent observed components, and broken lines give the calculated relative intensities on the basis of the known isotopic abundances for the elements present.

atomic labeling schemes for the two compounds. Bond distances and angles for **1** and **2** are presented in Tables III–VI Crystallographic parameters are summarized in Table VII.

The structure of **1** was solved in the monoclinic space group $P2_1/n$. Each molecule occupies a general position within the cell, and the molecules have no crystallographically imposed symmetry. The structure is very similar to that of the analogous iodide benzoate $Re_2(O_2CPh)_2I_4$[13] and the amidinato complex $Re_2[(PhN)_2CPh]_2Cl_4$.[4] In both of these compounds, as well as in **1**, the bridging groups adopt the transoid configuration; that is, there is a planar Re_2Cl_4 unit with the bridging ligands above and below this plane. The phenyl rings are rotated so that they are nearly perpendicular to the Re–N–C_{br} planes; the average of the four dihedral angles is 102°. In a manner similar to that observed in $Re_2[(PhN)_2CPh]_2Cl_4{\cdot}THF$,[4] compound **1** also has a rotational conformation that is twisted from the fully eclipsed conformation. The twist here is ca. 3.8° (see Table VIII) in contrast to the 6° twist in $Re_2[(PhN)_2CPh]_2Cl_4{\cdot}THF$.[4] The Re–Re

Table VII. Crystallographic Parameters

parameter	compd 1	compd 2
space group	$P2_1/n$	$I4/mmm$
a, Å	14.774 (4)	14.235 (2)
b, Å	12.008 (4)	14.235 (2)
c, Å	16.990 (5)	12.199 (2)
$\alpha = \gamma$, deg	90	90
β, deg	92.78	90
V, Å^3	3002 (3)	2472 (1)
Z	4	4
formula wt	932.76	1081.86
cryst size, mm	0.10 × 0.15 × 0.30	0.30 × 0.35 × 0.30
μ, cm^{-1}	88.91	110.28
2θ range, deg	0–45	0–45
no. data	3030	
$F_o^2 > 3\sigma(F_o^2)$	2159	432
no. of variables	333	36
R_1	0.044	0.049
R_2	0.054	0.068
esd	1.038	2.009
d_x, g/cm^3 (calcd)	2.063	2.907

Table VIII. Equations of Planes, P_i, of the form $AX + BY + CZ = D$ and Dihedral Angles for $Re_2[(PhN)_2CCH_3]_2Cl_4$ (1)

Equations of Planes

plane	atoms	A	B	C	D
P_1	Re(1), Re(2), N(2)	0.1510	−0.9810	−0.1220	−2.0550
P_2	Re(1), Re(2), Cl(3)	0.4903	0.1815	−0.8525	1.1636
P_3	Re(1), Re(2), N(4)	0.1374	−0.9856	−0.0985	−2.0863
P_4	Re(1), Re(2), Cl(4)	0.4883	0.1938	−0.8509	1.1893
P_5	Re(2), Re(1), N(1)	0.1129	−0.9920	−0.0562	−2.1382
P_6	Re(2), Re(1), Cl(2)	0.4984	0.1225	−0.8582	1.0386
P_7	Re(2), Re(1), N(3)	0.1109	−0.9924	−0.0528	−2.1422
P_8	Re(2), Re(1), C(1)	0.4988	0.1198	−0.8584	1.0327
P_9	Re(1), N(1), C(1)	0.1991	−0.9799	−0.0077	−1.7076
P_{10}	C(3), C(4), C(5), C(6), C(7), C(8)	0.7031	0.4914	−0.5140	4.9722
P_{11}	Re(2), N(2), C(1)	0.2210	−0.9722	−0.0777	−1.5195
P_{12}	C(9), C(10), C(11), C(12), C(13), C(14)	−0.0212	0.0730	−0.9971	−0.7381
P_{13}	Re(1), N(3), C(15)	0.1074	−0.9927	−0.0551	−2.1596
P_{14}	C(17), C(18), C(19), C(20), C(21), C(22)	0.0454	0.3204	−0.9462	−2.0991
P_{15}	Re(2), N(4), C(15)	0.0315	−0.9871	−0.1569	−2.8430
P_{16}	C(23), C(24), C(25), C(26), C(27), C(28)	0.8071	0.3345	−0.4866	2.5407

Dihedral Angles (P_i/P_j)

P_i/P_j	angle, deg	P_i/P_j	angle, deg
P_1/P_5	4.4	P_9P_{10}	109.7
P_2/P_8	3.6	P_{11}/P_{12}	89.9
P_3/P_7	3.0	P_{13}/P_{14}	105.1
P_4/P_6	4.1	P_{15}/P_{16}	103.2

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(13) Bratton, W. K.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 1299.

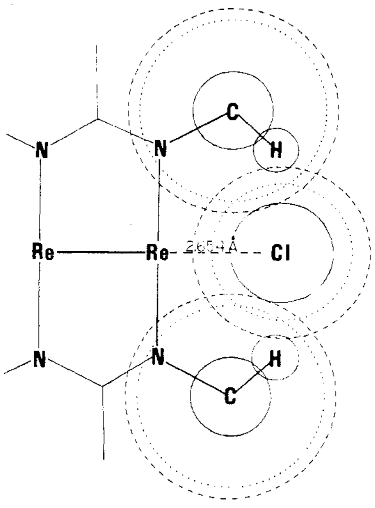

Figure 4. Scale diagram of the nonbonded contacts for the axial chlorine atoms in **2**. The full and dashed circles represent covalent and van der Waals radii and the dotted circles the average of the two.

bond length, 2.178 (2) Å, is essentially identical with that found in $Re_2[(PhN)_2CPh]_2Cl_4$,[4] 2.177 (2) Å. The average Re–Cl and Re–N distances, 2.314 (7) and 2.06 (2) Å, respectively, are also identical. Since the remaining distances and corresponding angles are essentially analogous to those found in $Re_2[(PhN)_2CPh]_2Cl_4 \cdot THF$, they will not be discussed.

The structure of **2** was solved in the tetragonal space group $I4/mmm$. All atoms except the ortho and meta carbon atoms of the phenyl rings reside on special positions within the cell. The phenyl group is disordered so that it appears to be rotated both to the right and to the left of the mirror plane that is perpendicular to the M–M bond and passes through C(1), C(2), and C(5). The dihedral angle between the two apparent ring planes is 39°.

The CCl_4 molecule occupies a position of $\bar{4}m2$ symmetry and is also disordered. The geometry about the central carbon atom, for a unique molecule, is essentially tetragonal, with an average Cl–C–Cl angle of 110°.

The Re–Re bond length, 2.208 (2) Å, is slightly longer (0.03 Å) than that in **1**. This lengthening of the bond in going from the bis to the tetrakis compound is analogous to that observed in the pivalato series where there is a difference of 0.025 Å.[6,7] The Re–Re distance is virtually identical with those found in $Re_2(hp)_4Cl_2$,[14] 2.206 (2) Å, $Re_2(O_2CCMe_3)_2Cl_4$,[6] 2.209 (2) Å, and $Re_2[(PhN)_2CPh]_2Cl_4 \cdot THF$,[4] 2.209 (1) Å. It is interesting to note that in all of these compounds there is some kind of axial interaction. In the carboxylate series, where axial interactions are also a predominant feature, the tetrakis compounds, $Re_2(O_2CCMe_3)_4Cl_2$,[7] $Re_2(O_2CCMe_3)_4Br_2$,[7] and $Re_2(O_2CPh)_4Cl_2$,[15] all have substantially longer, 2.234–2.236 Å, bond lengths than the corresponding bis compounds, $Re_2(O_2CCMe_3)Cl_4$,[6] $Re_2(O_2CPh)_2I_4$,[13] and $Re_2(O_2CCH_3)_2Cl_4$,[16] which have bond lengths of approximately 2.20 Å. It is uncertain at this time whether the occurrence of these axial interactions is the predominant factor contributing to the lengthening of the Re–Re bond, but there seems little doubt that they do have an impact on the bond length.

The Re–Cl distance, 2.654 (6) Å, is unusually long; longer even than in $Re_2(O_2CPh)_4Cl_2$ (2.489 (5) Å)[15] or $Re_2(O_2CMe_3)_4Cl_2$[7] (2.477 (3) Å). It is also longer than the 2.545 (7)-Å Re–Cl distance in $Re_2(hp)_4Cl_2$[14] (hp = 2-hydroxypyridine anion). The only comparable distances have been found in $Re_2(O_2CCMe_3)_3Cl_3$,[6] where the Re–Cl bridging distances are 2.632 (10) and 2.680 (8) Å, respectively, and in $Re_2Cl_5[(Ph_2P)_2CCH_2]_2 \cdot 2PhMe$,[17] which has a Re–Cl distance of 2.575 (6) Å for the axial chlorine atom. The weakness of the Re–Cl bond in **2** was already suggested by the mass spectroscopic analysis.

The rather long Re–Cl bond observed in this instance is a result of repulsions between the Cl atom and the four surrounding methyl groups. The Cl–C(methyl) distance is 3.137 Å, which is considerably less than the sum of the van der Waals radii, 3.7 Å. Figure 4 is a "to-scale" drawing showing the relationship between the methyl groups and the chlorine atom. The broken circles (- - -) in the figure represent the van der Waals contact distances for the methyl groups and chlorine atoms. It can be seen that the van der Waals spheres for the methyl groups and the chlorine atom overlap considerably, even at the actual Re–Cl distance of 2.654 Å. This might lead to the expectation that the methyl groups would bend away from the region of approach of the chlorine atom, but this does not, in fact, occur to any significant extent since the Re–N–C angles are about 118°. As we have noted before,[2] such a bending is probably impossible because the methyl groups are already making rather close contacts with the phenyl groups on the central carbon atoms. Thus, any tendency of the Re–Cl bonds to become as short as they are in the $Re_2(O_2CR)_4Cl_2$ case (ca. 2.48 Å) is tempered by the repulsions that are introduced by the presence of the methyl groups.

Also shown in Figure 4 are solid circles representing the covalent radii of the atoms. It is interesting to note that the dotted circles, which have radii halfway between those of the van der Waals and covalent circles, only slightly overlap. Thus, these averages of the two radii seem to be approximate, empirical "contact radii", appropriate to the type of problem at hand.

The structure of **2** is similar to that of $Cr_2[(MeN)_2CPh]_4$, which crystallizes from THF/hexane solution without any axially coordinated THF molecules. With use of the "contact radii" empirically derived for **2**, it appears that this is an understandable result. We must note first that because of the shorter M–M distance in the chromium compound, the methyl groups are bent in even closer to the axial ligand positions. With use of the same contact radii and considering also the repulsions arising from the CH_2 groups of the THF, it appears that the oxygen atom of a THF molecule could not approach more closely than perhaps 3.5 Å to the chromium atom, whereas in the case of many Cr_2 complexes where axial ligands are present, e.g., the carboxylates,[18] the distances are typically 2.25–2.35 Å. It is not unreasonable that, when the accessibility is so restricted that an approach distance of no better than ~3.5 Å is possible, there is too little bond energy to make axial bonding thermodynamically feasible. This is particularly true when, in contrast to the case with compound **2** where we have cation–anion attraction, the M_2 unit and the ligand are both neutral.

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Supplementary Material Available: Tables of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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(14) Cotton, F. A.; Gage, L. D. *Inorg. Chem.* **1979**, *18*, 1716.

(15) Bennett, M. J.; Bratton, W. K.; Cotton, F. A.; Robinson, W. R. *Inorg. Chem.* **1968**, *7*, 1570.

(16) Koz'min, P. A.; Surazhskaya, M. D.; Kuznetsov, V. G. *Zh. Strukt. Khim.* **1970**, *11*, 313.

(17) Cotton, F. A.; Shive, L. W.; Stults, B. R. *Inorg. Chem.* **1976**, *15*, 2239.

(18) Cotton, F. A.; Extine, M.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 176.