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Contribution from the Department of Chemistry,
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Studies of Metal–Nitrogen Multiple Bonds. IV. The Crystal and Molecular Structure of Trichloro(methylimino)bis(diphenylethylphosphine)rhenium(V)

By DAVID BRIGHT and JAMES A. IBERS

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The crystal structure of the alkylimino rhenium(V) complex trichloro(methylimino)bis(diphenylethylphosphine)rhenium(V), $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$, has been determined from three-dimensional X-ray data collected by counter methods and refined using least-squares techniques to a final R factor of 4.8% on F for the 2209 independent reflections above background. The material crystallizes in a monoclinic cell of dimensions a = 12.64 (3) Å, b = 17.85 (4) Å, c = 13.72 (3) Å, β = 101.30 (3)°, and space group C_{2h}^5-$P2_1/n$. The density of 1.64 g/cm³ calculated for four formula units in the unit cell agrees well with the observed density of 1.63 ± 0.01 g/cm³. The coordination about the Re atom is distorted octahedral, with the phosphine ligands *trans* to one another, and Cl atoms *trans* to one another in the basal plane and with the third Cl at the one vertex and the methylimino group (coordinated to the Re atom *via* the N atom) at the other. The Re–P distances are 2.482 (7) and 2.486 (7) Å, the Re–Cl distances in the basal plane are 2.408 (6) and 2.428 (6) Å, and the Re–Cl distance *trans* to the N atom is 2.411 (6) Å. The Re–N distance is 1.685 (11) Å and the Re–N–CH_3 angle is close to linearity at 173°. The molecule as a whole is very similar to the aryliminorhenium complexes reported earlier.

Introduction

Recently the preparation of a series of arylimino complexes of Re(V) of the general formula $ReCl_3(NC_6H_4X)(P(C_2H_5)_2C_6H_5)_2$, where X is *para* to the N atom on the arylimino ring, was reported by Chatt, Garforth, Johnson, and Rowe.[1] The observation that the dipole moments of the compounds in this series increase with increasing electron-releasing power of the group X led Chatt, *et al.*, to suggest that the formal Re–N double bond in these compounds has considerable triple-bond character and furthermore that the triple character of the bond should increase as the electron-releasing power of the group X increases.

In order to test this hypothesis, we recently determined and reported[2] the crystal structures of a compound from each end of the dipole moment range—one containing the strongly electron-releasing methoxy group, $ReCl_3(NC_6H_4OCH_3)(P(C_2H_5)_2C_6H_5)_2$, μ = 7.2 D, and one containing the strongly electron-withdrawing acetyl group, $ReCl_3(NC_6H_4COCH_3)(P(C_2H_5)_2C_6H_5)_2$, μ = 4.5 D. We found that the Re–N–Ar angle (Ar = aryl) is very close to linearity in both compounds (175.81 (8)° in the methoxy compound and 171.8 (4)° in the acetyl compound) consistent with a high degree of triple-bond character. However, in spite of the considerable change in electron distribution indicated by the dipole moment change, the difference in the Re–N bond lengths in the two compounds is only possibly significant. Moreover, if the change in bond length is real, it is in the direction opposite to that expected; *i.e.*, the Re–N bond in the methoxy compound, 1.709 (4) Å, is possibly longer than that in the acetyl compound, 1.690 (5) Å.

A methylimino analog of these compounds, $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$, has recently been prepared by the action of dimethylhydrazine dihydrochloride on oxotrichlorobis(triphenylphosphine)rhenium(V) followed by phosphine exchange.[3] Clearly the mesomeric and steric properties of an alkyl group should be rather different from those of an aryl group, and a structural analysis of this compound was undertaken to detect a possible change in the Re–N bond length. It was hoped that the magnitude and direction of any change would assist in our understanding of metal–nitrogen multiple bonds, in general, and of rhenium–nitrogen double bonds, in particular. The results of the structural analysis are reported here.

Collection and Reduction of the Intensity Data

Crystals of $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$ were kindly supplied by Dr. J. R. Dilworth and Professor J.

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(1) J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 1012 (1964).

(2) D. Bright and J. A. Ibers, *Inorg. Chem.*, 7, 1099 (1968).

(3) J. Chatt, J. R. Dilworth, and G. J. Leigh, private communication.

Chatt. Preliminary investigation of the blue needle-shaped crystals showed that their diffraction symmetry is 2/m.

From optical goniometry, the faces developed on the sides of the needles were identified as {100} and {110}. However, the faces at the ends of the needles could not be assigned indices in this manner as these faces were too small to give optical signals. The lattice constants at 22° were determined from a least-squares refinement of the setting angles of 11 strong X-ray reflections that had been carefully centered on a Picker automatic four-circle diffractometer[4] using Mo $K\alpha_1$ radiation (λ 0.70930 Å). The results are $a = 12.64$ (3) Å, $b = 17.85$ (4) Å, $c = 13.72$ (3) Å, and $\cos\beta = -0.1961$ (5). The systematic absences observed on precession and Weissenberg photographs of the material are $0k0$ for k odd and $h0l$ for $h + l$ odd. These extinctions are consistent only with space group $C_{2h}{}^5$-$P2_1/n$. The density calculated for four molecules per unit cell is 1.64 g/cm^3. This agrees well with the density 1.63 ± 0.01 g/cm^3 measured by suspending the crystals in aqueous potassium chloride. Thus no symmetry need be imposed on the molecule.

The intensity data were collected as previously described,[4] using a crystal with approximate dimensions 0.04 × 0.04 × 0.4 mm. This crystal was mounted on the diffractometer with the needle direction (c) almost coincident with the ϕ rotation axis. Since c is not a symmetry direction, this orientation does not increase the probability of multiple diffraction effects.

For the data collection Mo $K\alpha$ radiation was used, and the diffracted beams were filtered through 3 mils of Zr foil. The intensities were measured by the θ–2θ technique at a takeoff angle of 1.3°. At this angle the intensity of a reflection was about 80% of its maximum value as a function of takeoff angle.

A counter aperture 5 mm square was used, and the aperture was placed 35 cm from the crystal. A nonsymmetric scan range in 2θ was used, from -0.65 to 0.75 from the $K\alpha_1$ peak. Stationary counter–stationary crystal background counts of 10 sec were initially taken at each end of the scan. The scan rate was 1°/min. As a check on the stability of both the crystal and the electronic equipment, four reflections were measured every 12 hr throughout the data collection period. These reflections showed no significant change in intensity during this time.

Intensity data were collected for the unique hkl planes of the monoclinic form. After 1000 reflections had been measured, it became apparent that most of the reflections were rather weak, and to improve the signal-to-noise ratio of the peaks, the background counting times were increased to 20 sec for the remainder of the run. Data collection was terminated at $2\theta(\text{Mo } K\alpha_1) = 41°$ since beyond this angle very few reflections had significant intensity.

The data were then processed in the manner described previously.[4] After initial correction for background, the standard deviation of the corrected intensity I was calculated from the expression

$$\sigma(I) = (\text{CT} + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2)^{1/2}$$

where CT is the total integrated count obtained in time t_c, B_1 and B_2 are the background counts each obtained in time t_b, and $I = \text{CT} - 0.5(t_c/t_b)(B_1 + B_2)$. The value of p was initially taken as 0.06.

The intensities were next corrected for Lorentz and polarization factors. Transmission factors were then calculated for a set of reflections which would have been expected to show widely differing attenuation due to absorption. Based on a linear absorption coefficient of 41.16 cm^{-1}, the transmission factors for these reflections were found to vary very little, from 0.77 to 0.83. Since this variation was so small, no absorption correction was applied. Of the 3078 reflections collected 2209 were found to have $I \geq 3\sigma(I)$. These reflections will be referred to as being above background.

Solution and Refinement of the Structure

In the least-squares refinements the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and $w = 1/\sigma^2(F_o)$. The standard deviation of F_o, $\sigma(F_o)$, was taken as $\sigma(F_o{}^2)/2F_o$. The agreement factors R_1 and R_2 are defined as $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $R_2 = \Sigma(w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2)^{1/2}$.

The scattering factors used for P, Cl, N, and C were from the usual tabulation[5] and those for Re were by Cromer and Waber.[6] The hydrogen scattering factors were those of Stewart, *et al.*[7]

The effects of anomalous scattering were included in the structure factor calculations.[8] The values of $\Delta f'$ and $\Delta f''$ were those given by Cromer.[9]

The Re atom was readily located by inspection of the three-dimensional Patterson function,[10] and successive Fourier syntheses and least-squares refinements served to locate the remaining nonhydrogen atoms in the structure. The four independent phenyl rings were refined as planar rigid groups (D_{6h} symmetry, C–C = 1.390 Å), in the manner described previously.[11]

With all nonhydrogen atoms included with isotropic thermal parameters, the values of the agreement factors were $R_1 = 6.9\%$ and $R_2 = 7.8\%$. Refinement of anisotropic thermal parameters for the Re, P, and Cl atoms led to $R_1 = 5.4\%$ and $R_2 = 6.2\%$, and refinement of anisotropic parameters for all of the nonhydrogen, nongroup atoms gave $R_1 = 4.9\%$ and $R_2 = 5.6\%$. Both

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[4] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[5] J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

[6] D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[8] J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

[9] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[10] The programs used in this work were PICK and PICKOUT, for generating and processing the data, NUCLS, the group-refinement program, and local modifications of Zalkin's FORDAP Fourier summation program, the Busing-Levy ORFFE error function program, and Johnson's ORTEP thermal ellipsoid plotting program.

[11] S. J. La Placa and J. A. Ibers, *Acta Cryst.*, **18**, 511 (1965).

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS × 10) FOR $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$

K	L	FO	FC
**** H = 0 *****			
0	2	4986	5046
0	4	2341	2259
0	6	3128	3125
0	8	2187	2243
0	10	1740	1393
0	12	1604	1666
1	2	648	626
1	3	541	529
1	4	560	485
1	6	422	327
1	8	497	461
1	9	349	232
1	10	456	343
2	0	3892	3575
2	1	2838	2811
2	2	3063	3124
2	4	2001	1977
2	5	1725	1714
2	6	2724	2694
2	7	1647	1643
2	8	1795	1784
2	9	977	936
2	10	1030	1029
2	11	713	731
2	12	1149	1123
2	13	769	760
3	1	997	946
3	2	306	316
3	3	944	975
3	5	962	985
3	8	317	354
3	9	389	385
3	11	379	359
4	0	1143	1101
4	1	2807	2743
4	2	664	647

K	L	FO	FC
3	-4	901	868
3	-3	2276	2206
3	-2	899	891
3	-1	2557	2449
3	0	1224	1174
3	1	2128	2062
3	2	432	487
3	3	2407	2402
3	4	2055	2105
3	5	1811	1838
3	6	1328	1334
3	7	1609	1621
3	9	1203	1201
3	10	366	347
3	11	933	927
3	12	497	535
4	-12	977	923
4	-11	506	474
4	-10	1029	1024
4	-9	1312	1340
4	-7	509	477
4	-6	2057	2079
4	-5	597	603
4	-4	2564	2554
4	-3	249	141
4	-2	1458	1443
4	-1	338	376
4	0	871	831
4	1	1376	1329
4	2	1092	1078
4	4	1377	1310
4	5	939	880
4	6	927	882
4	7	523	494
4	8	789	753
4	9	537	552
4	10	473	513
4	12	306	177
5	-11	884	841

TABLE II

FINAL PARAMETERS FOR $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	0.11318(5)[b]	0.05597(4)	0.24638(4)	0.00535(5)	0.00250(2)	0.00334(4)	-0.00035(4)	0.00104(3)	-0.00013(4)
Cl_1	0.1145(3)	0.1745(2)	0.3307(3)	0.0081(4)	0.0025(2)	0.0073(3)	-0.0004(2)	0.0013(3)	-0.0013(2)
Cl_2	0.1329(3)	-0.0033(2)	0.4065(3)	0.0079(4)	0.0036(2)	0.0038(2)	0.0005(2)	0.0013(2)	0.0008(2)
Cl_3	0.0949(3)	0.1301(3)	0.0957(3)	0.0064(3)	0.0050(2)	0.0047(3)	-0.0002(2)	0.0012(2)	0.0017(2)
P_1	0.3116(3)	0.0746(2)	0.2780(3)	0.0052(3)	0.0026(2)	0.0046(3)	-0.0001(2)	0.0008(2)	-0.0003(2)
P_2	-0.0834(3)	0.0503(2)	0.2463(3)	0.0060(4)	0.0022(1)	0.0036(2)	-0.0003(2)	0.0014(2)	-0.0001(2)
N	0.1150(8)	-0.0224(6)	0.1783(7)	0.0050(10)	0.0034(5)	0.0015(7)	-0.0003(5)	0.0013(7)	-0.0013(5)
Me[c]	0.1182(13)	-0.0820(10)	0.1130(12)	0.0070(15)	0.0054(9)	0.0075(13)	0.0041(9)	0.0018(11)	-0.0023(9)
Et_1C_1	0.3647(12)	0.1036(10)	0.4036(12)	0.0049(13)	0.0052(8)	0.0077(13)	0.0014(9)	-0.0003(11)	-0.0007(9)
Et_1C_2	0.4851(16)	0.1152(12)	0.4304(14)	0.0114(21)	0.0079(12)	0.0094(17)	-0.0004(13)	-0.0019(15)	-0.0028(12)
Et_2C_1	-0.1181(13)	0.0961(8)	0.3531(11)	0.0073(15)	0.0032(6)	0.0049(11)	-0.0004(8)	0.0036(10)	-0.0003(7)
Et_2C_2	-0.2370(14)	0.0932(9)	0.3626(11)	0.0088(16)	0.0038(7)	0.0057(12)	0.0010(9)	0.0010(11)	0.0006(8)

Group	x_c[d]	y_c	z_c	δ	ϵ	η	B_1[e]	B_2	B_3	B_4	B_5	B_6
Ph_{11}	0.3763(5)	0.1958(4)	0.1287(6)	3.134(10)	2.364(7)	-1.766(9)	3.4(3)	4.4(4)	6.8(5)	6.9(5)	7.7(5)	5.8(4)
Ph_{12}	0.4479(5)	-0.0776(4)	0.2670(4)	2.191(6)	-2.672(6)	0.122(6)	3.1(3)	4.3(4)	5.4(4)	4.7(4)	4.8(4)	3.5(3)
Ph_{21}	-0.2526(5)	0.1292(4)	0.0701(5)	-0.654(6)	3.093(6)	0.628(6)	3.3(3)	4.2(3)	5.5(4)	5.1(4)	4.4(4)	3.9(3)
Ph_{22}	-0.1450(5)	-0.1229(4)	0.2556(5)	-0.202(7)	2.522(6)	-1.585(8)	3.0(3)	4.2(4)	5.4(4)	5.3(4)	5.4(4)	4.1(4)

[a] The form of the anisotropic thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses here and in subsequent tables are estimated standard deviations in the least significant digits. [c] Me is the CH_3 group attached to the N atom, Et_1C_2 is carbon 2 of ethyl group 1 attached to P_1. Ph_{11} and Ph_{12} are the phenyl groups attached to P_1. [d] The angles δ, ϵ, and η (in radians) which bring about alignment (except for translation) of an internal coordinate system within the group with a fixed external system have been defined in previous papers.[11] [e] B_i is the isotropic thermal parameter of atom i. The rings are numbered such that atom 1 is attached to phosphorus.

of these changes in the agreement factors are, according to Hamilton's R factor ratio test,[12] highly significant.

The phenyl and methylene hydrogen atoms were next included in the structure as fixed contributions to F_c in positions calculated from the well-known stereochemistry of such groups. The H–C–H angle in the methylene groups was taken to be 109.47°, and for both the phenyl and methylene groups the C–H distance was set at 0.9 Å. This C–H distance is short compared with the value of 1.1 Å frequently reported for C–H distances derived from spectroscopic data, but it is well-known that light-atom–hydrogen distances in structures determined by X-ray diffraction are often abnormally short compared with the spectroscopic values. The reasons for this are the subjects of some discussion.[13] However, for the determination of the structure of a rhenium compound closely related to the present structure, we were fortunate in having a highly accurate set of data,[2] and we found that in this structure inclusion of the hydrogen atoms at 0.9 Å from the carbon atoms gave slightly better agreement between observed and calculated structure amplitudes than inclusion of the hydrogens with C–H = 1.1 Å. In accordance with this experience we again used the shorter distance in the present structure, although the quality of the present data is probably not sufficiently high to show any detectable difference from a model with C–H = 1.1 Å.

A difference Fourier synthesis was next calculated using only those planes for which $(\sin \theta)/\lambda$ was less than 0.35 Å^{-1}. The synthesis showed peaks around the three independent methyl groups in the structure and for the phosphine ethyl CH_3 groups. These peaks could be interpreted as the CH_3 hydrogen atoms lying in a staggered orientation with respect to the methylene hydrogens. The assignment of peaks to the CH_3 group attached to the nitrogen atom was less certain. However, after inclusion of the ethyl hydrogen atoms in the structure, the nitrogen methyl hydrogen atoms were included in positions consistent with the crystal packing and the observed electron density. The inclusion of these 33 hydrogen atoms reduced the values of the agreement factors to $R_1 = 4.8\%$ and $R_2 = 5.4\%$.

An inspection of the data revealed no evidence that a correction for secondary extinction was necessary.

At this stage the value of the estimated standard deviation of an observation of unit weight was 1.07 electrons. Since the theoretical value of this quantity is 1.00, this suggests that the absolute weighting scheme is correct. However, a good test of the validity of a weighting scheme is that the contribution to $\Sigma w(|F_o| - |F_o|)^2$ should be reasonably constant for all classes of reflection, and an inspection of the data showed that this was not so. The strong reflections were greatly underweighted. To correct this, the value

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(12) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

(13) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968.

TABLE III

DERIVED PARAMETERS FOR GROUP CARBON ATOMS IN $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$

	x	y	z
		Ph_{11}	
C_1	0.3540 (13)[a]	0.1424 (6)	0.1955 (7)
C_2	0.3646 (12)	0.1210 (5)	0.1005 (8)
C_3	0.3869 (8)	0.1745 (7)	0.0336 (6)
C_4	0.3985 (14)	0.2493 (6)	0.0618 (9)
C_5	0.3879 (13)	0.2706 (5)	0.1569 (10)
C_6	0.3656 (8)	0.2172 (6)	0.2237 (6)
		Ph_{12}	
C_1	0.3881 (8)	−0.0123 (4)	0.2671 (7)
C_2	0.4885 (8)	−0.0100 (4)	0.2400 (7)
C_3	0.5482 (6)	−0.0753 (6)	0.2400 (8)
C_4	0.5076 (9)	−0.1430 (5)	0.2668 (8)
C_5	0.4073 (9)	−0.1453 (4)	0.2940 (7)
C_6	0.3475 (6)	−0.0799 (5)	0.2941 (7)
		Ph_{21}	
C_1	−0.1786 (7)	0.0926 (5)	0.1429 (6)
C_2	−0.2747 (8)	0.0574 (4)	0.1001 (7)
C_3	−0.3486 (6)	0.0940 (6)	0.0273 (7)
C_4	−0.3266 (7)	0.1658 (6)	−0.0027 (7)
C_5	−0.2305 (9)	0.2009 (4)	0.0401 (7)
C_6	−0.1565 (6)	0.1643 (5)	0.1129 (7)
		Ph_{22}	
C_1	−0.1219 (10)	−0.0471 (4)	0.2501 (8)
C_2	−0.1304 (11)	−0.0788 (6)	0.3407 (6)
C_3	−0.1536 (8)	−0.1546 (6)	0.3463 (6)
C_4	−0.1681 (11)	−0.1987 (4)	0.2612 (9)
C_5	−0.1597 (11)	−0.1669 (6)	0.1705 (7)
C_6	−0.1364 (7)	−0.0911 (6)	0.1650 (6)

[a] The estimated standard deviations are derived from those of the group parameters and are meant to be used in error analyses on inter-ring distances. Intra-ring distances, of course, are fixed (C–C = 1.390 Å).

of p in the expression for $\sigma(I)$ (see previous section) was changed to 0.03. A cycle with this weighting scheme gave residuals $R_1 = 4.8\%$ and $R_2 = 4.5\%$, and the standard deviation of an observation of unit weight now calculated as 1.23 electrons. The contributions to the least-squares residual were now reasonably constant for all classes of reflection, based on $|F_o|$, scattering angle, and Miller indices, suggesting that the amended weighting scheme is a reasonable one.

No parameter shifted by more than 1.5 times its estimated standard deviation upon this change of weights. The final values of $|F_o|$ and $|F_c|$ (in electrons × 10) are listed in Table I. Table II lists the final values of the least-squares parameters together with their standard deviations, and Table III lists the atomic coordinates of the group atoms derived from the least-squares parameters.

Results

The structure consists of well-separated molecules of $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$. Excluding possible hydrogen contacts, the shortest intermolecular distance in the structure is 3.61 Å between Me and $Ph_{21}C_6$.

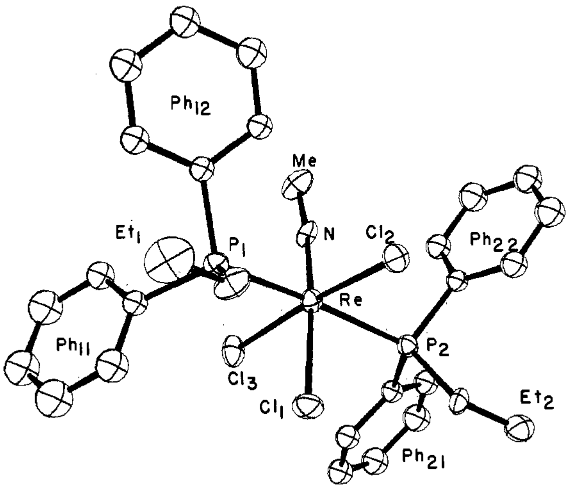

Figure 1.—A perspective drawing of the molecular structure of $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$.

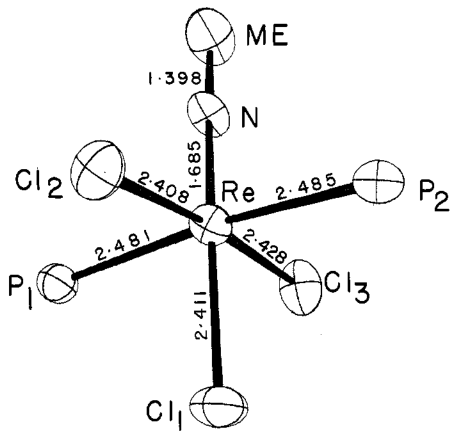

Figure 2.—A perspective drawing of the $ReCl_3(NCH_3)P_2$ portion of $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$.

The over-all molecular configuration is shown in Figure 1, and the $ReCl_3(NCH_3)P_2$ portion of the molecule, labeled with bond distances, is shown in Figure 2. Listings of selected interatomic distances and angles are given in Tables IV and V, respectively. As is usually found, the relative values of the bond lengths are not affected by the thermal motions of the atoms. For this molecule it is most reasonable to assume that the ligand atoms ride on the rhenium atom, and corrections to the bond lengths with this assumption[14] do not exceed twice the appropriate standard deviations.

The principal magnitudes of thermal vibration for the atoms that were refined anisotropically are listed in Table VI, and the directions of these vibrations can be seen, at least approximately, from the figures. With the exception of the nitrogen atom the anisotropy is small. The vibration envelope for the nitrogen atom is, however, very flat, indicating that this atom is apparently undergoing highly anisotropic motion, although a change in the minimum amplitude of only

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[14] W. R. Busing and H. A. Levy, *Acta Cryst.*, **17**, 142 (1964).

TABLE IV

SELECTED INTERATOMIC DISTANCES (Å) IN $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$

Re–N	1.685 (11)	Cl$_1$–N	4.091 (14)
Re–Cl$_1$	2.411 (6)	Cl$_1$–Cl$_2$	3.336 (9)
Re–Cl$_2$	2.408 (6)	Cl$_1$–Cl$_3$	3.282 (9)
Re–Cl$_3$	2.428 (6)	Cl$_1$–P$_1$	3.258 (8)
Re–P$_1$	2.482 (7)	Cl$_1$–P$_2$	3.373 (8)
Re–P$_2$	2.486 (7)	Cl$_2$–Cl$_3$	4.826 (11)
N–Me	1.398 (18)	Cl$_2$–P$_1$	3.421 (8)
P$_1$–Et$_1$C$_1$	1.799 (17)	Cl$_2$–P$_2$	3.296 (8)
P$_1$–Ph$_{11}$C$_1$	1.808 (14)	Cl$_3$–P$_1$	3.471 (8)
P$_1$–Ph$_{12}$C$_1$	1.849 (14)	Cl$_3$–P$_2$	3.634 (8)
P$_2$–Et$_2$C$_1$	1.805 (14)	Cl$_2$–N	3.114 (13)
P$_2$–Ph$_{21}$C$_1$	1.834 (15)	Cl$_3$–N	2.941 (13)
P$_2$–Ph$_{22}$C$_1$	1.808 (15)	P$_1$–N	3.116 (12)
Et$_1$C$_1$–Et$_1$C$_2$	1.508 (23)	P$_2$–N	3.123 (12)
Et$_2$C$_1$–Et$_2$C$_2$	1.534 (21)		

TABLE V

SELECTED INTERATOMIC ANGLES (IN DEG) FOR $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$

Re–N–Me	173.4 (10)	P$_2$–Re–N	95.0 (4)
Cl$_1$–Re–N	174.6 (4)	Re–P$_1$–Et$_1$C$_1$	112.3 (5)
Cl$_1$–Re–Cl$_2$	87.6 (2)	Re–P$_1$–Ph$_{11}$C$_1$	113.2 (4)
Cl$_1$–Re–Cl$_3$	85.4 (2)	Re–P$_1$–Ph$_{12}$C$_1$	113.6 (5)
Cl$_1$–Re–P$_1$	83.5 (1)	Re–P$_2$–Et$_2$C$_1$	112.5 (5)
Cl$_1$–Re–P$_2$	87.1 (1)	Re–P$_2$–Ph$_{21}$C$_1$	119.1 (4)
Cl$_2$–Re–N	97.5 (4)	Re–P$_2$–Ph$_{22}$C$_1$	108.3 (5)
Cl$_2$–Re–Cl$_3$	173.0 (1)	P$_1$–Et$_1$C$_1$–Et$_1$C$_2$	116.2 (13)
Cl$_2$–Re–P$_1$	88.8 (1)	P$_2$–Et$_2$C$_1$–Et$_2$C$_2$	116.9 (11)
Cl$_2$–Re–P$_2$	84.7 (1)	Et$_1$C$_1$–P$_1$–Ph$_{11}$C$_1$	107.9 (10)
Cl$_3$–Re–N	89.4 (4)	Et$_1$C$_1$–P$_1$–Ph$_{12}$C$_1$	102.5 (10)
Cl$_3$–Re–P$_1$	90.0 (1)	Ph$_{11}$C$_1$–P$_1$–Ph$_{12}$C$_1$	106.7 (9)
Cl$_3$–Re–P$_2$	95.4 (1)	Et$_2$C$_1$–P$_2$–Ph$_{21}$C$_1$	102.4 (11)
P$_1$–Re–N	94.9 (4)	Et$_2$C$_1$–P$_2$–Ph$_{22}$Cl	107.6 (9)
P$_1$–Re–P$_2$	168.7 (1)	Ph$_{21}$C$_1$–P$_2$–Ph$_{22}$C$_1$	106.2 (10)

TABLE VI

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION ALONG PRINCIPAL ELLIPSOID AXES (Å)

Atom	Min	Intermed	Max
Re	0.173 (1)	0.192 (1)	0.212 (1)
Cl$_1$	0.182 (7)	0.253 (6)	0.272 (6)
Cl$_2$	0.176 (7)	0.237 (6)	0.257 (6)
Cl$_3$	0.182 (7)	0.222 (6)	0.300 (6)
P$_1$	0.193 (7)	0.204 (6)	0.215 (6)
P$_2$	0.177 (7)	0.187 (7)	0.219 (7)
N	0.084 (37)	0.195 (19)	0.247 (17)
Me	0.208 (28)	0.240 (25)	0.329 (25)
Et$_1$C$_1$	0.179 (29)	0.259 (25)	0.314 (23)
Et$_1$C$_2$	0.224 (30)	0.333 (28)	0.394 (27)
Et$_2$C$_1$	0.156 (27)	0.223 (23)	0.265 (23)
Et$_2$C$_2$	0.214 (26)	0.244 (25)	0.278 (24)

TABLE VII

IMPORTANT DISTANCES AND ANGLES IN THE RHENIUM(V)–IMINO COMPLEXES: (A) $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$, (B) $ReCl_3(NC_6H_4OCH_3)(P(C_2H_5)_2C_6H_5)_2$, AND (C) $ReCl_3(NC_6H_4COCH_3)(P(C_2H_5)_2C_6H_5)_2$

	A	B	C
Re–N, Å	1.685 (11)	1.709 (4)	1.690 (5)
Re–Cl(*trans*),[a] Å	2.411 (6)	2.432 (2)	2.410 (3)
Re–Cl(*cis*),[a] Å	2.408 (6) 2.428 (6)	2.421 (1)	2.399 (3) 2.433 (3)
Re–P(*cis*),[a] Å	2.482 (7) 2.486 (7)	2.470 (1)	2.457 (4) 2.461 (4)
N–C, Å	1.40 (2)	1.37 (1)	1.38 (1)
Re–N–C, deg	173 (1)	175.8 (1)	171.8 (4)

[a] *cis* and *trans* in this table are used to indicate positions relative to the N atom.

two standard deviations would be sufficient to give the vibration envelope a more normal shape. The occurrence of a distorted ellipsoid in this structure is of interest as some workers have used the shape of the vibration ellipsoid as a method for distinguishing between different species of light atom, *e.g.*, between N and O[15] and between N and C.[16] Applying the arguments of these workers that the ellipsoid is contracted because, in the structure model, insufficient electron density is placed at the atom position, the N atom in the present structure could be taken to be an oxygen atom. However, the analytical data on this compound definitely show the presence of nitrogen, and since all of the atoms in the structure save the N atom and the atom attached to N are clearly identified either by stereochemistry or by peak heights, the assumption that the atom labeled N in our structure is in reality an oxygen atom means that the atom labeled Me must be the N atom. In other words we have a nitrosyl group attached to the rhenium atom *via* oxygen. This seems highly improbable particularly as there is no evidence in the infrared spectrum supporting such a structure. It seems far more likely that we do have a Re–N–CH_3 system and that the nitrogen appears flat owing to deficiencies in our data. However, this experience shows that caution should be exercised in distinguishing between species of atom by this method unless the data are of exceptionally high quality so that the vibrational ellipsoids are very well defined.

The over-all molecular structure is very similar to those of the aryliminorhenium(V) complexes previously described, and to facilitate comparison of the three compounds the important bond lengths and angles are listed in Table VII. As can be seen from this table, the bond lengths in the three compounds are very similar, and hence the comments made previously on these distances in the arylimino complexes[2] apply here as well.

In common with the arylimino complexes, and also with the related oxo complex,[17] $ReOCl_3(P(C_2H_5)_2C_6H_5)_2$, the major distortion from an ideal octahedral configuration about the rhenium atom is a movement of the ligands *cis* to the nitrogen atom away from this atom. This distortion appears to be due to steric effects and will be discussed in detail in the following paper.[18]

The N–CH_3 distance is 1.40 (2) Å. This, rather unexpectedly, agrees well with the distances 1.37 (1)

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and 1.38 (1) Å found for the corresponding distances in the arylimino complexes. One would expect a longer bond here since the radius of sp^3-hybridized carbon is larger than that of sp^2-hybridized carbon. It does, however, compare well with the distance 1.42 Å reported for the $N-CH_3$ bond in methyl isocyanide.[19]

The $Re-N-CH_3$ angle is close to linearity at 173 (1)°. This compares well with the corresponding angles in the arylimino complexes (see Table VII) and suggests that, as originally proposed by Chatt and coworkers,[1] the Re–N bond has considerable triple-bond character or at least confirms that the N atom is formally sp hybridized in the complexes so that its orbitals are in a suitable configuration for formation of a triple bond.

The Re–N distance in the present structure is 1.685 (11) Å. This bond length is very similar to those found in the other complexes and thus the Re–N bond length appears to be largely independent of the group attached to N. This observation, although surprising, is at least consistent with our previous findings that the Re–N bond length is unexpectedly insensitive to change of the *para* substituent on the arylimino ring. The bonding in this compound will be further discussed in the following paper[18] which describes the structure of the six-coordinate nitrido complex anion $OsNCl_5^{2-}$.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201

Studies of Metal–Nitrogen Multiple Bonds. V. The Crystal Structure of Potassium Nitridopentachloroosmate(VI), K_2OsNCl_5

BY DAVID BRIGHT AND JAMES A. IBERS

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The crystal structure of potassium nitridopentachloroosmate(VI), K_2OsNCl_5, has been determined from three-dimensional X-ray data collected by counter methods and has been refined by least-squares techniques to a final R factor, based on F, of 3.3% for the 687 reflections above background. The material crystallizes in space group D_{2h}^{16}-Pnma of the orthorhombic system in a cell with dimensions $a = 13.27$ (2) Å, $b = 9.85$ (1) Å, and $c = 6.84$ (1) Å. The density of 3.45 g/cm³ calculated for four formula units in the unit cell agrees with the observed density of 3.4 ± 0.1 g/cm³. The $OsNCl_5^{2-}$ ion is required crystallographically to possess m symmetry. The coordination about the Os atom is distorted octahedral. The Cl atoms *cis* to the nitrido ligand are bent away from the N atom. The Os–N distance is 1.614 (13) Å. The three independent Os–Cl distances *cis* to the N atom do not differ significantly from one another and average 2.362 (2) Å, but the Os–Cl distance *trans* to the N atom is considerably longer at 2.605 (4) Å. This contradicts the results from a previously reported structure of K_2OsNCl_5 in which the *trans* Os–Cl distance was reported to be much shorter than the *cis* distances. The results on a number of compounds with metal–nitrogen multiple bonding are intercompared and trends are rationalized in terms of nonbonded interactions.

Introduction

This is the fifth paper in a series that describes structural studies of compounds that contain metal–nitrogen multiple bonding. In previous papers the structures of five compounds of Re(V) have been reported: $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$,[1] $ReNCl_2(P(C_6H_5)_3)_2$,[2] $ReCl_3(NC_6H_4OCH_3)(P(C_2H_5)_2C_6H_5)_2$,[3] $ReCl_3(NC_6H_4COCH_3)(P(C_2H_5)_2C_6H_5)_2$,[3] and $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$.[4] The Re–N bond lengths in the latter four complexes are reasonably consistent with current theory; *i.e.*, the formal triple bond in the five-coordinate nitrido compound $ReNCl_2(P(C_6H_5)_3)_2$, 1.602 (9) Å, is shorter than the formal Re–N double bonds in the arylimino complexes $ReCl_3(NC_6H_4OCH_3)(P(C_2H_5)_2C_6H_5)_2$, 1.709 (4) Å, $ReCl_3(NC_6H_4COCH_3)(P(C_2H_5)_2C_6H_5)_2$, 1.690 (5) Å, and $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$, 1.685 (11) Å. In the six-coordinate nitrido complex $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$ the situation is different. The formal Re–N triple bond in this compound is 1.788 (11) Å, almost 0.2 Å longer than that in the related five-coordinate compound, and almost 0.1 Å longer than the formal double bonds in the arylimino complexes. Moreover, the Re–Cl bond which is *trans* to the N atom in this compound is considerably longer at 2.563 (4) Å than the Re–Cl bond *cis* to the N atom, 2.454 (4) Å. In the arylimino complexes the Re–Cl bond length

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