Inorg. Chem. **1984**, *23*, 159–164 **159**

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907,
and the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Synthesis and Structural Characterization of the Dirhenium Polyhydride Complex $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$

JOE D. ALLISON,[1a] F. A. COTTON,*[1b] GREGORY L. POWELL,[1b] and RICHARD A. WALTON*[1a]

Received May 3, 1983

In contrast to the very sluggish reaction between the dirhenium octahydride $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ and *tert*-butyl isocyanide, the corresponding paramagnetic salt $[Re_2(\mu\text{-}H)_4H_4(PPh_3)_4]PF_6$ reacts extremely rapidly to form the dirhenium pentahydride complex $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$. This complex has been structurally characterized by X-ray crystallography. It crystallizes in space group $P\bar{1}$, and the unit cell dimensions are a = 13.840 (3) Å, b = 23.951 (4) Å, c = 12.667 (3) Å, α = 96.10 (2)°, β = 111.80 (3)°, γ = 76.51 (2)°, V = 3790 (3) Å^3, and Z = 2. The molecule consists of two $ReH(PPh_3)_2(t\text{-}BuNC)$ halves joined by three bridging hydrogen atoms and a Re–Re bond (2.604 (1) Å). There is an approximate twofold axis of symmetry passing through one bridging hydrogen atom and bisecting the Re–Re bond. All hydrogen atoms except for those in the *tert*-butyl groups were included in the refined structure. ^1H and ^{31}P NMR spectroscopy shows that this basic structure is preserved in solution over the temperature range +35 to –70 °C. The bridging (H_b) and terminal (H_t) Re–H resonances are quite distinct (δ –5.60 (singlet) and δ –6.75 (triplet), respectively), with the Re–H_t triplet arising from coupling of the two terminal PPh_3 ligands on each rhenium to the single terminal hydride ligand attached to each.

Introduction

In the period since Bau et al.[2] first structurally characterized the so-called "agnohydrides" of rhenium $[ReH_x(PR_3)_2]_2$ (PR_3 = PPh_3 or a mixed alkyl-phenyl phosphine)[3] as the hydrido-bridged complexes $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$, dirhenium polyhydride complexes have attracted increasing interest. Not only has the bonding in the $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$ molecules prompted a theoretical investigation,[4] but new synthetic methods have been developed,[5] and various aspects of the chemical reactivity of these complexes have been explored, including their reactions with organic halides,[6] nitriles,[7] alkyl isocyanides,[7] and phosphite ligands.[8] Furthermore, the isolation and characterization of other dirhenium polyhydride species that are closely related electronically and structurally to $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$ have recently been accomplished.[8-10] Thus, several complexes of the type $Re_2(\mu\text{-}H)_3H_3(PR_3)_5$,[9,10] have been generated photochemically from mononuclear rhenium polyhydrides, whereas the mixed phosphine–phosphite complex $Re_2(\mu\text{-}H)_3H(PMe_2Ph)_4[P(OCH_2)_3CEt]_2$ can be prepared thermally from $Re_2H_8(PMe_2Ph)_4$.[8] This tetrahydride has been protonated to give its conjugated acid $[Re_2(\mu\text{-}H)_3H_2(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]^+$, a species which was structurally characterized as its BF_4^- salt.[8]

In the course of investigating ways of activating the relatively inert triphenylphosphine complex $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$,[7] we have been able to convert it to the dirhenium pentahydride complex $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$ following its prior oxidation to the paramagnetic salt $[Re_2(\mu\text{-}H)_4H_4(PPh_3)_4]PF_6$. The structural and spectroscopic characterization of this dirhenium pentahydride and its relationship to the species $[Re_2(\mu\text{-}H)_3H_2(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]^+$ serve as the focus of the present report.

Table I. Summary of Crystal Data, Data Collection Parameters, and Refinement Residuals for $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2](PF_6)$

formula	$[Re_2H_5[P(C_6H_5)_3]_4(C_4H_9NC)_2](PF_6)$; $Re_2P_5F_6N_2C_{82}H_{83}$
fw	1737.84
space group	$P\bar{1}$
a, Å	13.840 (3)
b, Å	23.951 (4)
c, Å	12.667 (3)
α, deg	96.10 (2)
β, deg	111.80 (3)
γ, deg	76.51 (2)
V, Å^3	3790 (3)
Z	2
d_{calcd}, g/cm^3	1.523
cryst size, mm	0.16 × 0.22 × 0.50
μ(Mo Kα), cm^{-1}	33.96
data collection instrument	CAD-4
radiation	Mo Kα (λ_α = 0.710 73 Å), graphite monochromated
scan method	2θ–ω
data collection range, deg	$5 \leqslant 2\theta \leqslant 50$
no. of unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	7225
no. of parameters refined	856
R^a	0.0413
$R_w{}^b$	0.0466
quality-of-fit indicator^c	1.131
largest shift/esd, final cycle	0.08

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)^2$, $\sigma(|F_o|)^2 = [\sigma_{count}{}^2(I) + (p|F_o|^2)^2]^{1/2}$, p = 0.05 for CAD-4. ^{c} Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

Experimental Section

Materials. All solvents and reagents were reagent grade. Solvents were dried and deoxygenated prior to use. The complex $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ was prepared with use of the method of Chatt and Coffey[3] whereby a suspension of $ReH_7(PPh_3)_2$ in ethanol was refluxed for 3 h. Its oxidation with a dichloromethane solution of $Ph_3C^+PF_6^-$ afforded $[Re_2H_8(PPh_3)_4]PF_6$.[7] *tert*-Butyl isocyanide was prepared with use of the procedure of Weber et al.[11]

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Table II. Table of Positional and Isotropic-Equivalent Thermal Parameters and Their Estimated Standard Deviations for $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2](PF_6)$[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^3
Re(1)	0.19847 (3)	0.22697 (2)	0.17807 (3)	2.012 (8)	C(J6)	−0.0059 (8)	0.3122 (5)	0.3890 (9)	4.2 (3)
Re(2)	0.27472 (3)	0.27365 (2)	0.37878 (3)	2.017 (8)	C(K1)	0.1721 (8)	0.4263 (5)	0.3694 (9)	3.3 (3)
P(1)	0.3041 (2)	0.2097 (1)	0.0632 (2)	2.52 (6)	C(K2)	0.165 (1)	0.4787 (5)	0.429 (1)	4.9 (3)
P(2)	0.0127 (2)	0.2386 (1)	0.0766 (2)	2.69 (6)	C(K3)	0.170 (1)	0.5272 (5)	0.384 (1)	6.3 (4)
P(3)	0.4073 (2)	0.2095 (1)	0.5156 (2)	2.36 (6)	C(K4)	0.181 (1)	0.5258 (5)	0.282 (1)	5.6 (4)
P(4)	0.1670 (2)	0.3599 (1)	0.4243 (2)	2.63 (6)	C(K5)	0.191 (1)	0.4750 (5)	0.224 (1)	6.8 (4)
H(1)	0.147 (6)	0.268 (3)	0.063 (6)	2 (2)*	C(K6)	0.188 (1)	0.4256 (5)	0.268 (1)	5.4 (4)
H(2)	0.239 (6)	0.270 (3)	0.476 (6)	3 (2)*	C(L1)	0.1887 (8)	0.3818 (4)	0.5739 (9)	3.4 (3)
H(3)	0.208 (6)	0.299 (4)	0.231 (6)	3 (2)*	C(L2)	0.109 (1)	0.3985 (6)	0.616 (1)	5.8 (4)
H(4)	0.157 (5)	0.233 (3)	0.299 (6)	1.1	C(L3)	0.131 (1)	0.4199 (7)	0.728 (1)	6.9 (4)
H(5)	0.324 (7)	0.224 (4)	0.300 (7)	4 (3)*	C(L4)	0.229 (1)	0.4247 (6)	0.795 (1)	6.7 (5)
N(1)	0.1957 (7)	0.0955 (4)	0.1451 (8)	4.1 (2)	C(L5)	0.310 (1)	0.4073 (7)	0.757 (1)	7.4 (5)
N(2)	0.4496 (7)	0.3475 (4)	0.4604 (8)	4.5 (3)	C(L6)	0.291 (1)	0.3850 (6)	0.646 (1)	6.0 (4)
C(1)	0.1953 (7)	0.1444 (4)	0.1510 (8)	2.8 (2)	P(5)	0.000	0.000	0.500	4.02 (9)*
C(11)	0.1987 (9)	0.0339 (5)	0.133 (1)	5.1 (4)	P(6)	0.500	0.500	0.000	7.1 (2)*
C(12)	0.303 (1)	0.0041 (6)	0.227 (1)	7.1 (5)	F(1)	−0.0043 (6)	0.0671 (4)	0.5151 (7)	7.4 (2)*
C(13)	0.201 (1)	0.0158 (6)	0.011 (1)	7.1 (4)	F(2)	−0.0996 (6)	0.0116 (4)	0.3878 (7)	7.5 (2)*
C(14)	0.098 (1)	0.0251 (6)	0.149 (1)	7.5 (4)	F(3)	0.0736 (6)	−0.0064 (4)	0.4263 (7)	7.7 (2)*
C(2)	0.3849 (8)	0.3203 (4)	0.4307 (8)	2.7 (3)	F(4)	0.4794 (7)	0.5633 (4)	0.0501 (8)	9.0 (3)*
C(21)	0.5308 (9)	0.3822 (5)	0.495 (1)	5.2 (4)	F(5)	0.5793 (8)	0.4785 (5)	0.1233 (8)	10.5 (3)*
C(22)	0.537 (1)	0.4075 (6)	0.617 (1)	6.8 (4)	F(6)	0.5959 (8)	0.5132 (5)	−0.0296 (8)	10.7 (3)*
C(23)	0.636 (1)	0.3412 (6)	0.497 (1)	7.3 (4)	H(A2)	0.4137	0.1242	0.2387	5
C(24)	0.497 (1)	0.4286 (6)	0.409 (1)	6.9 (5)	H(A3)	0.5556	0.0459	0.2729	6
C(A1)	0.4076 (7)	0.1434 (4)	0.0839 (8)	2.6 (2)	H(A4)	0.6350	0.0153	0.1359	7
C(A2)	0.4460 (8)	0.1127 (5)	0.1834 (8)	3.5 (3)	H(A5)	0.5727	0.0664	−0.0304	7
C(A3)	0.5302 (9)	0.0659 (5)	0.204 (1)	4.3 (3)	H(A6)	0.4283	0.1448	−0.0686	6
C(A4)	0.5777 (9)	0.0478 (5)	0.123 (1)	4.7 (3)	H(B2)	0.5301	0.2111	0.1317	5
C(A5)	0.5396 (9)	0.0781 (5)	0.024 (1)	4.9 (3)	H(B3)	0.6286	0.2802	0.1661	6
C(A6)	0.4543 (9)	0.1254 (5)	0.0012 (9)	4.2 (3)	H(B4)	0.5461	0.3772	0.1464	8
C(B1)	0.3851 (8)	0.2639 (5)	0.0903 (7)	3.0 (3)	H(B5)	0.3593	0.4026	0.0886	7
C(B2)	0.4946 (8)	0.2503 (5)	0.1231 (9)	3.4 (3)	H(B6)	0.2598	0.3332	0.0591	5
C(B3)	0.5534 (9)	0.2914 (5)	0.144 (1)	4.6 (3)	H(C2)	0.2375	0.2883	−0.1275	6
C(B4)	0.505 (1)	0.3486 (5)	0.132 (1)	5.6 (4)	H(C3)	0.1496	0.2790	−0.3243	9
C(B5)	0.3943 (9)	0.3634 (5)	0.098 (1)	4.9 (3)	H(C4)	0.0944	0.1971	−0.4044	9
C(B6)	0.3349 (8)	0.3222 (5)	0.0795 (9)	4.0 (3)	H(C5)	0.1255	0.1189	−0.2908	6
C(C1)	0.2372 (7)	0.2071 (5)	−0.0918 (7)	3.1 (3)	H(C6)	0.2097	0.1273	−0.0929	6
C(C2)	0.2162 (9)	0.2535 (6)	−0.1599 (9)	4.5 (3)	H(D2)	0.0525	0.1840	0.2883	5
C(C3)	0.1630 (9)	0.2478 (6)	−0.277 (1)	5.9 (4)	H(D3)	−0.0357	0.1314	0.3506	7
C(C4)	0.130 (1)	0.1997 (7)	−0.324 (1)	6.3 (4)	H(D4)	−0.2048	0.1174	0.2384	8
C(C5)	0.1482 (9)	0.1533 (6)	−0.2574 (9)	4.9 (4)	H(D5)	−0.2862	0.1588	0.0590	8
C(C6)	0.2000 (9)	0.1581 (5)	−0.1401 (9)	4.1 (3)	H(D6)	−0.1958	0.2075	−0.0116	8
C(D1)	−0.0613 (7)	0.2009 (5)	0.1315 (8)	3.2 (3)	H(E2)	−0.1993	0.3012	0.0630	7
C(D2)	−0.0158 (8)	0.1783 (4)	0.2397 (9)	3.4 (3)	H(E3)	−0.2935	0.3962	0.0257	8
C(D3)	−0.0693 (9)	0.1474 (6)	0.2770 (9)	5.0 (3)	H(E4)	−0.2126	0.4643	−0.0051	9
C(D4)	−0.1693 (9)	0.1389 (6)	0.212 (1)	5.7 (3)	H(E5)	−0.0330	0.4400	0.0205	10
C(D5)	−0.2160 (9)	0.1629 (6)	0.105 (1)	5.6 (4)	H(E6)	0.0628	0.3462	0.0617	9
C(D6)	−0.1630 (8)	0.1928 (5)	0.063 (1)	4.3 (3)	H(F2)	−0.0139	0.1316	−0.0453	9
C(E1)	−0.0598 (8)	0.3133 (5)	0.0634 (8)	3.2 (3)	H(F3)	−0.0768	0.1007	−0.2346	12
C(E2)	−0.1646 (9)	0.3293 (5)	0.054 (1)	4.9 (4)	H(F4)	−0.1398	0.1674	−0.3769	12
C(E3)	−0.222 (1)	0.3860 (6)	0.031 (1)	5.9 (4)	H(F5)	−0.1250	0.2605	−0.3316	11
C(E4)	−0.173 (1)	0.4264 (6)	0.015 (1)	6.1 (4)	H(F6)	−0.0636	0.2926	−0.1422	6
C(E5)	−0.068 (1)	0.4116 (6)	0.028 (1)	7.0 (5)	H(G2)	0.5178	0.2353	0.3792	4
C(E6)	−0.0104 (9)	0.3557 (6)	0.052 (1)	6.0 (4)	H(G3)	0.6780	0.1943	0.3501	6
C(F1)	−0.0313 (7)	0.2149 (5)	−0.0719 (8)	3.4 (3)	H(G4)	0.7774	0.1074	0.4287	6
C(F2)	−0.037 (1)	0.1591 (6)	−0.103 (1)	6.4 (4)	H(G5)	0.7183	0.0581	0.5345	7
C(F3)	−0.075 (1)	0.1401 (7)	−0.216 (1)	8.3 (5)	H(G6)	0.5586	0.0987	0.5644	6
C(F4)	−0.110 (1)	0.1790 (8)	−0.300 (1)	8.5 (5)	H(H2)	0.2454	0.1452	0.4029	4
C(F5)	−0.104 (1)	0.2339 (8)	−0.272 (1)	7.5 (5)	H(H3)	0.1889	0.0683	0.4424	6
C(F6)	−0.0658 (9)	0.2532 (6)	−0.1592 (9)	4.8 (3)	H(H4)	0.2739	0.0274	0.6200	6
C(G1)	0.5216 (7)	0.1723 (4)	0.4751 (8)	2.6 (2)	H(H5)	0.4080	0.0638	0.7576	6
C(G2)	0.5581 (8)	0.1994 (5)	0.4118 (8)	3.1 (3)	H(H6)	0.4660	0.1397	0.7189	5
C(G3)	0.6541 (8)	0.1749 (5)	0.3942 (9)	4.0 (3)	H(I2)	0.3519	0.2553	0.7086	6
C(G4)	0.7124 (8)	0.1235 (5)	0.4401 (9)	4.1 (3)	H(I3)	0.4350	0.2945	0.8870	7
C(G5)	0.678 (1)	0.0943 (5)	0.503 (1)	5.0 (4)	H(I4)	0.6117	0.3019	0.9411	7
C(G6)	0.5825 (9)	0.1186 (5)	0.5210 (9)	4.0 (3)	H(I5)	0.7022	0.2735	0.8158	7
C(H1)	0.3652 (8)	0.1504 (4)	0.5544 (8)	2.8 (3)	H(I6)	0.6228	0.2314	0.6413	5
C(H2)	0.2807 (8)	0.1283 (4)	0.4755 (8)	3.2 (3)	H(J2)	−0.0314	0.4434	0.3198	5
C(H3)	0.2459 (9)	0.0828 (5)	0.498 (1)	4.1 (3)	H(J3)	−0.2111	0.4453	0.2804	7
C(H4)	0.2957 (9)	0.0592 (5)	0.6033 (9)	4.1 (3)	H(J4)	−0.2610	0.3652	0.3133	8
C(H5)	0.376 (1)	0.0803 (5)	0.6845 (9)	4.5 (3)	H(J5)	−0.1350	0.2814	0.3774	8
C(H6)	0.4102 (8)	0.1254 (5)	0.6611 (8)	3.7 (3)	H(J6)	0.0455	0.2778	0.4146	6
C(I1)	0.4773 (7)	0.2389 (4)	0.6549 (8)	2.6 (2)	H(K2)	0.1570	0.4807	0.5008	7
C(I2)	0.4241 (8)	0.2583 (5)	0.7306 (9)	4.2 (3)	H(K3)	0.1652	0.5625	0.4253	9
C(I3)	0.4730 (9)	0.2819 (6)	0.8370 (9)	4.6 (3)	H(K4)	0.1824	0.5599	0.2508	8
C(I4)	0.5768 (9)	0.2865 (6)	0.8683 (9)	4.8 (3)	H(K5)	0.2006	0.4735	0.1530	9
C(I5)	0.6311 (9)	0.2688 (6)	0.7943 (9)	4.8 (3)	H(K6)	0.1977	0.3901	0.2280	8

Table II (*Continued*)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(I6)	0.5835 (8)	0.2445 (5)	0.6901 (8)	3.7 (3)	H(L2)	0.0383	0.3956	0.5692	8
C(J1)	0.0244 (8)	0.3605 (5)	0.3738 (8)	3.1 (3)	H(L3)	0.0739	0.4313	0.7557	10
C(J2)	−0.0524 (8)	0.4104 (5)	0.3322 (9)	3.9 (3)	H(L4)	0.2416	0.4404	0.8701	10
C(J3)	−0.1588 (9)	0.4116 (6)	0.309 (1)	5.1 (4)	H(L5)	0.3802	0.4100	0.8058	11
C(J4)	−0.1882 (8)	0.3642 (6)	0.327 (1)	5.8 (4)	H(L6)	0.3488	0.3720	0.6200	9
C(J5)	−0.1132 (9)	0.3144 (6)	0.366 (1)	5.8 (4)					

[a] Atoms marked with an asterisk were refined isotropically. Parameters for which no esd's appear were not refined. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Preparation of $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$. A dichloromethane solution containing $[Re_2(\mu\text{-}H)_4H_4(PPh_3)_4]PF_6$ was obtained by oxidizing $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ (0.218 g, 0.153 mmol) with 0.06 g (0.155 mmol) of $Ph_3C^+PF_6^-$. The resulting dark blue solution was maintained at 0 °C and treated with 0.15 mL (1.5 mmol) of *tert*-butyl isocyanide and the mixture stirred for 5 min. It was then filtered and evaporated to dryness and the residue washed with diethyl ether. The dark green powder was recrystallized from aqueous acetone to give maroon prisms, yield 0.24 g (83% based upon $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$). Anal. Calcd for $C_{82}H_{83}F_6N_2P_5Re_2$: C, 56.67; H, 4.80. Found: C, 57.79; H, 4.91.

Preparation of Single Crystals of $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$. Crystals suitable for an X-ray crystallographic study were grown by dissolving the crude reaction product in a minimum volume of acetone and then carefully adding water until a slight cloudiness developed. This mixture when kept in a refrigerator at ca. 0 °C deposited maroon crystals of the complex.

X-ray Crystallography. Data Collection. A maroon crystal was coated with epoxy cement and mounted in a random orientation on the end of a glass fiber; all measurements were made at 25 ± 2 °C. Pertinent crystallographic parameters are summarized in Table I. With use of the 2θ–ω scan technique, a total of 13 788 data were collected in the range $5° \leq 2\theta \leq 50°$. The scan range in ω was calculated as $(0.70 + 0.35 \tan\theta)$ with a 25% extension on either end for background determination.

After the data were corrected for Lorentz and polarization effects,[12] an empirical absorption correction[13] based on azimuthal scans of nine reflections with χ near 90° was applied. Equivalent reflections were averaged with agreement factors of 0.026 based on intensity and 0.018 based on F_o. Weak intensity data were rejected to leave 7225 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$ for use in structural refinement.

Structure Solution and Refinement. The positions of the two independent rhenium atoms were determined from a three-dimensional Patterson map. The remaining nonhydrogen atoms were located through alternating series of least-squares cycles and difference Fourier maps. Five hydride hydrogen atoms were located in a difference Fourier search which followed refinement of all non-hydrogen atoms. The hydride atoms and the atoms associated with PF_6^- ions were refined isotropically; all other atoms were refined anisotropically. All phenyl hydrogen atoms were included (but not refined) at calculated positions with isotropic thermal values about 1.5 times as large as those of the corresponding phenyl carbon atoms. In the final stages of refinement, the thermal parameter for one of the hydride hydrogen atoms, H(4), took on a negative value (−0.73); this parameter was subsequently fixed at an arbitrary value of +1.10. Convergence of full-matrix least-squares refinement gave residuals of $R = 0.0413$ and $R_w = 0.0466$. A final difference Fourier map contained six peaks above 1.0 e/Å^3; however, all of these peaks were within 0.8 Å from atoms in the two independent PF_6^- anions.

Final atomic coordinates and thermal parameters are listed in Table II. Important bond distances and angles are given in Table III. Complete tables of anisotropic thermal parameters, bond distances and angles, and structure factors are available as supplementary material.

Physical Measurements. Infrared spectra as Nujol mulls were recorded in the region 4000–400 cm^{-1} with a Beckman IR-12 spectrophotometer. ^{1}H NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer operated at 90 MHz while ^{31}P NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock, using $P(OMe)_3$ as an external standard. Analysis of volatile gases was carried out with a Carle Series-S analytical gas chromatograph (Model 111-H 156A) equipped with a Linear Model 1201 strip-chart recorder. Reactions were sampled with use of the setup previously described.[6] Microanalyses were performed by Dr. H. D. Lee of the Purdue Microanalytical Laboratory.

Results and Discussion

(a) Synthesis. We have, in an earlier communication,[14] described the reversible one-electron oxidation of the dirhenium polyhydride complex $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ to the paramagnetic, ESR-active, blue-purple monocation $[Re_2(\mu\text{-}H)_4H_4(PPh_3)_4]^+$ and have subsequently reported the isolation of its PF_6^- salt.[7] In seeking to make comparisons between the chemical reactivity of the diamagnetic 18-electron neutral complex $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ and its 17-electron cation, we have explored the reactions of both these species with *tert*-butyl isocyanide.[15] In contrast to the extremely sluggish nature of the reaction between $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ and *tert*-butyl isocyanide in refluxing tetrahydrofuran, the analogous reaction with $[Re_2(\mu\text{-}H)_4H_4(PPh_3)_4]PF_6$ in dichloromethane is complete within a few minutes and maroon crystals of the dirhenium pentahydride complex $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$ can be isolated in high yield. GC analysis shows that the only volatile product of this reaction is H_2. Although the true identity of this molecule was not immediately apparent from our preliminary analysis of its spectroscopic properties, these results when taken in conjunction with an X-ray crystallographic investigation provided a definitive structural identification of this molecule.

(b) Crystal Structure. Figure 1 illustrates the geometry and atom-labelling scheme for the $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]^+$ cation. Along with the phenyl hydrogen atoms, the two PF_6^- anions positioned on independent inversion centers are not pictured. In Figure 2, all of the phenyl and *tert*-butyl groups are omitted to give a clear view of the central portion of the cation. The environments about the two eight-coordinate rhenium atoms are essentially equivalent, and the structure may be described as two face-sharing distorted pentagonal bipyramids. Although the cation in its entirety possesses no element of symmetry, its central portion has idealized C_2 symmetry. The idealized C_2 axis passes through H(5) and bisects the Re–Re bond. It is approximately vertical in Figure 2 and perpendicular to the page in Figure 1.

The most interesting structural feature of the cation is the presence of three bridging and two terminal hydride ligands. The three bridging hydrogen atoms form a triangle that is equilateral within the relatively large errors. It has the following edge lengths: H(3)–H(4), 2.24 (11) Å; H(3)–H(5),

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[12] Computing was done with the Enraf-Nonius Structure Determination Package on a PDP-11/60 computer at B. A. Frenz and Associates, Inc., College Station, TX.

[13] North, A. C. T.; Phillips, D. C.; Matthews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

[14] Allison, J. D.; Cameron, C. J.; Wild, R. E.; Walton, R. A. *J. Organomet. Chem.* **1981**, *218*, C62.

[15] The enhanced substitution lability of 17-electron organometallic species compared to that of their 18-electron analogues is a topic of considerable current interest. See, for example: Shi, Q.-Z.; Richmond, T. G.; Trogler; W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 4032.

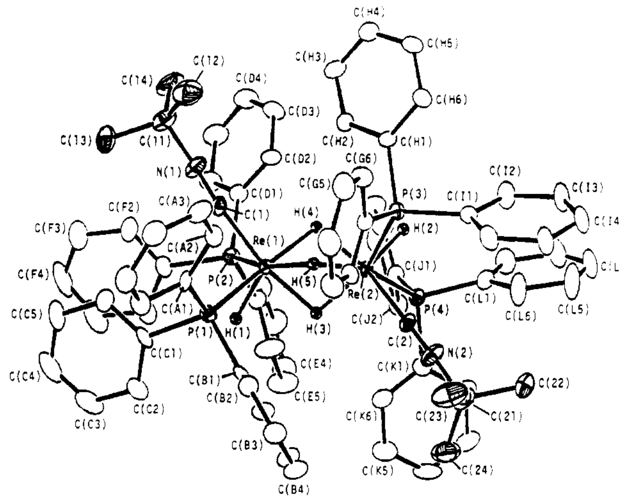


Figure 1. Structure and labeling scheme for the complex cation $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]^+$. Hydrogen atoms were given an arbitrary isotropic thermal parameter. All other atoms are represented by their 25% probability ellipsoids. Designations for unlabeled ring atoms follow from those given by an obvious pattern. Phenyl hydrogen atoms (not shown) were given the same labels as the corresponding carbon atoms.

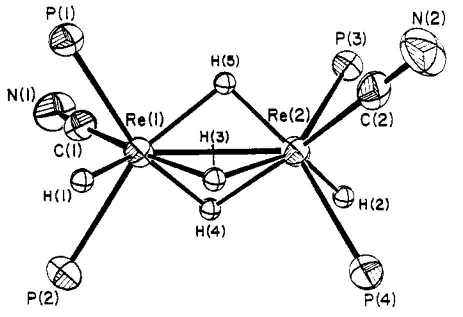
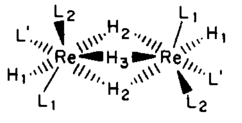


Figure 2. View of the central portion of the cation. Atoms are represented by their 50% probability ellipsoids except for hydrogens, which are represented by spheres with arbitrary radii.

2.12 (12) Å; H(4)–H(5), 2.27 (11) Å. The two terminal hydrogen atoms are each essentially coplanar with one of the three bridges: H(1) is only 0.056 Å out of the plane formed by Re(1), H(3), and Re(2) while H(2) is only 0.136 Å out of the plane formed by Re(1), H(4), and Re(2).

The $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]^+$ ion is quite similar to the recently characterized $[Re_2H_5(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]^+$ cation.[8] Both of these cations can be represented as $Re_2H_5L_4L'_2{}^+$ species with a structure of type **1**. This schematic representation incorporates the idealized C_2 symmetry (the twofold axis would pass through H_3 perpendicular to the page) so that the four ligands L occupy two unique positions (L_1 and L_2) and the five hydride ligands occupy three unique positions, one terminal (H_1) and two bridging (H_2 and H_3). A comparison of important average bond distances and angles for the two cations appears in Table IV. The Re–Re bond lengths are essentially identical. In both cases the Re–H bond distances for terminal hydrides are shorter than those for bridging hydrides.



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The striking similarity between these two cations is somewhat surprising considering the opposite approaches taken to produce them. Virtually all structural differences may be attributed to the greater steric bulkiness of PPh_3 vs. that of PMe_2Ph, which apparently forces the non-hydrogen terminal ligands in $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]^+$ further away from the center of the cation and the terminal hydride ligands closer to the center.

Table III. Important Bond Distances and Angles for the $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]^+$ Cation

	Distances (Å)		
Re(1)–Re(2)	2.604 (1)	P(1)–C(A1)	1.841 (10)
–P(1)	2.366 (3)	–C(B1)	1.832 (11)
–P(2)	2.372 (3)	–C(C1)	1.835 (10)
–H(1)	1.68 (7)	P(2)–C(D1)	1.855 (11)
–H(3)	1.80 (8)	–C(E1)	1.826 (11)
–H(4)	1.81 (7)	–C(F1)	1.821 (10)
–H(5)	1.85 (9)	P(3)–C(G1)	1.845 (10)
–C(1)	1.978 (11)	–C(H1)	1.825 (10)
Re(2)–P(3)	2.370 (3)	–C(I1)	1.825 (10)
–P(4)	2.402 (3)	P(4)–C(J1)	1.832 (11)
–H(2)	1.50 (8)	–C(K1)	1.828 (11)
–H(3)	1.85 (8)	–C(L1)	1.843 (11)
–H(4)	1.99 (7)	C(1)–N(1)	1.164 (12)
–H(5)	1.65 (9)	C(2)–N(2)	1.156 (13)
–C(2)	1.976 (11)	N(1)–C(11)	1.460 (14)
		N(2)–C(21)	1.462 (15)

	Angles (deg)		
Re(2)–Re(1)–P(1)	117.73 (7)	P(4)–Re(2)–H(2)	64 (3)
–P(2)	121.88 (7)	–H(3)	84 (3)
–H(1)	120 (3)	–H(4)	97 (2)
–H(3)	45 (3)	–H(5)	159 (3)
–H(4)	50 (2)	–C(2)	82.9 (3)
–H(5)	39 (3)	H(2)–Re(2)–H(3)	135 (4)
–C(1)	123.9 (3)	–H(4)	81 (4)
P(1)–Re(1)–P(2)	114.92 (9)	–H(5)	133 (5)
–H(1)	67 (3)	–C(2)	108 (3)
–H(3)	103 (3)	H(3)–Re(2)–H(4)	71 (3)
–H(4)	162 (2)	–H(5)	74 (4)
–H(5)	86 (3)	–C(2)	98 (3)
–C(1)	84.8 (3)	H(4)–Re(2)–H(5)	76 (4)
P(2)–Re(1)–H(1)	63 (3)	–C(2)	170 (2)
–H(3)	101 (3)	H(5)–Re(2)–C(2)	100 (3)
–H(4)	82 (2)	Re(1)–P(1)–C(A1)	118.6 (4)
–H(5)	159 (3)	–C(B1)	111.3 (3)
–C(1)	83.0 (3)	–C(C1)	118.4 (3)
H(1)–Re(1)–H(3)	74 (4)	C(A1)–P(1)–C(B1)	100.5 (5)
–H(4)	128 (3)	–C(C1)	100.5 (5)
–H(5)	130 (4)	C(B1)–P(1)–C(C1)	105.2 (5)
–C(1)	117 (3)	Re(1)–P(2)–C(D1)	116.9 (3)
H(3)–Re(1)–H(4)	77 (3)	–C(E1)	114.1 (4)
–H(5)	71 (4)	–C(F1)	117.9 (3)
–C(1)	169 (3)	C(D1)–P(2)–C(E1)	104.9 (5)
H(4)–Re(1)–H(5)	77 (4)	–C(F1)	100.3 (5)
–C(1)	94 (2)	C(E1)–P(2)–C(F1)	100.5 (5)
H(5)–Re(1)–C(1)	101 (3)	Re(2)–P(3)–C(G1)	115.0 (3)
Re(1)–Re(2)–P(3)	114.13 (6)	–C(H1)	116.6 (3)
–P(4)	117.39 (7)	–C(I1)	118.1 (3)
–H(2)	125 (3)	C(G1)–P(3)–C(H1)	102.7 (5)
–H(3)	44 (3)	–C(I1)	100.1 (5)
–H(4)	44 (2)	C(H1)–P(3)–C(I1)	101.7 (5)
–H(5)	45 (3)	Re(2)–P(4)–C(J1)	114.9 (4)
–C(2)	127.4 (3)	–C(K1)	115.8 (4)
P(3)–Re(2)–P(4)	124.32 (9)	–C(L1)	120.2 (3)
–H(2)	70 (3)	C(J1)–P(4)–C(K1)	103.6 (5)
–H(3)	151 (3)	–C(L1)	99.3 (5)
–H(4)	106 (2)	C(K1)–P(4)–C(L1)	100.2 (5)
–H(5)	77 (3)	C(1)–N(1)–C(11)	177 (1)
–C(2)	82.3 (3)	C(2)–N(2)–C(21)	178 (1)
Re(1)–H(3)–Re(2)	91 (4)	Re(1)–C(1)–N(1)	174.1 (9)
Re(1)–H(4)–Re(2)	87 (3)	Re(2)–C(2)–N(2)	180 (1)
Re(1)–H(5)–Re(2)	96 (5)		

(c) Spectroscopic Properties. This complex is soluble in polar solvents such as acetonitrile, dichloromethane, acetone, and tetahydrofuran, slightly soluble in alcohols, and insoluble in benzene, pentane, diethyl ether, and water. Its IR spectrum (Nujol mull) shows $\nu(C{\equiv}N)$ modes at 2090 m–s and 2040 s cm^{-1}, thereby demonstrating the presence of terminal *tert*-butyl isocyanide ligands only. These absorptions obscure the

Table IV. Selected Average Bond Distances and Angles for Two $Re_2H_5L_4L'_2{}^+$ Species[a]

	$Re_2H_5(PMe_2Ph)_4$-$[P(OCH_2)_3CEt]_2{}^+$ [b]	$Re_2H_5(PPh_3)_4$-$(CN\text{-}t\text{-}Bu)_2{}^+$ [c]
	Distances (Å)	
Re–Re	2.605 (2)[d]	2.604 (1)
Re–L_1	2.366 [2]	2.368 [2]
Re–L_2	2.348 [12]	2.387 [15]
Re–L′	2.228 [4]	1.977 [1]
Re–H_1	1.46 [14]	1.59 [9]
Re–H_2	1.73 [6]	1.86 [4]
Re–H_3	1.91 [7]	1.75 [10]
	Angles (deg)	
Re–Re–L_1	111.0 [8]	116 [2]
–L_2	114.6 [8]	120 [2]
–L′	123.4 [4]	126 [2]
–H_1	142 [2]	122 [2]
Re–H_2–Re	97 [3]	89 [2]
Re–H_3–Re	86 (5)	96 (5)
L_1–Re–L_2	123.1 [6]	120 [5]
–L′	90.6 [2]	84 [1]
–H_1	63 [0]	68 [2]
–H_3	83 [1]	82 [4]
L_2–Re–L′	91.2 [5]	83.0 [1]
–H_1	60 [1]	64 [1]
–H_3	154 [1]	159 [0]
L′–Re–H_1	94 [2]	112 [4]
–H_3	88 [4]	100 [1]
H_1–Re–H_3	146 [2]	132 [2]
H_2–Re–H_2	74 [3]	76 [2]
–H_3	70 [1]	74 [1]

[a] For the first cation, L = PMe_2Ph (=L_1, L_2) and L′ = $P(OCH_2)_3CEt$. For the second cation, L = PPh_3 (=L_1, L_2) and L′ = *t*-BuNC. [b] Reference 8. [c] This paper. [d] A number in parentheses is an esd for a given value while a number in brackets is equal to $[\Sigma_n \Delta_i^2/n(n-1)]^{1/2}$, where Δ_i is the deviation of the *i*th of *n* values from the arithmetic mean of the *n* values.

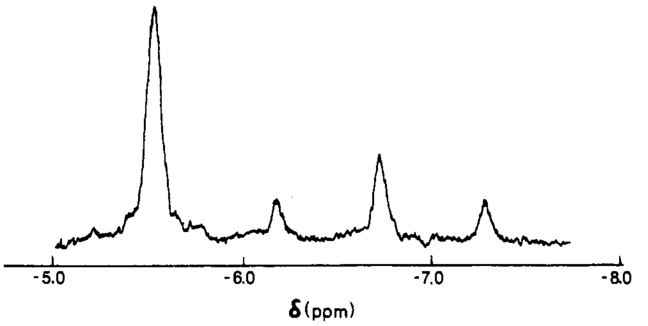

Figure 3. ^1H NMR spectrum of $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$ (in CD_2Cl_2 at 10 °C) in the region of the hydrido resonances.

much less intense bands arising from ν(Re–H) vibrations.

At room temperature (+22 °C) the ^1H NMR spectrum of a CD_2Cl_2 solution of the complex displays a multiplet at δ 7.25 (phenyl) and a singlet at δ 0.75 (*tert*-butyl) showing the correct integration for a formulation with a phosphine: isocyanide ligand ratio equal to 2:1. The Re–H resonances of this complex were examined over the temperature range +35 to −70 °C (90 MHz, CD_2Cl_2 as solvent). The spectrum was essentially unchanged over this range of temperature, showing a singlet at δ −5.60 and a triplet centered at δ −6.75 (J(P–H) = 50 Hz). The spectrum recorded at +10 °C is shown in Figure 3. The resonances at δ −5.60 and δ −6.75 integrate to a relative intensity of 3:2, and the overall intensity of these Re–H resonances, when compared to those of the PPh_3 and *t*-BuNC ligands, is in accord with the formulation $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$. The upfield shift of the triplet assigned to the terminal Re–H units, relative to the resonance(s) due to Re–H–Re, is in accord with related assignments made by Green et al.[8] for the two types of hydride ligand in $[Re_2(\mu\text{-}H)_3H_{n+1}(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]^{n+}$ (n = 0 or 1). Interestingly, the inequivalent bridging Re–H bonds of $[Re_2(\mu\text{-}H)_3H_2(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]^+$ are differentiated at −60 °C in the ^1H NMR (δ −5.93 br s, 1 H; δ −6.75 br s, 2 H)[8] but these resonances coalesce upon raising the temperature, although the terminal Re–H triplet (arising from coupling to the two PMe_2Ph ligands but *not* the terminal phosphite) is affected very little. Thus, the ^1H NMR spectrum of $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$ between +35 and −70 °C is essentially the same as that reported at +16 °C for $[Re_2(\mu\text{-}H)_3H_2(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]BF_4$[8] and shows that while the bridging hydrides are equivalent on the NMR time scale, there is no process that leads to the exchange of terminal and bridging Re–H bonds under our experimental conditions.

The ^{31}P NMR spectrum of $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$ is quite simple. In acetone-d_6 (at +22 °C) a doublet at δ +29.9 is observed, arising from the coupling of the pairs of terminal PPh_3 ligands with the single terminal Re–H on each rhenium (J(P–H) = 49 Hz). As expected, the corresponding $^{31}P\{^1H\}$ spectrum displays only a singlet at δ 29.9. Thus, as in the case of $[Re_2(\mu\text{-}H)_3H_{n+1}(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]^{n+}$ (n = 0 or 1),[8] measurable phosphorus–hydride coupling involves only the terminal Re–H units, an observation that can, in the absence of fluxionality, be extremely useful in probing the solution structures of dirhenium polyhydride complexes since Re–H_t and Re–H_b units can be quite easily differentiated.

(d) Concluding Remarks. The isolation and characterization of the cation $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]^+$ constitutes only the second example of such a complex containing the monocationic dirhenium pentahydride unit. However, its preparation from $[Re_2(\mu\text{-}H)_4H_4(PPh_3)_4]^+$, through the reductive elimination of H_2, constitutes a different synthetic strategy from that employed by Green et al.[8] in the protonation of the neutral dirhenium tetrahydride complex $Re_2(\mu\text{-}H)_3H(PMe_2Ph)_4[P(OCH_2)_3CEt]_2$. Further studies are under way to explore the scope of this chemistry.

The diamagnetism of the cation and the short Re–Re distance, 2.604 (1) Å, indicate that a bond exists between the metal atoms. An electron count prior to allowance for the formation of any such bond yields 15 electrons per metal atom. If it is appropriate to invoke the 18-electron rule, a rhenium–rhenium bond order of 3 would be indicated. It is of course possible to relax the 18-electron rule and propose only a single bond. From another point of view, one could observe that the rhenium atoms have a formal oxidation number of +3, making them d^4 ions. Thus, they are capable of forming bonds of order 2 or 4 while still conforming to the requirement that the ion be diamagnetic. The observed bond length is surely too long for a bond order of 4 and perhaps even for 3, although the latter value cannot, perhaps, be entirely excluded.

It would seem that the metal–metal bonding in this hydride-bridged species (and in others of similar type) is not amenable to a satisfying formulation using either of the above qualitative approaches. They lead us to nothing more definitive than the range of 1–3 for the bond order. It is, of course, not clear just how meaningful the concept of bond order really is in this type of compound. We believe that the electronic structure of this and similar species ought to be examined by some sort of first-principles calculation (as was the $[Mo_2Cl_8H]^{3-}$ ion[16]) from which it may then be possible to infer some serviceable qualitative rules for metal–metal bonding in multiply hydrido-bridged systems.

Acknowledgments. Support from the National Science Foundation (Grant No. CHE82-06117 to R.A.W. and Grant

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[16] Bino, A.; Bursten, B. E.; Cotton, F. A.; Fang, A. *Inorg. Chem.* **1982**, *21*, 3755.

No. CHE77-00448 to F.A.C.) is gratefully acknowledged. The Varian XL-200 spectrometer was purchased with funds from the National Science Foundation (Grant No. CHE80-04246 to Purdue). This support is gratefully acknowledged.

Registry No. [$Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2$]$PF_6$, 86676-29-1; [$Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$]$PF_6$, 86664-86-0.

Supplementary Material Available: Tables of all bond distances and angles, anisotropic thermal parameters, least-squares planes for all phenyl rings, and observed and calculated structure factors (52 pages). Ordering information is given on any current masthead page.

Contribution from the Institute of Inorganic Chemistry, University of Münster, D-4400 Münster, Federal Republic of Germany,
and Chemistry Department A, Technical University of Denmark, DK-2800 Lyngby, Denmark

$NbAlCl_8$: A Molecular Dinuclear Complex in the Solid, Melt, and Vapor Phases. Synthesis, Crystal Structure, and Raman Spectra

BERNT KREBS,*[1a,e] HOLGER JANSSEN,[1a] NIELS J. BJERRUM,*[1b] ROLF W. BERG,[1b]
and G. N. PAPATHEODOROU[1c,d]

Received March 10, 1983

Crystalline $NbAlCl_8$ was prepared as a new type of dinuclear halide complex by the direct reaction of Al_2Cl_6 with Nb_2Cl_{10} at ~200 °C in evacuated sealed glass ampoules. The yellow compound is orthorhombic, space group *Cmcm*, with $a = 8.016$ (2) Å, $b = 17.139$ (4) Å, $c = 8.116$ (2) Å, $V = 1115.1$ Å^3, $D_{\text{measd}} = 2.40$ (2) g·cm^{-3}, and $D_{\text{calcd}} = 2.403$ g·cm^{-3} for $Z = 4$. The crystal and molecular structure determination was based on three-dimensional X-ray diffractometer data refined to a final conventional R factor of 0.030 for 639 independent reflections with $I \geq 2\sigma(I)$. The crystals contain dinuclear $Cl_4NbCl_2AlCl_2$ molecules with *mm* symmetry, consisting of an $AlCl_4$ tetrahedron sharing a common edge with a distorted $NbCl_6$ octahedron. Al–Cl bond lengths of 2.078 (2) and 2.200 (2) Å and Nb–Cl bond lengths of 2.219 (1), 2.288 (1), and 2.643 (1) Å were observed. The Nb–Cl bridge bonds are longer than in the Nb_2Cl_{10} molecule, thus indicating a higher Lewis acidity of $AlCl_3$ compared to that of $NbCl_5$. Polarized Raman spectra of $NbAlCl_8$ single crystals were obtained at room temperature. The factor-group analysis of vibrations in crystalline $NbAlCl_8$ was used for the assignment of the observed Raman bands. Raman spectra of melt mixtures of $NbCl_5$ with $AlCl_3$ at 235 °C were characterized by a superposition of bands due to Al_2Cl_6(l), Nb_2Cl_{10}(l), and $NbCl_5$(l), together with $NbAlCl_8$(l). Measurements of relative Raman band intensities in the mixtures showed two strongly polarized bands at 416 and 364 cm^{-1} and other weaker bands due to $NbAlCl_8$ complexes present in the melts. Raman spectra of vapors over the liquid mixtures at temperatures between 235 and 350 °C were mainly due to Al_2Cl_6(g) and $NbCl_5$(g) molecules. Two new polarized bands observed in the spectra at 418 and 369 cm^{-1} were attributed to the formation of the $NbAlCl_8$ gaseous molecule.

Introduction

The chlorides and bromides of aluminum, gallium, and indium are able to form ternary complex halides with a large number of other metal and nonmetal halides in the gas phase or in the condensed state.[2] These complex halides sometimes occur as molecules; as volatile "gas complexes" they are important for many types of chemical transport reactions,[2,3] e.g. in the case of a halide transport according to

$$MCl_x(\text{solid}) + 0.5nAl_2Cl_6(\text{gas}) \rightleftarrows MCl_x{\cdot}nAlCl_3(\text{gas})$$

On the other hand, they can form various aggregates in the solid state, in which more or less pronounced heteropolar bonding is present according to the Lewis acid and base properties of the components. For Al_2Cl_6 (or just $AlCl_3$), by far the most important of the mentioned complex-forming trihalides, a considerable number of ternary compounds with dihalides and tetrahalides have been isolated as solids, and some of them are structurally well characterized by X-ray diffraction. The latter include trinuclear $CuAl_2Cl_8$[4] and $PdAl_2Cl_8$[5] as well as the two- or three-dimensionally polymeric compounds $CoAl_2Cl_8$,[6] $NiAl_2Cl_8$,[7] $SCl_3{}^+AlCl_4{}^-$,[8] $SeCl_3{}^+AlCl_4{}^-$,[9] and $TeCl_3{}^+AlCl_4{}^-$.[10] Little is known about complex formation in the solid among two trichlorides.

Concerning possible complex formation between trihalides and pentahalides, however, all chemical and structural knowledge is restricted to results of vibrational, electron, and mass spectroscopic as well as thermoanalytic and potentiometric work. The gas complexes $UAlCl_8$[11] and $TaAlCl_8$[12] have been shown to exist, ionic structures $PCl_4{}^+MCl_4{}^-$ are derived from vibrational spectra of the PCl_5–MCl_3 systems (M = B, Al, Ga),[13] and the complex $NbGaCl_8$ was postulated from liquid and solid-state Raman spectra[14] and by DTA measurements.[15] Some evidence on the nature of possible complexes between $NbCl_5$ and $AlCl_3$ is obtained from investigations in KCl–$AlCl_3$–$NbCl_5$ melts[16] and from mass spectroscopy in the gas phase.[12] In the following we report the preparation and characterization of the crystalline 1:1 complex between $NbCl_5$ and $AlCl_3$, which is the first example of structural analysis of this novel type of binuclear molecular addition compound. Also, Raman spectra of the complex in the solid, liquid, and gaseous phases are obtained.

Synthesis of Crystalline $NbAlCl_8$

Because of the extreme sensitivity of the compounds toward hydrolysis and partial oxidation, all operations had to be done under exclusion of moisture and oxygen by means of standard glovebox and sealed-cell techniques. The starting materials used for the synthesis

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(1) (a) University of Münster. (b) Technical University of Denmark. (c) University of Patras, Patras, Greece. (d) Visiting Professor at TUD in 1982. (e) Visiting Professor at TUD in 1981.

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