Crystal and Molecular Structure of $[ReH(CH_3CN)_3(PMe_2Ph)_3][BF_4]_2$

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(Received December 23, 1986)

While virtually all transition-metal phosphine polyhydrides adhere to the 18-electron rule, reactive ligand-deficient species can be created by thermal or photochemical means, or by acidolysis [1]. The reaction of polyhydrides with acids can result in simple protonation [2], formation of non-classical polyhydrides [3], or, most commonly, multiple hydride loss by H_2 extrusion. When a hydrohalic acid is used, the product is a metal phosphine halide complex. The reaction with the acid of a non-coordinating anion (e.g. HBF_4) can result (in weakly-coordinating solvents) in anion degradation by the strongly electrophilic metal cation generated [4] or the formation of solvento complexes when more coordinating solvents are used [5–8]. Some of these solvento compounds have been used for stoichiometric or catalytic alkane activation [9].

In a previous paper, we reported the preparation of $[ReH(CH_3CN)_3(PMe_2Ph)_3][BF_4]_2$ (**1**), the product of the reaction of $ReH_5(PMe_2Ph)_3$ with HBF_4 in CH_3CN [6]. NMR evidence showed that one hydride was present and that the phosphine and nitrile ligands were equivalent, suggesting either stereochemical non-rigidity (not established in variable-temperature NMR studies [8]) or a rigid capped octahedral geometry where the phosphine and nitrile ligands were in a *fac* arrangement. In order to answer this question we carried out a single-crystal X-ray diffraction study of **1**.

Experimental

1 was prepared as described previously [3]. Suitable single crystals were grown by dissolving 50 mg of the compound in CH_3CN (2 ml) under argon, slowly adding Et_2O (15 ml) as a top layer and cooling to −15 °C for 2 days.

A suitable single crystal of $C_{30}H_{43}N_3P_3B_2F_8Re$ ($M = 898.4$, monoclinic unit cell, space group $P2_1/c$, $a = 13.309(5)$, $b = 12.789(2)$, $c = 22.816(6)$ Å, $\alpha = 101.57(2)°$, $V = 3804.6(19)$ Å^3, $Z = 4$, $D_{calc} = 1.568$ g cm^{-3}, (Mo Kα) = 34.22 cm^{-1}, (Mo Kα) = 0.71069 Å) was examined using a Syntex P3 automated diffractometer. Of 8208 data points 4664 reflections were considered observed [$I \geqslant 3.0(I)$]. The structure was solved for heavy atom positions by direct methods using MULTAN80 [10]. Successive least-squares/difference Fourier cycles allowed location of the remainder of the non-hydrogen atoms. Refinement of the scale factor, positional and anisotropic thermal parameters was carried to convergence [11]. Phenyl and methyl hydrogen positional parameters were determined from a difference Fourier synthesis and were included in the final cycles of refinement with assigned isotropic thermal parameters of $U = 0.03$. All parameters associated with hydrogen atoms were held invariant. The final cycle of refinement led to an R factor of 4.8% (unit weights were used throughout). Anomalous dispersion corrections were made for Re and P. Scattering factors were taken from Cromer and Mann [12].

Results and Discussion

The structure of the dication of **1** is shown in Fig. 1, positional parameters are given in Table I with selected bond distances and angles given in Tables II and III. The three phosphorus atoms coordinated to Re (Re–P, 2.374(3)–2.403(3) Å) form a triangle (P...P, 3.730(5)–3.817(4) Å) skewed to the triangle of nitrogen atoms (N...N, 2.80(1)–2.86(1) Å) bound

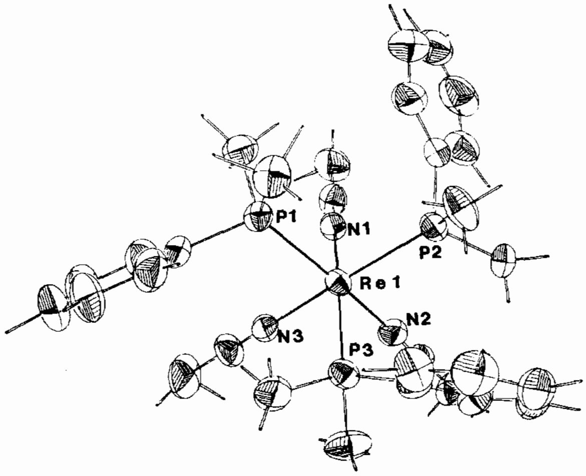

Fig. 1. ORTEP diagram of the $[ReH(CH_3CN)_3(PMe_2Ph)_3]$-$[BF_4]_2$ cation.

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0020-1693/87/$3.50

TABLE 1. Positional Parameters for $ReP_3C_{30}N_3H_{43}B_2F_8$

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$
Re1	0.23642(3)	0.21648(3)	0.60811(2)
P1	0.1284(2)	0.3571(2)	0.6282(1)
P2	0.3884(2)	0.3078(2)	0.5963(1)
P3	0.2864(2)	0.1242(2)	0.6997(1)
B1	0.8575(11)	0.2282(14)	0.4289(7)
F1	0.7625(9)	0.2308(16)	0.4217(7)
F2	0.8880(11)	0.1945(18)	0.3838(6)
F3	0.9005(16)	0.3092(14)	0.4457(12)
F4	0.8929(20)	0.1729(22)	0.4722(9)
B2	0.3187(13)	0.0678(14)	0.3773(7)
F5	0.3026(15)	0.1069(12)	0.4251(6)
F6	0.2998(12)	−0.0352(10)	0.3796(6)
F7	0.2595(9)	0.1096(11)	0.3298(5)
F8	0.4123(11)	0.0716(15)	0.3738(8)
N1	0.1820(7)	0.2533(7)	0.5167(4)
C11	0.1559(8)	0.2689(10)	0.4673(5)
C12	0.1241(11)	0.2957(12)	0.4052(6)
N2	0.3008(7)	0.0856(7)	0.5707(4)
C21	0.3320(9)	0.0149(9)	0.5498(5)
C22	0.3759(11)	−0.0727(11)	0.5245(6)
N3	0.1028(7)	0.1216(7)	0.5976(4)
C31	0.0326(9)	0.0717(9)	0.5890(6)
C32	−0.0594(11)	0.0080(13)	0.5758(10)
C1	0.0662(10)	0.4319(10)	0.5631(6)
C2	0.1878(10)	0.4609(11)	0.6782(6)
C111	0.0166(9)	0.3207(9)	0.6604(5)
C112	−0.0699(10)	0.2804(12)	0.6232(7)
C113	−0.1517(11)	0.2518(12)	0.6496(10)
C114	−0.1514(16)	0.2618(17)	0.7081(11)
C115	−0.0659(16)	0.3080(17)	0.7440(9)
C116	0.0177(11)	0.3355(12)	0.7208(7)
C3	0.4592(10)	0.3846(11)	0.6570(6)
C4	0.4914(9)	0.2298(12)	0.5804(7)
C211	0.3694(8)	0.3999(9)	0.5342(5)
C212	0.3854(11)	0.3695(11)	0.4779(6)
C213	0.3637(12)	0.4378(14)	0.4296(7)
C214	0.3259(12)	0.5326(13)	0.4353(8)
C215	0.3107(13)	0.5665(12)	0.4884(9)
C216	0.3317(12)	0.5009(11)	0.5386(7)
C5	0.2807(11)	−0.0177(9)	0.6934(6)
C6	0.2085(10)	0.1423(12)	0.7551(6)
C311	0.4160(9)	0.1449(9)	0.7404(5)
C312	0.4395(9)	0.2139(12)	0.7879(5)
C313	0.5394(12)	0.2314(13)	0.8157(6)
C314	0.6186(10)	0.1837(12)	0.7951(7)
C315	0.5972(10)	0.1168(11)	0.7475(6)
C316	0.4988(9)	0.0969(10)	0.7210(5)

TABLE II. Selected Bond Distances (Å) for $[ReH(CH_3CN)_3(PMe_2Ph)_3][BF_4]_2$ (e.s.d.s in parentheses)

Re–P(1)	2.403(3)	P(2)–C(3)	1.80(1)
Re–P(2)	2.398(3)	P(2)–C(4)	1.79(1)
Re–P(3)	2.374(3)	P(2)–C(211)	1.82(1)
Re–N(1)	2.118(9)	P(3)–C(5)	1.82(1)
Re–N(2)	2.134(10)	P(3)–C(6)	1.80(2)
Re–N(3)	2.127(9)	P(3)–C(311)	1.81(1)
N(1)–C(11)	1.13(1)	P(1)...P(2)	3.730(5)
N(2)–C(21)	1.14(2)	P(2)...P(3)	3.768(4)
N(3)–C(31)	1.11(1)	P(1)...P(3)	3.817(4)
C(11)–C(12)	1.43(1)	N(1)...N(2)	2.80(1)
C(21)–C(22)	1.44(2)	N(2)...N(3)	2.86(1)
C(31)–C(32)	1.45(2)	N(1)...N(3)	2.85(1)
P(1)–C(1)	1.82(1)		
P(1)–C(2)	1.82(1)		
P(1)–C(111)	1.84(1)		

TABLE III. Selected Bond Angles (°) for $[ReH(CH_3CN)_3(PMe_2Ph)_3][BF_4]_2$ (e.s.d.s in parentheses)

P(1)–Re–P(2)	102.0(1)	P(3)–Re–N(1)	163.0(3)
P(1)–Re–P(3)	106.1(1)	P(3)–Re–N(2)	84.1(2)
P(2)–Re–P(3)	104.3(1)	P(3)–Re–N(3)	84.0(2)
N(1)–Re–N(2)	82.3(3)	Re–N(1)–C(11)	176(1)
N(1)–Re–N(3)	84.4(3)	Re–N(2)–C(21)	178(1)
N(2)–Re–N(3)	84.3(3)	Re–N(3)–C(31)	176(1)
P(1)–Re–N(1)	85.5(2)	N(1)–C(11)–C(12)	176(1)
P(1)–Re–N(2)	165.1(3)	N(2)–C(21)–C(22)	178(1)
P(1)–Re–N(3)	86.0(2)	N(3)–C(31)–C(32)	178(2)
P(2)–Re–N(1)	84.8(2)		
P(2)–Re–N(2)	85.5(3)		
P(2)–Re–N(3)	166.1(2)		

to Re (Re–N, 2.118(9)–2.134(10) Å). When the hydride ligand is not considered the Re coordination geometry is a distorted *fac* octahedron.

While hydride ligands have a low steric demand, they do occupy regular coordination positions and do exert a structural influence in hydrido compounds [13]. The position of the hydride ligand in **1** could not be located in the difference-Fourier map but it can be inferred by comparison of the structure to that of *fac*-$[Os(CH_3CN)_3(PMe_2Ph)_3][PF_6]_2$ (**2**), similarly prepared by reaction of $OsH_4(PMe_2Ph)_3$ with $[Ph_3C][PF_6]$ [7]. The average M–N (2.126 Å) and M–P (2.392 Å) distances in **1** are slightly longer than those in **2** (Os–N, 2.091 Å (av.); Os–P, 2.327 Å (av.)). While the average N–Re–N and N–Os–N angles are similar (84.1° *versus* 84.4°), the average P–Re–P angle (104.1°) is much greater than the average P–Os–P angle (95.4°), strongly implying that the hydride ligand caps the octahedron on the face defined by the triangle of phosphine ligands – a less desirable position from a steric standpoint – rather than on the face defined by the triangle of acetonitrile ligands. The *cis* N–Re–P angles average 85°, considerably more compressed than the analogous *cis* N–Os–P angles, which average 90°. The ligands themselves in **1** are completely normal: N–C and C–CH_3 distances are identical within 1–2σ, the Re–N–C and N–C–CH_3 bond angles are little perturbed from linearity, and angles and distances within the phosphine ligands show no anomalies.

The seven-coordinate geometry established for **1** is different to that of the related seven-coordinate solvento complex $[ReH(CH_3CN)_4(PPh_3)_2][BF_4]_2$ (**3**) [6, 8]. While an X-ray diffraction study of **3** has yet to be done, ^1H and ^{31}P NMR spectra indicate two types of nitrile ligands are present but that the phosphines are equivalent [8]. This can be explained in terms of a pentagonal biprismatic geometry for **3**, in which the hydride and four nitrile ligands lie in an equatorial plane with equivalent phosphines in axial positions.

Supplementary Material

A complete list of bond angles and distances, hydrogen positional parameters, anisotropic thermal parameters, and calculated and observed structure factors can be obtained from the authors.

Acknowledgement

We thank the Army Research Office for support.

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