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Contribution from the Department of Industrial Chemistry,
University of Tokyo, Hongo, Tokyo, Japan

Preparation and Properties of Dinitrogen–Molybdenum Complexes. 3.[1] Preparation and Molecular Structure of 1-(η-Hydrazido(2–))fluorobis[1,2-bis(diphenylphosphino)ethane]molybdenum Tetrafluoroborate–Dichloromethane Solvate, $[Mo(N_2H_2)F(Ph_2PCH_2CH_2PPh_2)_2][BF_4]\cdot CH_2Cl_2$

MASANOBU HIDAI,* TERUYUKI KODAMA, MAKI SATO, MICHIHARU HARAKAWA,
and YASUZO UCHIDA

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The compound $[Mo(N_2H_2)F(Ph_2PCH_2CH_2PPh_2)_2][BF_4]\cdot CH_2Cl_2$ was prepared by the reaction of $[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ with excess aqueous fluoboric acid. The structure of the complex has been determined from three-dimensional x-ray counter data collected on a single crystal. The material crystallizes in space group D_2^4-$P2_12_12_1$ of the orthorhombic system with four formula units of the complex in a cell of dimensions $a = 18.966$ (7) Å, $b = 20.740$ (7) Å, $c = 13.362$ (5) Å, and $V = 5256.1$ Å^3. The structure has been refined by block-diagonal least-squares techniques to a final R index of 0.0841 based on 4992 reflections above background. The molybdenum atom has octahedral coordination with Mo–P = 2.541 (3) Å (average), Mo–F = 1.992 (8) Å, and Mo–N(1) = 1.762 (12) Å. The hydrazido(2–) ligand lies in a plane approximately perpendicular to the least-squares plane through the four phosphorus atoms. The N(1)–N(2) bond length is 1.333 (24) Å and the Mo–N(1)–N(2) angle is 176.4 (13)°. A hydrogen bond is observed between the hydrazido(2–) ligand and tetrafluoroborate anion.

Introduction

Recent extensive studies of the reactivity of molybdenum- and tungsten–dinitrogen complexes have disclosed that the end-on coordinated dinitrogen of these complexes reacts with mineral acids, acyl halides, and alkyl halides to give ammonia and several complexes containing a ligand derived from the dinitrogen ligand.[2] In a previous paper,[1] we reported the preparation of a new series of molybdenum–dinitrogen complexes of the type $[Mo(N_2)(RCN)(dpe)_2]$ (dpe = $Ph_2PCH_2CH_2PPh_2$), and formation of the benzoylazo complex $[MoCl(N_2COPh)(dpe)_2]$ from their reaction with benzoyl chloride. During the course of our studies on the reactions of these molybdenum–dinitrogen complexes with carbonium salts, we have found that the complex $[Mo(N_2H_2)F(dpe)_2][BF_4]\cdot CH_2Cl_2$ is prepared by the reaction of $[Mo(N_2)_2(dpe)_2]$ with excess aqueous fluoboric acid. Chatt and his co-workers have recently prepared a similar complex $[M(N_2H_2)F(dpe)_2][BF_4]$ (M = Mo or W) from $[M(N_2)_2(dpe)_2]$ (M = Mo or W) and anhydrous fluoboric acid in tetrahydrofuran.[3] In this paper we wish to describe the preparation and the molecular structure of $[Mo(N_2H_2)F(dpe)_2][BF_4]\cdot CH_2Cl_2$.[4]

Experimental Section

All reactions were carried out under an atmosphere of pure nitrogen. Solvents were dried and distilled under nitrogen. $[Mo(N_2)_2(dpe)_2]$ was prepared by the method described in a previous paper.[5] ^{31}P (40.5 MHz), ^1H (100 MHz), and ^{19}F (94 MHz) spectra were recorded on a computer-assisted JEOL PS-100 spectrometer.

Preparation of $[Mo(N_2H_2)F(dpe)_2][BF_4]\cdot CH_2Cl_2$. To a solution of $[Mo(N_2)_2(dpe)_2]$ (0.200 g, 0.211 mmol) in tetrahydrofuran (10 ml) was added 48% aqueous HBF_4 (116 μl, 0.850 mmol) at –40 °C. After the mixture was stirred at ambient temperature for about 20 h, addition of *n*-hexane yielded yellowish brown crystals. Recrystallization of these crystals from dichloromethane/*n*-hexane gave orange crystals, which were washed with *n*-hexane and dried in vacuo (0.159 g, 67.8% yield). Anal. Calcd for $C_{53}H_{52}N_2BF_5Cl_2P_4Mo$: C, 57.2; H, 4.7; N, 2.5; F, 8.5; Cl, 6.4. Found: C, 57.0; H, 4.8; N, 2.2; F, 7.7; Cl, 6.4.

Reaction of $[Mo(N_2)_2(dpe)_2]$ with $Et_3O^+BF_4^-$. To a solution of $[Mo(N_2)_2(dpe)_2]$ (0.480 g, 0.50 mmol) in dichloromethane (17 ml) was added $Et_3O^+BF_4^-$ (0.383 g, 2.0 mmol) at –40 °C. The solution

Table I. Crystallographic Data of $[Mo(N_2H_2)F(dpe)_2][BF_4]\cdot CH_2Cl_2$

a	18.966 (7) Å
b	20.740 (7) Å
c	13.362 (5) Å
V	5256.1 Å^3
Density (by flotation in aqueous potassium carbonate)	1.40 g/cm^3 (calcd) 1.35 (found)
Crystal dimensions	0.4 × 0.5 × 1.0 mm
Systematic absences	$h00$: $h = 2n + 1$ $0k0$: $k = 2n + 1$ $00l$: $l = 2n + 1$
Space group	$D_2{}^4$-$P2_12_12_1$ (orthorhombic)
μ	5.26 cm^{-1}
Scan	2θ-ω
2θ limits	$0° \leqslant 2\theta \leqslant 60°$
Backgrounds	Measd for 10 s at each end of the scan
Total data	8457
Unique data ($F_o{}^2 > 3\sigma(F_o{}^2)$)	4992
Final R	0.0841

was gradually warmed to room temperature. At around 15 °C the solution quickly changed from yellow to red. After 5 h of stirring at ambient temperature, *n*-hexane (40 ml) was added to the solution to give red crystals, which were rather sticky and were washed with a small amount of methanol at −78 °C. Recrystallization from dichloromethane/*n*-hexane afforded red crystals (0.236 g, yield 51.1%). Anal. Calcd for $C_{105}H_{100}N_2P_8Cl_4B_3F_{13}Mo_2$: C, 56.0; H, 4.5; N, 1.2; P, 11.0; F, 11.0; Cl, 6.3. Found: C, 56.7; H, 4.5; N, 1.6; P, 10.1; F, 10.3; Cl, 5.5.

From the filtrate were isolated orange crystals (0.052 g, yield 6.0%). Anal. Calcd for $C_{53}H_{52}N_2BF_5Cl_2P_4Mo$: C, 57.2; H, 4.7; N, 2.5; F, 8.5. Found: C, 57.0; H, 4.8; N, 2.6; F, 8.3. This complex was identical with the complex $[Mo(N_2H_2)F(dpe)_2][BF_4]\cdot CH_2Cl_2$ described above.

X-Ray Analysis for $[Mo(N_2H_2)F(dpe)_2][BF_4]\cdot CH_2Cl_2$.[6] Crystals were sealed in a Pyrex capillary under nitrogen. Intensity measurements were made with Mo Kα (0.7107 Å) radiation monochromatized by LiF, using a Rigaku automated diffractometer. Lorentz and polarization corrections were applied, but no absorption correction was made since μ was low. Table I shows the crystallographic data. The structure was solved by the heavy-atom method and refined by block-diagonal least squares using anisotropic temperature factors for nonhydrogen atoms. The quantity minimized was $w(|F_o| - k|F_c|)^2$ and the weighting scheme was $w = 0.7$ for $|F_o| < 18$, $w = 1.0$ for $18 \leq |F_o| < 75$, and $w = (75/|F_o|)^2$ for $|F_o| \geq 75$. The atomic scattering factors were taken from the usual tabulation[7a] and the anomalous terms for Mo, Cl, and P were those of Cromer and Liberman[7b] and were included in F_c. At this stage a difference-Fourier synthesis showed clear peaks of hydrogen atoms on carbons of phenyl rings and methylene groups of dpe. Furthermore two hydrogen peaks were observed for N(2), but no such peak was seen for N(1). Then we carried out block-diagonal least-squares calculations including positional parameters of hydrogen atoms while their temperature parameters were fixed at 5.0 Å^2.

Results and Discussion

Preparation and Spectroscopic Properties of $[Mo(N_2H_2)F(dpe)_2][BF_4]\cdot CH_2Cl_2$. Trialkyloxonium salts are well known to attack the nitrogen atom of organonitriles affording *N*-alkylnitrilium salts. Expecting the analogous attack of these electrophilic reagents on the terminal nitrogen atom of coordinated dinitrogen, we treated $[Mo(N_2)_2(dpe)_2]$ with triethyloxonium salt in dichloromethane. Though two kinds of crystalline compounds were obtained in moderate yields from this reaction, they had unexpected structures containing no ethyl group. The one is a red crystalline complex, the structure of which will be described in the Appendix. The other is an orange compound with the formula $[Mo(N_2H_2)F(dpe)_2][BF_4]\cdot CH_2Cl_2$. This complex is obtained in a higher yield from the reaction of $[Mo(N_2)_2(dpe)_2]$ with excess aqueous fluoboric acid. Presumably triethyloxonium tetrafluoroborate generates protons in some way, perhaps in a reaction with a trace of water, and yields the same compound. The complex shows the symmetric and asymmetric N–H stretching frequencies at 3350 and 3250 cm^{-1} respectively. The ^{1}H NMR spectrum shows a broad band at 5.2 ppm assigned to two hydrogen atoms attached to the terminal nitrogen. Sellman[8] has pointed out that the hydrogen atom attached to a nitrogen atom adjacent to a transition metal ion has an ^{1}H NMR resonance at much lower than 6 ppm. The ^{19}F NMR resonance shows a sharp band with a shoulder at 87.1 ppm above benzotrifluoride assigned to the tetrafluoroborate anion and a quintet band at 88.1 ppm (J_{F-P} = 30 Hz) in a ratio of about 4:1. These spectral features indicate that the N_2H_2 group is bound to the metal as a hydrazido(2−) group and this ligand and fluoride anion are trans to each other.

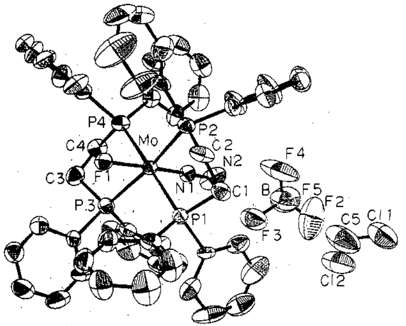
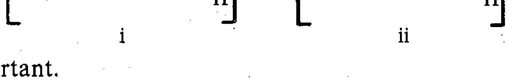


Figure 1. Perspective view of $[Mo(N_2H_2)F(dpe)_2][BF_4]\cdot CH_2Cl_2$. The shapes of the atoms in this drawing represent 50% probability contours of thermal motion.

Description of the Structure. The structure of $[Mo(N_2H_2)F(dpe)_2][BF_4]\cdot CH_2Cl_2$ consists of discrete cations, anions, and solvent molecules. The atomic positions are shown in Tables II and III and selected bond distances and angles in Table IV. The labeling scheme is shown in Figure 1. The shortest intermolecular contacts are H(114)···H(122) = 1.76 (27) Å, and the shortest C···H intermolecular contact is 2.43 (21) Å. The molybdenum atom is displaced by 0.124 Å above the plane defined by four phosphorus atoms in the direction of the hydrazido(2−) group. This is probably due to the steric hindrance of the hydrazido(2−) group toward the phenyl groups attached to the phosphorus atoms. The C–Cl distances in dichloromethane are 1.651 (49) and 1.756 (49) Å, and the Cl–C–Cl angle is 114.3 (28)°. It is hard to attach any significance to the result. The essential linearity of Mo–N(1)–N(2) linkage precludes protonation of N(1) and indicates the ligand as η^1-hydrazido(2−), which is compatible with the spectroscopic data. The N(1)–N(2) bond length 1.333 (24) Å indicates a bond order of aproximately 1.6 and the Mo–N(1) bond distance is consistent with considerable multiple bonding between the metal and ligand. From these results the two resonance structures can be considered where the contribution of canonical structure i would be more important.



$$\left[(dpe)_2FMo^{-}{=}N^{+}{=}N^{+}\begin{matrix}H\\ \\H\end{matrix}\right]^{+} \leftrightarrow \left[(dpe)_2FMo{\equiv}N^{+}{-}N\begin{matrix}H\\ \\H\end{matrix}\right]^{+}$$

i ii

The metal–ligand and intraligand bond lengths in several hydrazido(2−) complexes are shown in Table V. The N(1)–N(2) bond length of the hydrazido(2−)–tungsten complex $[W(N_2H_2)Cl(dpe)_2][BPh_4]$[9] is 1.37 (2) Å, which indicates a bond order of approximately 1.35. This suggests that the canonical structure of type ii is more important in contrast to the molybdenum complex above. These results are reflected on the ^{1}H NMR resonance spectra of the N proton. The tungsten complex shows a broad band due to the N proton

Table II. Positional and Thermal Parameters for the Nonhydrogen Atoms of $[Mo(N_2H_2)F(dpe)_2][BF_4]\cdot CH_2Cl_2$

Atom	x^a	y	z	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	1071(1)	1900(1)	1891(1)	156(2)	135(2)	298(4)	-10(5)	15(7)	-21(6)
Cl(1)	-1321(5)	147(4)	-1729(7)	870(38)	466(22)	1798(83)	-29(46)	-200(97)	654(75)
Cl(2)	-1872(4)	-1031(5)	-916(8)	627(32)	745(35)	2166(99)	-205(55)	-103(96)	1220(101)
P(1)	1532(2)	1730(2)	123(2)	200(9)	149(7)	334(16)	34(13)	41(21)	81(18)
P(2)	537(2)	813(2)	1455(3)	180(9)	143(7)	421(18)	-50(14)	-33(22)	-4(20)
P(3)	1390(2)	3069(2)	2173(2)	223(9)	147(7)	449(18)	-12(16)	27(21)	-43(22)
P(4)	588(2)	2081(2)	3655(2)	239(10)	191(8)	286(16)	-70(15)	-1(22)	-68(19)
F(1)	179(4)	2260(4)	1337(6)	179(20)	205(19)	452(44)	-3(33)	-61(52)	55(50)
F(2)	4510(11)	540(9)	2559(16)	967(90)	804(79)	2287(213)	529(145)	-322(249)	-1505(220)
F(3)	3961(7)	1432(6)	2933(11)	483(42)	501(41)	1501(125)	46(78)	21(148)	817(123)
F(4)	3554(8)	525(8)	3555(18)	491(54)	721(67)	3557(300)	-340(98)	-396(213)	2278(252)
F(5)	4565(7)	920(8)	4090(11)	4967(50)	752(63)	1250(118)	39(97)	-323(133)	429(148)
N(1)	1869(6)	1599(6)	2381(8)	171(29)	241(31)	397(63)	135(51)	-98(73)	210(74)
N(2)	2478(7)	1408(10)	2779(12)	260(44)	716(77)	685(105)	293(96)	-84(113)	577(149)
C(1)	1399(8)	859(6)	-178(10)	316(46)	162(31)	419(78)	-17(63)	45(103)	-37(84)
C(2)	645(8)	704(7)	116(11)	359(51)	186(34)	444(81)	-197(71)	35(112)	55(90)
C(3)	872(8)	3330(7)	3248(13)	307(50)	215(35)	702(112)	28(66)	176(125)	-249(108)
C(4)	943(8)	2854(7)	4105(11)	299(50)	216(34)	451(81)	-109(67)	-68(105)	-245(88)
C(5)	-1134(17)	-568(16)	-1255(36)	565(109)	667(121)	3464(568)	-96(211)	-570(473)	1525(456)
C(111)	2473(6)	1841(7)	-31(9)	178(31)	203(33)	450(71)	-27(60)	179(81)	211(94)
C(112)	2733(9)	2397(9)	-544(14)	307(56)	344(55)	688(121)	66(90)	212(140)	-240(137)
C(113)	3460(10)	2493(13)	-613(16)	305(63)	646(90)	841(157)	-458(126)	276(167)	137(204)
C(114)	3914(10)	2072(11)	-150(15)	236(46)	612(82)	942(140)	-76(120)	77(169)	31(182)
C(115)	3671(10)	1548(13)	372(16)	299(61)	676(95)	850(147)	48(124)	-112(161)	-446(199)
C(116)	2945(8)	1439(9)	434(12)	259(47)	397(57)	433(87)	91(86)	53(109)	202(119)
C(121)	1134(8)	2124(6)	-951(9)	290(43)	204(31)	264(56)	-50(67)	30(96)	-36(69)
C(122)	696(9)	2658(8)	-821(11)	316(53)	270(44)	434(87)	118(81)	32(115)	-105(103)
C(123)	399(9)	2944(9)	-1645(13)	316(52)	350(55)	736(123)	304(89)	54(131)	100(129)
C(124)	538(11)	2749(8)	-2599(12)	510(73)	326(53)	470(97)	245(107)	-362(148)	32(116)
C(125)	995(14)	2236(11)	-2752(13)	798(109)	474(70)	410(91)	357(160)	-262(191)	-350(134)
C(126)	1282(11)	1925(10)	-1942(13)	672(90)	351(51)	538(94)	248(123)	-202(167)	-448(150)
C(211)	969(7)	104(6)	1992(11)	251(41)	148(26)	497(78)	14(54)	10(105)	-79(83)
C(212)	1316(10)	165(7)	2909(12)	529(73)	191(36)	648(110)	20(82)	-303(144)	123(103)
C(213)	1648(14)	-387(9)	3343(17)	830(121)	225(48)	1096(185)	163(130)	-511(255)	251(152)
C(214)	1624(11)	-969(8)	2857(15)	506(74)	240(43)	862(145)	274(95)	-108(173)	341(130)
C(215)	1262(9)	-1028(7)	1997(15)	378(59)	201(36)	883(130)	64(73)	-56(155)	27(127)
C(216)	937(9)	-497(7)	1519(14)	405(65)	193(37)	851(129)	80(80)	-87(152)	-10(116)
C(221)	-412(7)	652(5)	1649(11)	287(44)	85(24)	599(93)	-138(53)	104(103)	-59(73)
C(222)	-626(10)	405(11)	2548(18)	277(58)	420(68)	1314(191)	210(107)	70(180)	331(191)
C(223)	-1344(12)	319(11)	2745(22)	537(89)	377(67)	1808(269)	8(125)	1059(258)	731(218)
C(224)	-1814(9)	432(11)	1984(19)	218(50)	546(78)	1239(185)	-278(105)	311(185)	-145(228)
C(225)	-1606(11)	714(18)	1120(20)	294(68)	1125(158)	1036(203)	-117(183)	-265(202)	-286(313)
C(226)	-875(9)	799(15)	926(17)	204(49)	891(122)	858(160)	-167(129)	-45(146)	-104(241)
C(311)	2313(7)	3228(6)	2520(10)	229(38)	172(35)	478(77)	-63(58)	-52(92)	158(84)
C(312)	2839(8)	2908(8)	2052(12)	237(41)	328(49)	631(108)	-126(71)	-27(113)	-263(118)
C(313)	3559(9)	3010(9)	2267(16)	312(53)	315(55)	1135(155)	-174(94)	-0(155)	-197(156)
C(314)	3719(9)	3452(9)	2981(17)	347(59)	308(49)	1098(164)	-242(86)	-186(173)	359(159)
C(315)	3179(11)	3793(9)	3509(17)	458(72)	324(55)	1053(171)	-278(106)	-547(192)	-367(161)
C(316)	2476(10)	3679(8)	3278(13)	420(60)	251(43)	561(121)	-91(83)	-159(142)	-97(114)
C(321)	1193(7)	3679(6)	1207(10)	259(43)	126(26)	462(76)	80(54)	156(94)	-52(75)
C(322)	477(7)	3879(6)	1083(12)	172(37)	165(32)	762(110)	-103(58)	-95(106)	-77(97)
C(323)	336(8)	4319(8)	312(13)	267(48)	216(39)	795(121)	-2(71)	-30(129)	6(115)
C(324)	836(10)	4529(10)	-325(15)	363(62)	375(59)	906(145)	65(98)	44(156)	584(159)
C(325)	1529(10)	4319(12)	-185(19)	331(64)	614(88)	1371(214)	236(125)	701(204)	950(159)
C(326)	1700(9)	3895(9)	585(14)	275(50)	313(50)	842(125)	-60(84)	360(137)	359(133)
C(411)	-378(7)	2194(6)	3874(11)	216(39)	179(32)	521(88)	-39(58)	116(98)	-107(88)
C(412)	-833(7)	2022(8)	3142(13)	231(38)	401(55)	631(94)	-100(75)	207(120)	-350(143)
C(413)	-1567(8)	2121(8)	3272(13)	232(43)	337(48)	774(124)	-38(74)	327(127)	-32(127)
C(414)	-1800(9)	2368(8)	4170(15)	241(50)	296(48)	925(138)	132(82)	489(144)	168(134)
C(415)	-1320(9)	2547(10)	4928(16)	304(58)	359(53)	877(139)	212(92)	476(154)	-118(145)
C(416)	-617(10)	2468(9)	4753(12)	387(63)	339(51)	545(104)	148(95)	220(136)	-244(122)
C(421)	873(7)	1531(7)	4616(9)	295(46)	238(35)	155(53)	53(64)	9(79)	-115(73)
C(422)	1592(8)	1473(8)	4827(11)	234(43)	297(43)	464(83)	144(72)	-182(105)	-114(102)
C(423)	1835(10)	1030(10)	5542(12)	469(70)	405(62)	447(98)	164(109)	-544(143)	-363(133)
C(424)	1400(12)	646(9)	6020(13)	669(98)	297(51)	467(95)	105(117)	-116(161)	57(115)
C(425)	641(11)	692(9)	5849(16)	493(78)	294(53)	891(145)	-232(109)	-136(181)	126(148)
C(426)	398(10)	1114(8)	5124(12)	435(65)	225(40)	535(96)	-159(84)	-0(136)	-18(106)
B	4135(11)	830(12)	3302(20)	349(66)	391(71)	1047(209)	-56(110)	-409(191)	610(209)

[a] The quantities given in the table are the posisional coefficients X 10^4.

[b] The form of the anisotropic thermal ellipsoid is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$. The quantities given in the table are the thermal coefficients X 10^5.

Table III. Positional Parameters for the Hydrogen Atoms of $[Mo(N_2H_2)F(dpe)_2][BF_4]\cdot CH_2Cl_2$

Atom	x^a	y	z
H(11)	173 (9)	49 (8)	23 (13)
H(12)	156 (9)	88 (9)	−108 (14)
H(21)	29 (9)	91 (9)	−34 (14)
H(22)	54 (9)	24 (9)	4 (14)
H(31)	38 (9)	327 (8)	297 (14)
H(32)	106 (10)	373 (8)	351 (14)
H(41)	137 (9)	295 (9)	445 (14)
H(42)	75 (9)	308 (9)	467 (13)
H(112)	236 (9)	267 (9)	−68 (14)
H(113)	365 (10)	278 (9)	−113 (14)
H(114)	467 (9)	196 (9)	−10 (14)
H(115)	412 (9)	116 (9)	91 (14)
H(116)	269 (9)	100 (9)	87 (14)
H(122)	57 (9)	282 (8)	−1 (14)
H(123)	12 (9)	336 (9)	−159 (14)
H(124)	5 (10)	297 (9)	−322 (14)
H(125)	132 (10)	211 (9)	−351 (14)
H(126)	165 (9)	174 (8)	−204 (14)
H(212)	107 (10)	83 (9)	305 (15)
H(213)	188 (10)	−26 (9)	400 (15)
H(214)	206 (9)	−137 (9)	296 (15)
H(215)	129 (9)	−148 (9)	151 (14)
H(216)	72 (10)	−39 (9)	82 (14)
H(222)	11 (10)	35 (9)	311 (16)
H(223)	−176 (10)	36 (9)	316 (15)
H(224)	−246 (10)	23 (9)	198 (15)
H(225)	−189 (10)	99 (9)	38 (14)
H(226)	−58 (9)	106 (9)	33 (14)
H(312)	279 (9)	264 (9)	145 (14)
H(313)	387 (10)	282 (9)	189 (15)
H(314)	439 (9)	372 (8)	311 (15)
H(315)	345 (9)	398 (9)	407 (14)
H(316)	225 (9)	391 (9)	377 (14)
H(322)	9 (10)	378 (9)	187 (16)
H(323)	−27 (10)	448 (9)	28 (15)
H(324)	72 (10)	470 (9)	−89 (15)
H(325)	192 (10)	439 (10)	−52 (15)
H(326)	208 (11)	390 (10)	61 (16)
H(412)	−65 (10)	183 (10)	250 (14)
H(413)	−191 (9)	194 (10)	260 (13)
H(414)	−224 (10)	248 (10)	445 (15)
H(415)	−156 (10)	273 (9)	545 (15)
H(416)	−40 (10)	241 (10)	527 (15)
H(422)	200 (10)	176 (10)	440 (14)
H(423)	237 (10)	100 (10)	569 (15)
H(424)	148 (10)	33 (9)	666 (15)
H(425)	32 (10)	30 (10)	629 (16)
H(426)	−15 (10)	112 (9)	503 (15)
H(51)	−103 (11)	−60 (9)	−82 (15)
H(52)	−109 (11)	−94 (9)	−186 (16)
HN(1)	302 (11)	140 (10)	278 (16)
HN(2)	277 (11)	108 (10)	339 (16)

[a] The quantities given in the table are the positional coefficents $\times 10^3$.

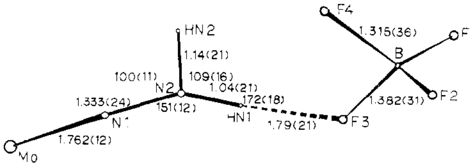


Figure 2. Hydrogen bond distances (Å) and angles (deg).

at 3.0 ppm,[2a] while the molybdenum complex shows a broad band at 5.2 ppm as described above.

The F(3) atom of the BF_4 anion makes a hydrogen bond to HN(1) and other fluorine atoms make no hydrogen bond, as shown in Figure 2. The bond length F(3)···HN(1) is 1.79 (21) Å and the N(2)–HN(1)–F(3) angle is 172 (18)°, while Mo, N(1), N(2), HN(1), and HN(2) atoms lie on the same plane. The BF_4 anion shows slight distortion from idealized tetrahedral symmetry. The B–F(3) distance 1.382 (31) Å is slightly longer than the other B–F distances (1.315 (36)–1.362 (34) Å). Though fewer data are available on NH···F systems than on OH hydrogen bonds, these data are compatible with the hydrogen-bond data observed in the case of $[Pt(P(C_2H_5)_3)_2(H_2NNHC_6H_4F)Cl][BF_4]$[10] and $LiN_2H_5BeF_4$.[11]

Appendix

The red complex, which is obtained from the reaction of $[Mo(N_2)_2(dpe)_2]$ with triethyloxonium salt in dichloro-

Table IV. Interatmic Distances (Å) and Angles (deg) in $[Mo(N_2H_2)F(dpe)_2][BF_4]\cdot CH_2Cl_2$

Atoms	Distance	Atoms	Angle
Mo–N(1)	1.762 (12)	N(1)–Mo–P(1)	90.1 (4)
Mo–P(1)	2.542 (3)	N(1)–Mo–P(2)	96.5 (4)
Mo–P(2)	2.539 (4)	N(1)–Mo–P(3)	94.5 (4)
Mo–P(3)	2.527 (4)	N(1)–Mo–P(4)	91.0 (4)
Mo–P(4)	2.557 (4)	N(1)–Mo–F(1)	178.7 (5)
Mo–F(1)	1.992 (8)	F(1)–Mo–P(1)	89.9 (2)
N(1)–N(2)	1.333 (24)	F(1)–Mo–P(2)	84.8 (2)
P(1)–C(1)	1.868 (15)	F(1)–Mo–P(3)	84.2 (2)
P(1)–C(111)	1.812 (15)	F(1)–Mo–P(4)	89.0 (2)
P(1)–C(121)	1.816 (16)	P(1)–Mo–P(2)	78.5 (1)
P(2)–C(2)	1.814 (16)	P(3)–Mo–P(4)	78.9 (1)
P(2)–C(211)	1.829 (15)	P(1)–Mo–P(3)	100.9 (1)
P(2)–C(221)	1.850 (15)	P(2)–Mo–P(4)	101.5 (1)
P(3)–C(3)	1.827 (18)	P(1)–Mo–P(4)	178.9 (1)
P(3)–C(311)	1.840 (14)	P(2)–Mo–P(3)	169.0 (1)
P(3)–C(321)	1.846 (14)	Mo–N(1)–N(2)	176.4 (13)
P(4)–C(4)	1.840 (15)	Cl(1)–C(5)–Cl(2)	114.3 (28)
P(4)–C(411)	1.870 (15)	F(2)–B–F(3)	105.3 (21)
P(4)–C(421)	1.802 (15)	F(2)–B–F(4)	114.3 (24)
C(5)–Cl(1)	1.651 (49)	F(2)–B–F(5)	108.4 (22)
C(5)–Cl(2)	1.756 (49)	F(3)–B–F(4)	109.0 (22)
B–F(2)	1.362 (34)	F(3)–B–F(5)	107.4 (21)
B–F(3)	1.382 (31)	F(4)–B–F(5)	112.0 (23)
B–F(4)	1.315 (36)		
B–F(5)	1.345 (36)		
N(2)–HN(1)	1.04 (21)	N(1)–N(2)–HN(1)	151 (12)
N(2)–HN(2)	1.14 (21)	N(1)–N(2)–HN(2)	100 (11)
		HN(1)–N(2)–HN(2)	109 (16)
F(3)· · ·HN(1)	1.79 (21)	N(2)–HN(1)· · ·F(3)	172 (18)
F(3)· · ·HN(2)	3.34 (21)		
F(4)· · ·HN(1)	2.32 (21)		
F(4)· · ·HN(2)	2.69 (21)		

Table V. Metal–Ligand and Intraligand Bond Lengths and Angles in Hydrazido(2–) Complexes

	M–N(1), Å	N(1)–N(2), Å	M–N(1)–N(2), deg
$[Mo(N_2H_2)F(dpe)_2]$-$[BF_4]\cdot CH_2Cl_2$[a]	1.762 (12)	1.333 (24)	176.4 (13)
$[W(N_2H_2)Cl(dpe)_2]$-$[BPh_4]$[b]	1.73 (1)	1.37 (2)	171 (1)
$[ReCl_2(NH_3)(N_2HPh)$-$(P(CH_3)_2Ph)_2][Br]$[c]	1.750 (12)	1.28 (2)	172 (1)
$[W(N_2HCH_3)Br(dpe)_2]$-$[Br]$[d]	1.768 (14)	1.32 (2)	174 (1)
$[Mo(S_2CN(CH_2)_5)_3$-$(N_2(C_2H_5)Ph)][BPh_4]$[d]	1.715 (16)	1.37 (2)	170 (2)

[a] This work. [b] Reference 9. [c] R. Mason, K. M. Thomas, J. A. Zubieta, P. G. Douglas, A. R. Golbraith, and B. L. Shaw, *J. Am. Chem. Soc.*, 96, 260 (1974). [d] F. C. March, R. Mason, and K. M. Thomas, *J. Organomet. Chem.*, 96, C43 (1975).

methane, has the formula $[Mo(N_2H_x)F(dpe)_2][MoCl_2(dpe)_2][BF_4]_3\cdot CH_2Cl_2$. X-ray analysis shows that there are two different compounds in a unit cell where one is a compound with two chloride ions in a trans position and the other is a compound containing the Mo–N–N linkage. Unfortunately the complex considerably shows disorder in crystals, so refinement is very difficult. The infrared spectrum shows a weak band at 3250 cm^{-1} assigned to the N–H stretching frequency. The phosphorus NMR spectrum shows a doublet band at 51 ppm (J_{F-P} = 30 Hz) below triphenylphosphine, whereas the fluorine NMR spectrum shows a quintet band at 97 ppm (J_{F-P} = 30 Hz) above benzotrifluoride, integrating for one fluorine, as well as bands at 83.5, 85, and 90 ppm assigned to undissociated and dissociated tetrafluoroborate anions. These data, in addition to the results of x-ray analysis, indicate the presence of the diamagnetic moiety $[Mo(N_2H_x)F(dpe)_2]$ in which the fluoride anion attached to molybdenum is all-cis to four phosphorus atoms of two dpe ligands. Since we have been unable to detect the ^1H NMR resonance of the N proton, we have been unable to assign its position and determine its number.

Registry No. $[Mo(N_2H_2)F(dpe)_2][BF_4]\cdot CH_2Cl_2$, 60104-25-8; $[Mo(N_2)_2(dpe)_2]$, 25145-64-6.

Supplementary Material Available: Table VI, a listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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