Electronic Supplementary Information

Molybdenum dinitrogen complexes supported by a silicon-centred tripod ligand and dppm or dmpm: Tuning the activation of N_2

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Crystal Structure of $[Mo(N_2)(SiP_3)(dppm)]$ (2):

Crystals suitable for X-ray crystal structure determination were obtained by slow diffusion of a 1:1 mixture of diethyl ether and *n*-hexane into a concentrated benzene solution of **2** in tetrahydrofuran over a period of 4 days.

CCDC-960643 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/.

Table 1. Crystal data and structure refinement for felix88.

Identification code	felix88	
Empirical formula	$C_{35}H_{49}MoN_2P_5Si$	
Formula weight	776.64	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.6764(8) Å	α= 90°.
	b = 18.1037(10) Å	β= 92.519(7)°.
	c = 16.6070(9) Å	γ = 90°.
Volume	3807.5(4) $Å^3$	
Z	4	
Density (calculated)	1.355 Mg/m^3	
Absorption coefficient	0.613 mm^{-1}	
F(000)	1616	
Crystal size	0.13 x 0.10 x 0.07 mm^3	
Theta range for data collection	2.35 to 27.00°.	
Index ranges	-16<=h<=16, -23<=k<=23, -21<=l<=21	
Reflections collected	40294	
Independent reflections	8037 [R(int) = 0.0626]	
Completeness to theta = 27.00°	96.7 %	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	8037 / 0 / 405
Goodness-of-fit on F^2	1.012
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0867
R indices (all data)	R1 = 0.0468, wR2 = 0.0920
Extinction coefficient	0.0063(5)
Largest diff. peak and hole	0.527 and -0.926 e.$Å^{-3}$

Remarks:
All non-hydrogen were refined anisotropic. All H atoms were located in difference map but were positioned with idealized geometry and refined using a riding model. A numerical absorption correction swas performed (Tmin/max: 0.8823/0.9469).

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Mo(1)	6378(1)	7274(1)	8257(1)	16(1)
N(1)	7190(2)	7908(2)	7427(2)	32(1)
N(2)	7545(3)	8215(2)	7073(2)	50(1)
P(1)	6017(1)	6330(1)	7243(1)	19(1)
C(1)	7284(2)	5825(1)	7370(1)	23(1)
P(2)	7787(1)	6340(1)	8276(1)	19(1)
C(11)	5012(2)	5594(1)	7281(2)	24(1)
C(12)	5155(3)	4975(2)	7768(2)	39(1)
C(13)	4351(3)	4456(2)	7822(2)	54(1)
C(14)	3414(3)	4542(2)	7396(2)	55(1)
C(15)	3255(2)	5153(2)	6907(2)	45(1)
C(16)	4044(2)	5675(2)	6853(2)	32(1)
C(21)	5942(2)	6476(1)	6143(1)	24(1)
C(22)	5944(2)	5876(2)	5617(2)	33(1)
C(23)	5948(3)	5979(2)	4791(2)	44(1)
C(24)	5953(3)	6682(2)	4479(2)	48(1)
C(25)	5945(3)	7285(2)	4988(2)	44(1)
C(26)	5947(2)	7184(2)	5820(2)	32(1)
C(31)	9169(2)	6493(1)	7995(2)	23(1)
C(32)	9548(2)	7192(2)	7830(2)	36(1)
C(33)	10560(2)	7280(2)	7545(2)	46(1)
C(34)	11197(2)	6679(2)	7429(2)	45(1)
C(35)	10835(2)	5983(2)	7605(2)	45(1)
C(36)	9833(2)	5893(2)	7881(2)	36(1)
C(41)	8072(2)	5622(1)	9046(2)	24(1)
C(42)	8534(3)	5853(2)	9780(2)	39(1)
C(43)	8752(3)	5346(2)	10393(2)	51(1)
C(44)	8518(3)	4608(2)	10286(2)	48(1)
C(45)	8083(2)	4373(2)	9562(2)	39(1)
C(46)	7866(2)	4876(1)	8945(2)	30(1)
Si(1)	4739(1)	8315(1)	9813(1)	34(1)
C(51)	3943(3)	8808(2)	10562(2)	55(1)
C(52)	4932(2)	7325(2)	10122(2)	36(1)
P(3)	5288(1)	6708(1)	9293(1)	26(1)
C(53)	5728(3)	5902(2)	9886(2)	43(1)
C(54)	3954(2)	6377(2)	8984(2)	42(1)
C(55)	4037(2)	8358(2)	8795(2)	35(1)
P(4)	4870(1)	8067(1)	7961(1)	24(1)
C(56)	3838(2)	7786(2)	7210(2)	39(1)
C(57)	5175(3)	8981(2)	7541(2)	41(1)
C(58)	6069(2)	8752(2)	9748(2)	36(1)
P(5)	7052(1)	8148(1)	9277(1)	25(1)
C(59)	7997(3)	8853(2)	8971(2)	47(1)
C(60)	7781(3)	7818(2)	10187(2)	45(1)

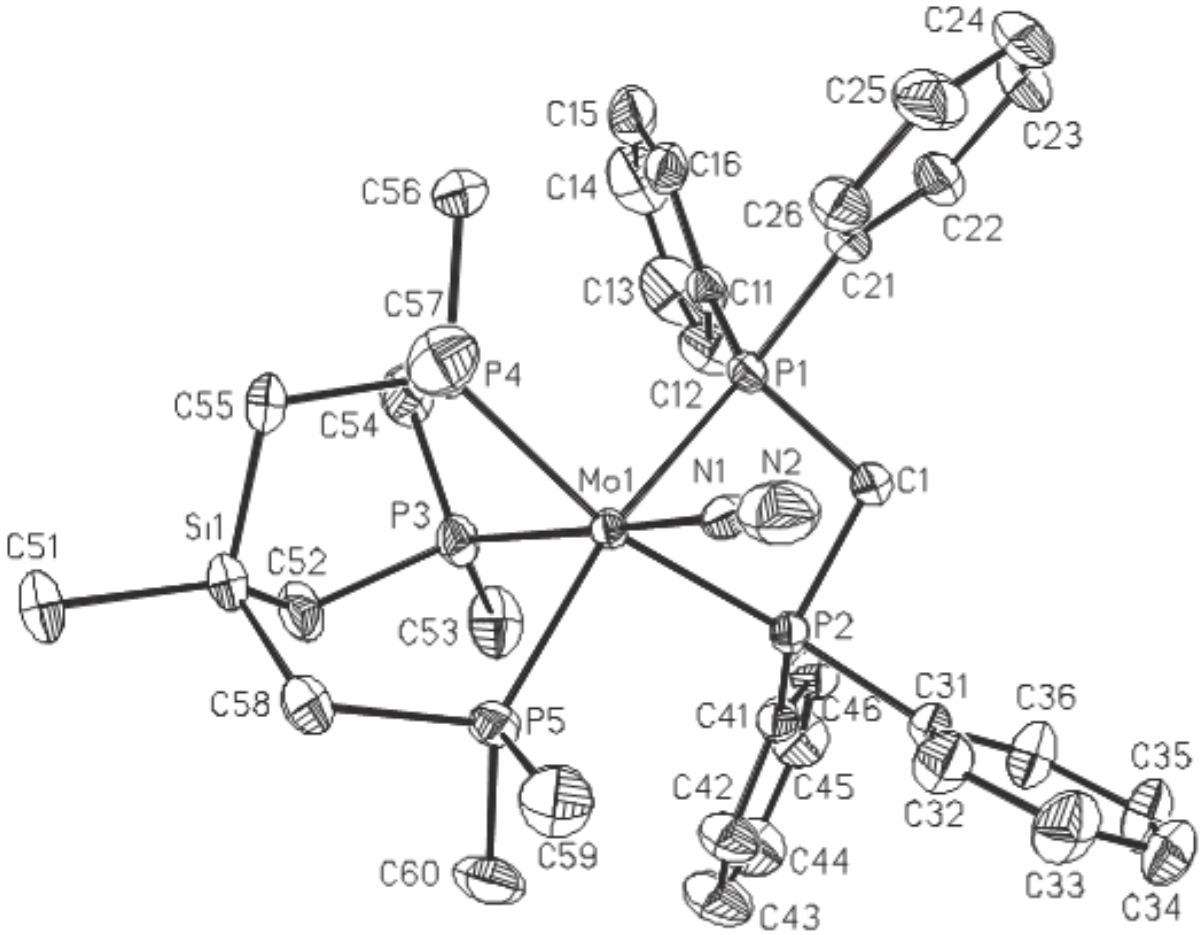


Figure 1: Crystal structure (50 % probability ellipsoids) of [Mo(N_2)(SiP_3)(dppm)] (2).

Table 3. Bond lengths [Å] and angles [°].

Mo(1)-N(1)	2.099(3)	Mo(1)-P(5)	2.4443(6)
Mo(1)-P(4)	2.4236(6)	Mo(1)-P(2)	2.4596(6)
Mo(1)-P(1)	2.4293(6)	Mo(1)-P(3)	2.4741(7)
N(1)-N(2)	0.938(4)	P(4)-Mo(1)-P(2)	167.37(2)
N(1)-Mo(1)-P(4)	87.04(6)	P(1)-Mo(1)-P(2)	68.83(2)
N(1)-Mo(1)-P(1)	90.72(6)	P(5)-Mo(1)-P(2)	101.83(2)
P(4)-Mo(1)-P(1)	98.81(2)	N(1)-Mo(1)-P(3)	171.15(6)
N(1)-Mo(1)-P(5)	86.23(6)	P(4)-Mo(1)-P(3)	85.82(2)
P(4)-Mo(1)-P(5)	90.35(2)	P(1)-Mo(1)-P(3)	95.52(2)
P(1)-Mo(1)-P(5)	170.19(2)	P(5)-Mo(1)-P(3)	88.60(2)
N(1)-Mo(1)-P(2)	90.40(6)	P(2)-Mo(1)-P(3)	97.69(2)
N(2)-N(1)-Mo(1)	176.8(3)		
C(21)-P(1)-Mo(1)	125.82(8)	C(41)-P(2)-Mo(1)	127.74(8)
C(11)-P(1)-Mo(1)	126.40(8)	C(31)-P(2)-Mo(1)	126.00(8)
C(1)-P(1)-Mo(1)	97.61(7)	C(1)-P(2)-Mo(1)	96.43(7)
C(53)-P(3)-Mo(1)	122.49(10)	C(60)-P(5)-Mo(1)	120.51(10)
C(52)-P(3)-Mo(1)	115.49(10)	C(59)-P(5)-Mo(1)	118.07(11)
C(54)-P(3)-Mo(1)	118.31(11)	C(58)-P(5)-Mo(1)	116.89(9)

Table 3. Bond lengths [Å] and angles [°].

P(1)-C(21)	1.844(2)	C(1)-P(2)	1.858(2)
P(1)-C(11)	1.846(2)	P(2)-C(41)	1.847(2)
P(1)-C(1)	1.852(2)	P(2)-C(31)	1.853(2)
C(11)-C(12)	1.388(4)	C(31)-C(32)	1.385(4)
C(11)-C(16)	1.399(4)	C(31)-C(36)	1.393(3)
C(12)-C(13)	1.392(4)	C(32)-C(33)	1.397(4)
C(13)-C(14)	1.365(6)	C(33)-C(34)	1.374(5)
C(14)-C(15)	1.381(5)	C(34)-C(35)	1.377(5)
C(15)-C(16)	1.382(4)	C(35)-C(36)	1.378(4)
C(21)-C(26)	1.389(4)	C(41)-C(46)	1.384(3)
C(21)-C(22)	1.395(3)	C(41)-C(42)	1.393(4)
C(22)-C(23)	1.385(4)	C(42)-C(43)	1.389(4)
C(23)-C(24)	1.375(5)	C(43)-C(44)	1.378(5)
C(24)-C(25)	1.382(5)	C(44)-C(45)	1.369(5)
C(25)-C(26)	1.393(4)	C(45)-C(46)	1.390(4)
C(21)-P(1)-C(11)	97.62(11)	C(23)-C(24)-C(25)	120.1(3)
C(21)-P(1)-C(1)	100.95(11)	C(24)-C(25)-C(26)	120.2(3)
C(11)-P(1)-C(1)	103.64(11)	C(21)-C(26)-C(25)	120.3(3)
P(1)-C(1)-P(2)	96.29(11)	C(32)-C(31)-C(36)	117.9(2)
C(41)-P(2)-C(31)	96.96(11)	C(32)-C(31)-P(2)	121.78(19)
C(41)-P(2)-C(1)	104.91(11)	C(36)-C(31)-P(2)	120.08(19)
C(31)-P(2)-C(1)	99.56(11)	C(31)-C(32)-C(33)	120.3(3)
C(12)-C(11)-C(16)	118.1(2)	C(34)-C(33)-C(32)	120.7(3)
C(12)-C(11)-P(1)	122.0(2)	C(33)-C(34)-C(35)	119.4(3)
C(16)-C(11)-P(1)	119.8(2)	C(34)-C(35)-C(36)	120.0(3)
C(11)-C(12)-C(13)	120.3(3)	C(35)-C(36)-C(31)	121.6(3)
C(14)-C(13)-C(12)	120.8(3)	C(46)-C(41)-C(42)	117.9(2)
C(13)-C(14)-C(15)	119.8(3)	C(46)-C(41)-P(2)	124.88(19)
C(14)-C(15)-C(16)	119.9(3)	C(42)-C(41)-P(2)	117.2(2)
C(15)-C(16)-C(11)	121.0(3)	C(43)-C(42)-C(41)	120.4(3)
C(26)-C(21)-C(22)	118.5(2)	C(44)-C(43)-C(42)	120.8(3)
C(26)-C(21)-P(1)	120.98(19)	C(45)-C(44)-C(43)	119.4(3)
C(22)-C(21)-P(1)	120.5(2)	C(44)-C(45)-C(46)	120.2(3)
C(23)-C(22)-C(21)	121.1(3)	C(41)-C(46)-C(45)	121.3(3)
C(24)-C(23)-C(22)	119.9(3)		
Si(1)-C(51)	1.864(3)	Si(1)-C(52)	1.876(3)
Si(1)-C(58)	1.871(3)	Si(1)-C(55)	1.877(3)
C(52)-P(3)	1.845(3)	P(4)-C(57)	1.844(3)
P(3)-C(53)	1.834(3)	C(58)-P(5)	1.856(3)
P(3)-C(54)	1.846(3)	P(5)-C(60)	1.835(3)
C(55)-P(4)	1.855(3)	P(5)-C(59)	1.838(3)
P(4)-C(56)	1.840(3)	P(4)-C(55)-Si(1)	113.44(14)
C(51)-Si(1)-C(58)	110.55(15)	C(56)-P(4)-C(57)	98.48(15)
C(51)-Si(1)-C(52)	110.05(17)	C(56)-P(4)-C(55)	100.00(14)
C(58)-Si(1)-C(52)	108.23(14)	C(57)-P(4)-C(55)	99.42(15)
C(51)-Si(1)-C(55)	109.43(15)	C(56)-P(4)-Mo(1)	120.31(10)
C(58)-Si(1)-C(55)	108.86(14)	C(57)-P(4)-Mo(1)	115.56(10)
C(52)-Si(1)-C(55)	109.70(13)	C(55)-P(4)-Mo(1)	119.10(9)
P(3)-C(52)-Si(1)	114.04(15)	P(5)-C(58)-Si(1)	113.47(13)
C(53)-P(3)-C(52)	99.19(14)	C(60)-P(5)-C(59)	98.20(17)
C(53)-P(3)-C(54)	98.25(16)	C(60)-P(5)-C(58)	99.70(15)
C(52)-P(3)-C(54)	98.79(14)	C(59)-P(5)-C(58)	99.47(14)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

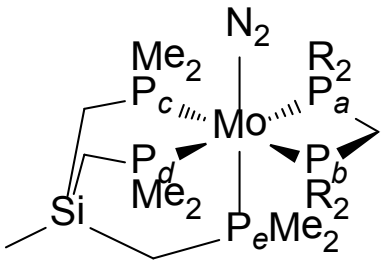
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	16(1)	17(1)	16(1)	-1(1)	2(1)	-1(1)
N(1)	19(1)	40(1)	35(1)	-15(1)	-7(1)	6(1)
N(2)	51(2)	49(2)	48(2)	1(1)	-13(2)	7(1)
P(1)	20(1)	20(1)	17(1)	-2(1)	1(1)	-1(1)
C(1)	23(1)	26(1)	21(1)	-3(1)	1(1)	3(1)
P(2)	19(1)	20(1)	18(1)	0(1)	2(1)	1(1)
C(11)	25(1)	24(1)	23(1)	-8(1)	5(1)	-6(1)
C(12)	47(2)	35(1)	34(2)	1(1)	-1(1)	-14(1)
C(13)	72(2)	43(2)	47(2)	2(1)	12(2)	-27(2)
C(14)	52(2)	60(2)	54(2)	-18(2)	17(2)	-37(2)
C(15)	26(1)	61(2)	49(2)	-24(2)	9(1)	-13(1)
C(16)	23(1)	38(1)	35(2)	-13(1)	4(1)	-3(1)
C(21)	24(1)	32(1)	17(1)	-2(1)	1(1)	2(1)
C(22)	38(1)	36(1)	25(1)	-7(1)	2(1)	4(1)
C(23)	49(2)	59(2)	24(1)	-13(1)	3(1)	3(1)
C(24)	48(2)	78(2)	18(1)	3(1)	2(1)	1(2)
C(25)	51(2)	51(2)	31(2)	11(1)	-3(1)	-2(1)
C(26)	37(1)	31(1)	27(1)	3(1)	-1(1)	0(1)
C(31)	19(1)	28(1)	22(1)	-1(1)	2(1)	2(1)
C(32)	32(1)	28(1)	48(2)	-5(1)	4(1)	-4(1)
C(33)	36(2)	39(2)	63(2)	-2(1)	10(2)	-15(1)
C(34)	25(1)	60(2)	51(2)	-5(2)	12(1)	-8(1)
C(35)	31(2)	47(2)	58(2)	0(1)	16(1)	10(1)
C(36)	31(1)	32(1)	47(2)	4(1)	13(1)	5(1)
C(41)	23(1)	28(1)	22(1)	3(1)	3(1)	4(1)
C(42)	48(2)	38(2)	29(1)	1(1)	-7(1)	1(1)
C(43)	68(2)	56(2)	28(2)	4(1)	-13(2)	3(2)
C(44)	58(2)	51(2)	34(2)	20(1)	-2(2)	4(2)
C(45)	43(2)	33(1)	40(2)	12(1)	3(1)	-1(1)
C(46)	33(1)	29(1)	26(1)	5(1)	1(1)	1(1)
Si(1)	33(1)	41(1)	28(1)	-13(1)	5(1)	8(1)
C(51)	50(2)	72(2)	43(2)	-27(2)	10(2)	16(2)
C(52)	40(2)	46(2)	24(1)	-6(1)	12(1)	0(1)
P(3)	27(1)	29(1)	23(1)	-1(1)	9(1)	-4(1)
C(53)	54(2)	40(2)	37(2)	14(1)	21(1)	-1(1)
C(54)	30(1)	58(2)	40(2)	-10(1)	14(1)	-17(1)
C(55)	29(1)	44(2)	34(2)	-10(1)	6(1)	12(1)
P(4)	21(1)	26(1)	24(1)	-3(1)	-1(1)	4(1)
C(56)	27(1)	54(2)	35(2)	-12(1)	-7(1)	9(1)
C(57)	43(2)	32(1)	48(2)	7(1)	-2(1)	7(1)
C(58)	39(2)	32(1)	37(2)	-16(1)	1(1)	3(1)
P(5)	25(1)	23(1)	27(1)	-6(1)	-3(1)	-1(1)
C(59)	43(2)	35(2)	64(2)	-15(1)	6(2)	-17(1)
C(60)	52(2)	46(2)	37(2)	-11(1)	-19(2)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(1A)	7736	5889	6905	28
H(1B)	7182	5292	7480	28
H(12)	5805	4906	8065	47
H(13)	4456	4037	8161	64
H(14)	2873	4182	7434	66
H(15)	2604	5214	6609	54
H(16)	3927	6096	6519	38
H(22)	5942	5388	5829	40
H(23)	5948	5564	4440	53
H(24)	5961	6753	3912	57
H(25)	5939	7770	4771	53
H(26)	5951	7601	6167	38
H(32)	9118	7613	7912	43
H(33)	10811	7762	7429	55
H(34)	11882	6743	7229	54
H(35)	11275	5565	7537	54
H(36)	9590	5409	7996	44
H(42)	8701	6359	9862	46
H(43)	9066	5510	10891	61
H(44)	8658	4266	10711	58
H(45)	7928	3864	9482	46
H(46)	7571	4705	8443	35
H(51A)	4297	8770	11098	82
H(51B)	3240	8584	10574	82
H(51C)	3875	9329	10410	82
H(52A)	5495	7301	10553	44
H(52B)	4272	7142	10350	44
H(53A)	6388	6020	10188	65
H(53B)	5845	5485	9523	65
H(53C)	5185	5769	10263	65
H(54A)	4010	5969	8600	64
H(54B)	3549	6781	8729	64
H(54C)	3594	6203	9459	64
H(55A)	3405	8037	8797	42
H(55B)	3793	8870	8694	42
H(56A)	3290	8167	7168	58
H(56B)	3523	7318	7377	58
H(56C)	4150	7721	6685	58
H(57A)	5558	8918	7046	62
H(57B)	5614	9260	7935	62
H(57C)	4517	9251	7420	62
H(58A)	5995	9214	9431	43
H(58B)	6337	8886	10298	43
H(59A)	8143	9196	9420	71
H(59B)	7697	9127	8506	71
H(59C)	8655	8614	8825	71
H(60A)	8497	7676	10050	68
H(60B)	7417	7390	10404	68
H(60C)	7818	8213	10591	68

^{31}P-NMR assignments for 2, 3 and 2-AlMe$_3$

^{31}P{^{1}H} NMR **(162 MHz, C_6D_6):**



	[Mo(N$_2$)(SiP$_3$)(dppm)] (**2**)	[Mo(N$_2$)(SiP$_3$)(dmpm)] (**3**)	[Mo(N$_2$AlMe$_3$)(SiP$_3$)(dppm)] (**2**-AlMe$_3$)
	δ / ppm		
P_a	11.7	-20.9	11.4
P_b	11.7	-20.9	11.4
P_c	4.2	7.4	2.8
P_d	4.2	7.4	2.8
P_e	-0.4	2.8	-12.1
	|J| / Hz		
$^{2}J_{ab}$	11.0	12.7	13.7
$^{2}J_{ac/bd}$	27.4	29.0	27.5
$^{2}J_{ad/bc}$	97.2	95.3	94.6
$^{2}J_{ae/be}$	18.3	20.6	21.6
$^{2/3}J_{cd}$	18.3	5.5	26.7
$^{2}J_{ce/de}$	25.4	24.0	26.7

Electronic Supplementary Material (ESI) for Dalton Transactions

Room temperature X-band EPR spectroscopy

Simulation parameters for $[Mo(SiP_3)(dmpm)(OTf)](OTf)_2$ (4) assuming a $[MoP_2P'_2P]$ core:

$g_{x\,y\,z}$	2.0159 2.0420 2.0115	$A(P'_2)_x$ / MHz	49.7
$A(Mo)_x$ / MHz	120.3	$A(P'_2)_y$ / MHz	48.1
$A(Mo)_y$ / MHz	120.0	$A(P'_2)_z$ / MHz	46.9
$A(Mo)_z$ / MHz	116.6	$A(P)_x$ / MHz	35.3
$A(P_2)_x$ / MHz	73.4	$A(P)_x$ / MHz	36.4
$A(P_2)_y$ / MHz	72.7	$A(P)_x$ / MHz	28.4
$A(P_2)_z$ / MHz	67.5	Linewidth / MHz	10.5