Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information for:

Coupling of Terminal Iridium Nitride Complexes

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1. Analytical Data

1.1 Cyclic Voltammetry

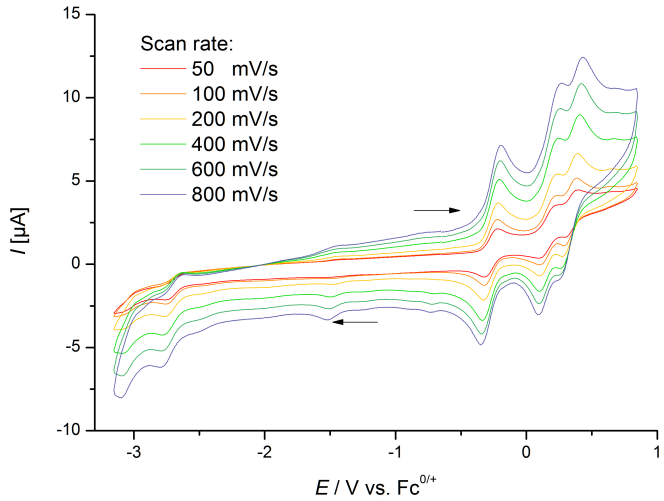

Figure S1. Cyclic voltammograms of **3** at different scan rates (THF, 10^{-3} M, 0.1 M [*n*-Bu_4N][PF_6], r.t., Ag/Ag^+-electrode).

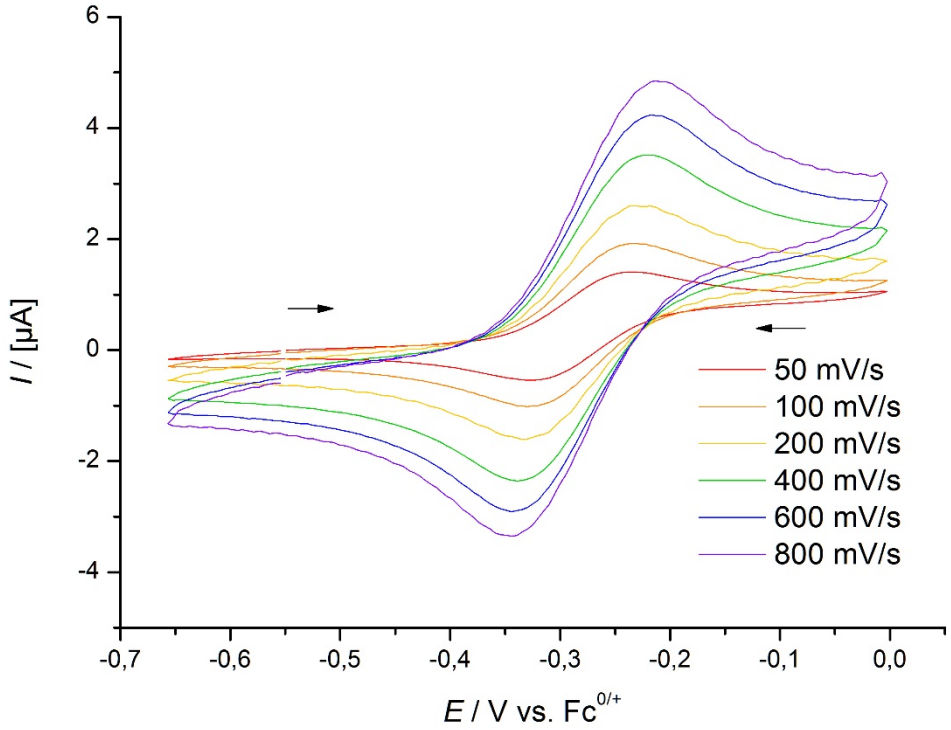

Figure S2. Cyclic voltammograms of **3** at different scan rates (THF, 10^{-3} M, 0.1 M [*n*-Bu_4N][PF_6], RT, Ag/Ag^+-electrode).

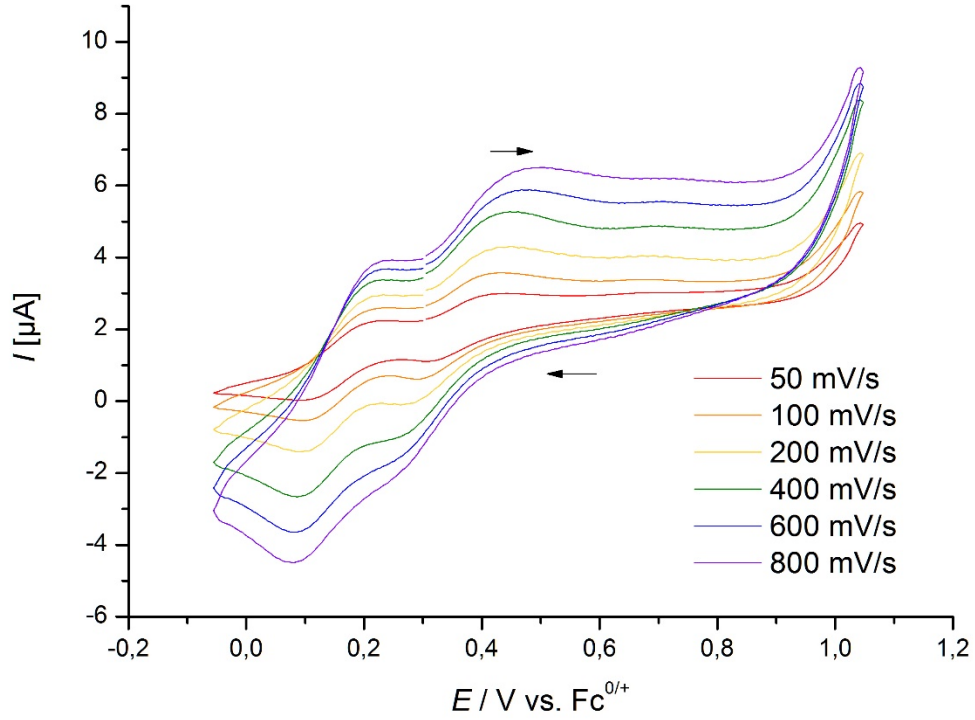

Figure S3. Cyclic voltammograms of **3** at different scan rates (THF, 10^{-3} M, 0.1 M [*n*-Bu_4N][PF_6], RT, Ag/Ag^+-electrode).

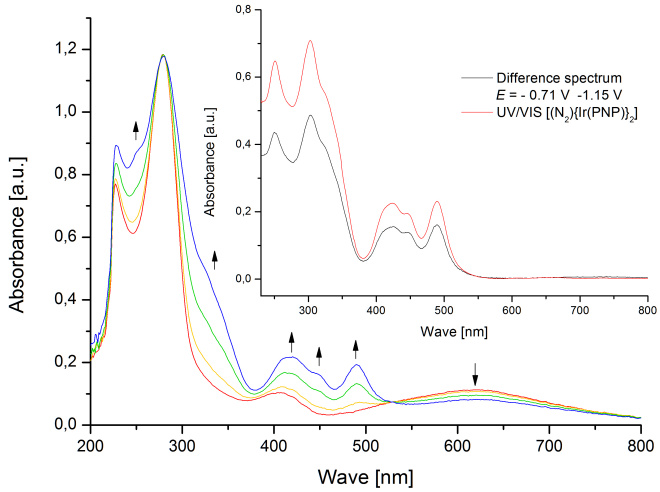

Figure S4. UV/VIS-Spectroelectrochemical reduction of **4** ($E_{1/2}$ = -0.86 V) at E = -0.71 V (red), E = -1.00 (yellow), E = -1.06 V (green) and E = -1.15 V (blue) in THF (c_4 = 10^{-3} M, 0.1 M [*n*-Bu_4N][PF_6], 0°C, 2.5 mV/s, Ag/Ag^+-electrode).

1.2 EPR Spectroscopy

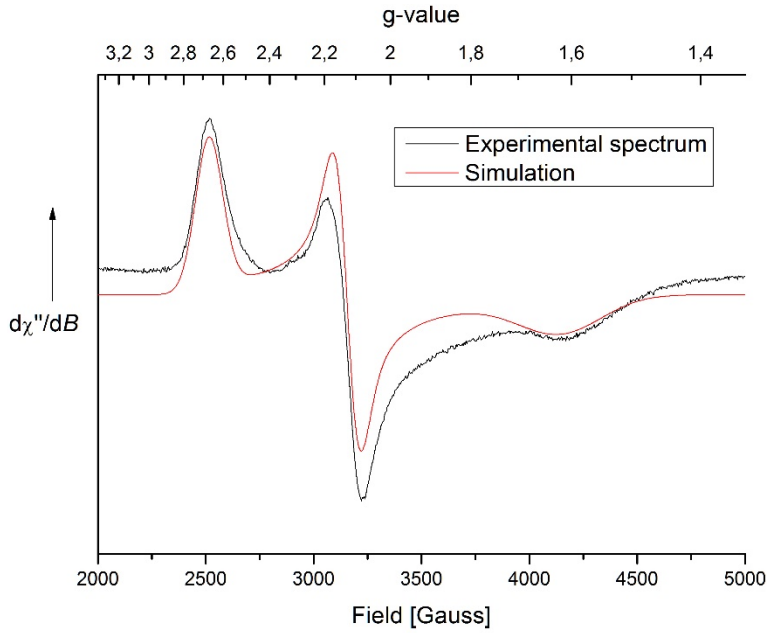

Figure S5. X-Band EPR spectrum of **5** (4 K, THF, Modulation: 3.00 G, Power: 1.00 mW, Frequency: 9.395 GHz).

1.3 IR Spectroscopy

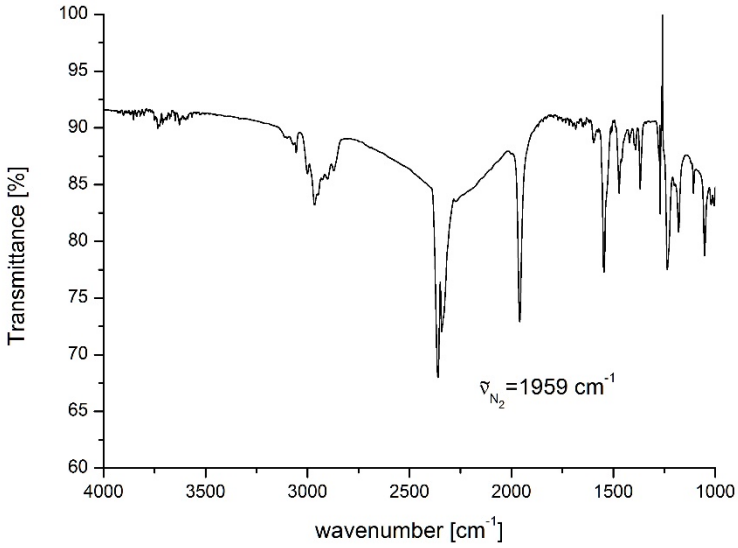

Figure S6. IR spectrum of **2** + 1 eq. of $[Fe(C_5H_5)_2][PF_6]$ (r.t., CH_2Cl_2, *c* = 6.7 mol/L).

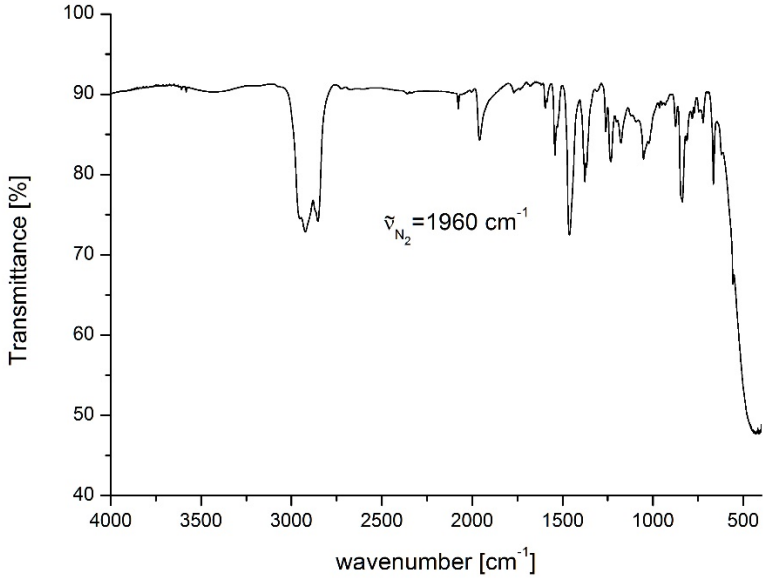

Figure S7. IR spectrum of **5** (nujol; minor amounts of $[IrN_2(PNP)]^1$ at ν_{N2} = 2077 cm^{-1} due to decomposition).

1.4 Electrospray Mass-Spectrommetry

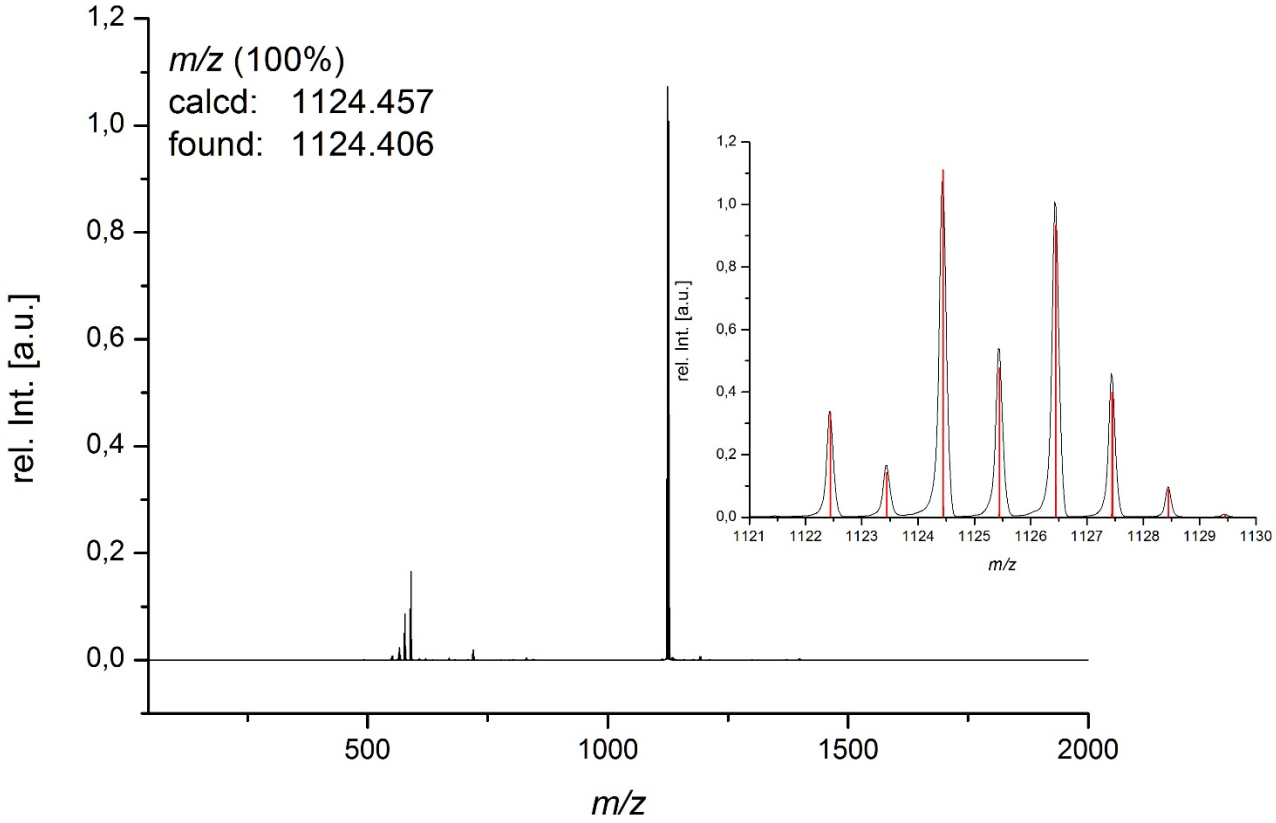

Figure S8. ESI-MS spectrum of **5**. The sample was injected (THF, c = 2 mM) by means of a syringe pump at a flow rate of 0.5 mLh^{-1}. The ESI source was operated with a voltage of U = 2500V and N_2 as nebulizer gas (flow rate of 5 L/min) and drying gas (0.7 bar backing pressure, T = 60°C to minimize decomposition of **5**). All generated ions with m/z = 50 - 2000 were allowed to pass the quadrupole mass filter and were detected after they had passed the TOF analyzer.

1.5 NMR Data and Kinetics

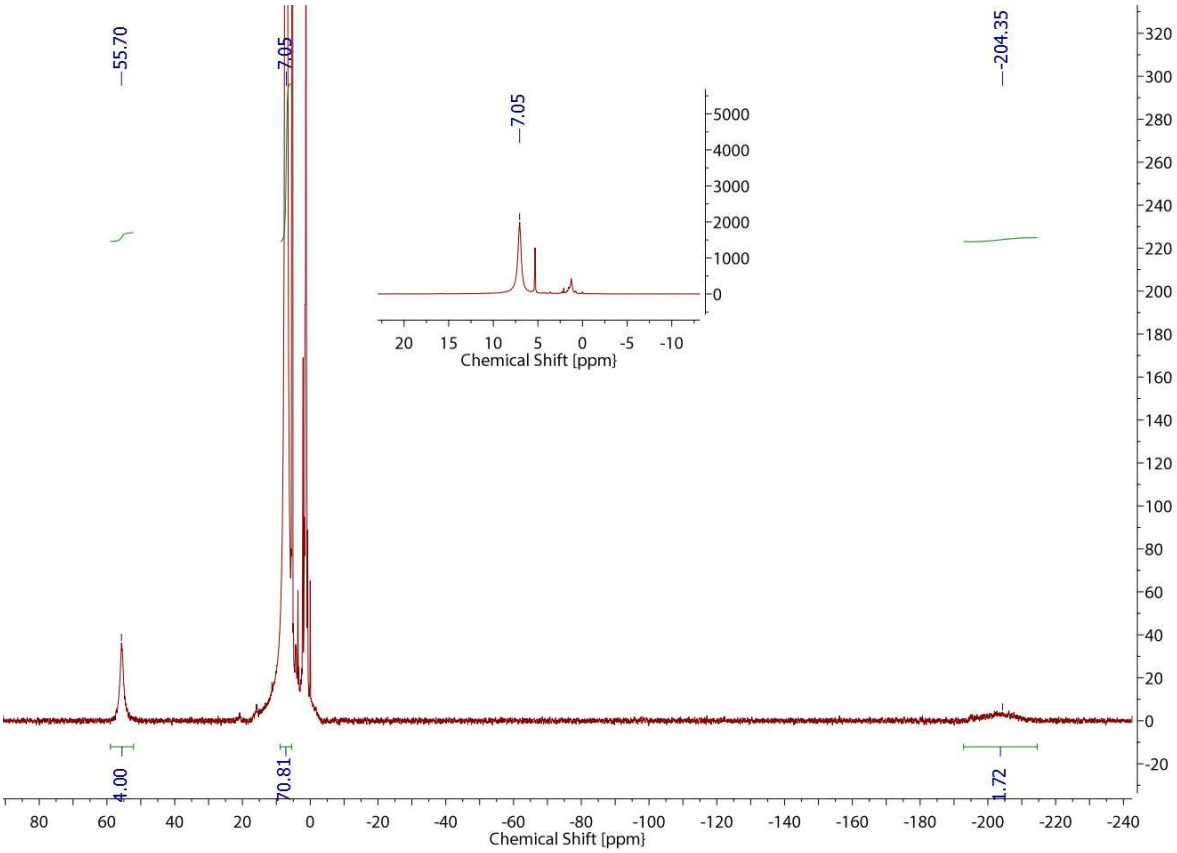

Figure S9. ^{1}H NMR spectrum of **5** (-70°C, CD_2Cl_2).

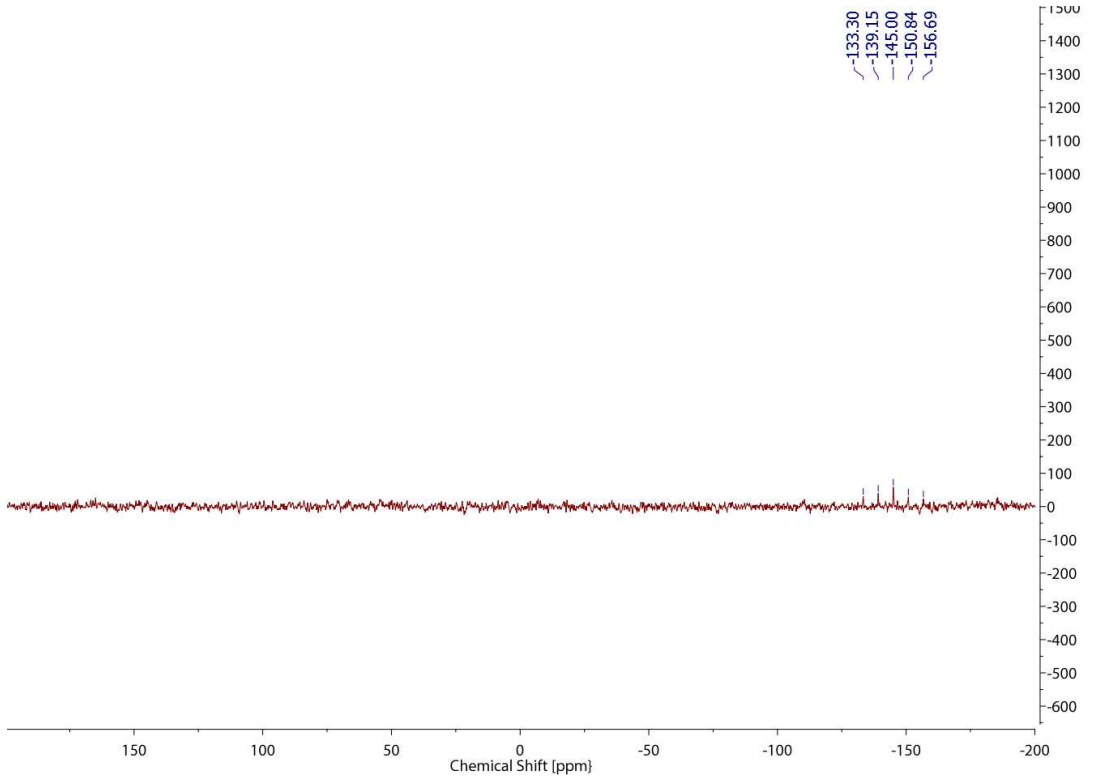

Figure S10. ^{31}P NMR spectrum of **5** (-70°C, CD_2Cl_2).

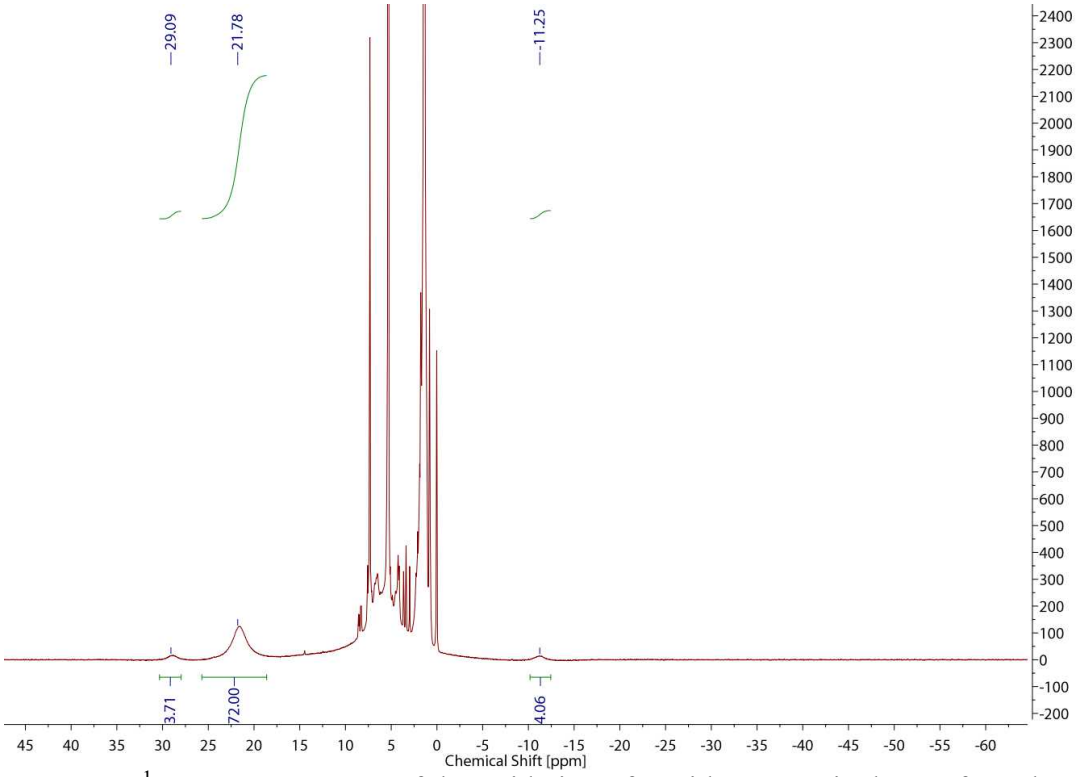

Figure S11. ^{1}H-NMR-spectrum of the oxidation of **2** with two equivalents of $AgSbF_6$ (-70°C, CD_2Cl_2).

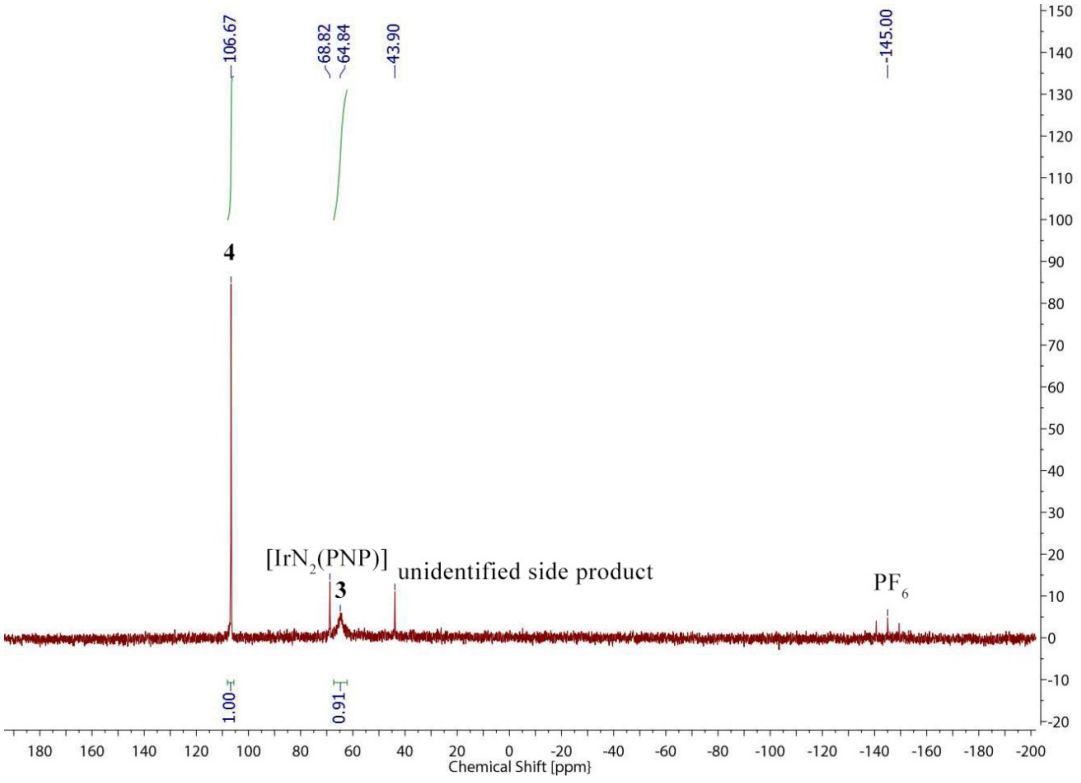

Figure S12. ^{31}P NMR spectrum of the reaction of 1eq. **4** + 1 eq. **2** (-70°C, CD_2Cl_2/Toluene-d_8 {1:1}).

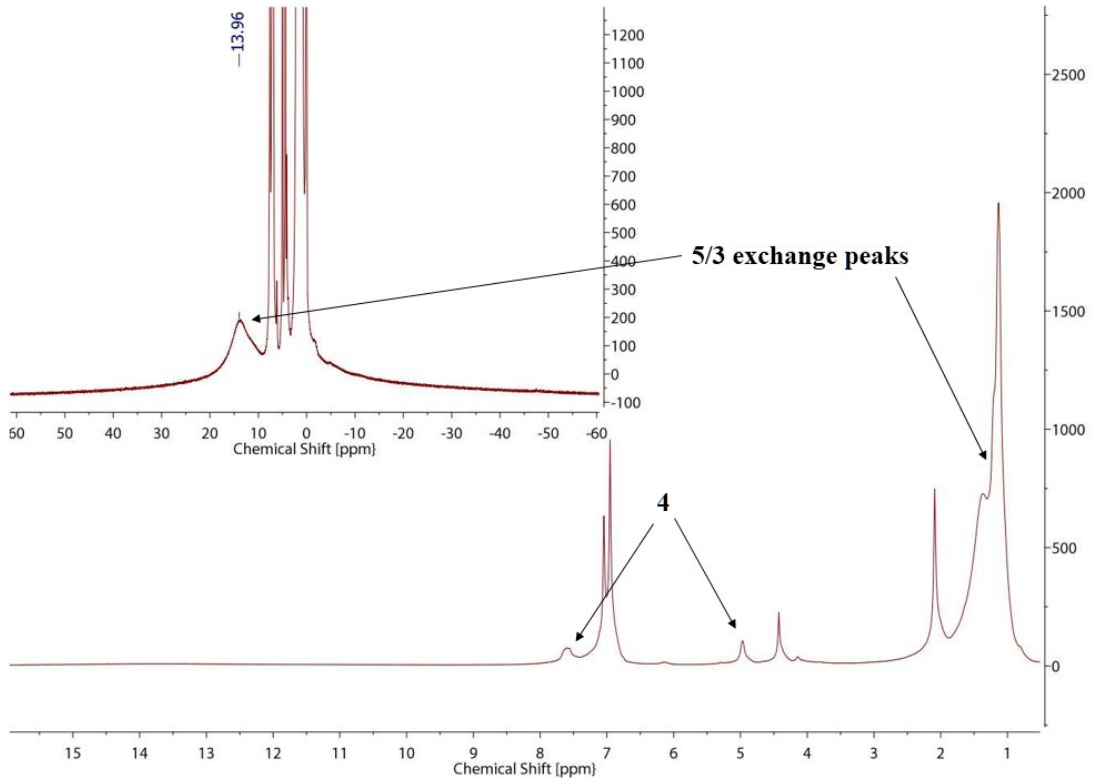

Figure S13. ^{1}H NMR spectrum of the reaction of 1eq. **4** + 1 eq. **2** (-70°C, CD_2Cl_2/Toluene-d_8 {1:1}).

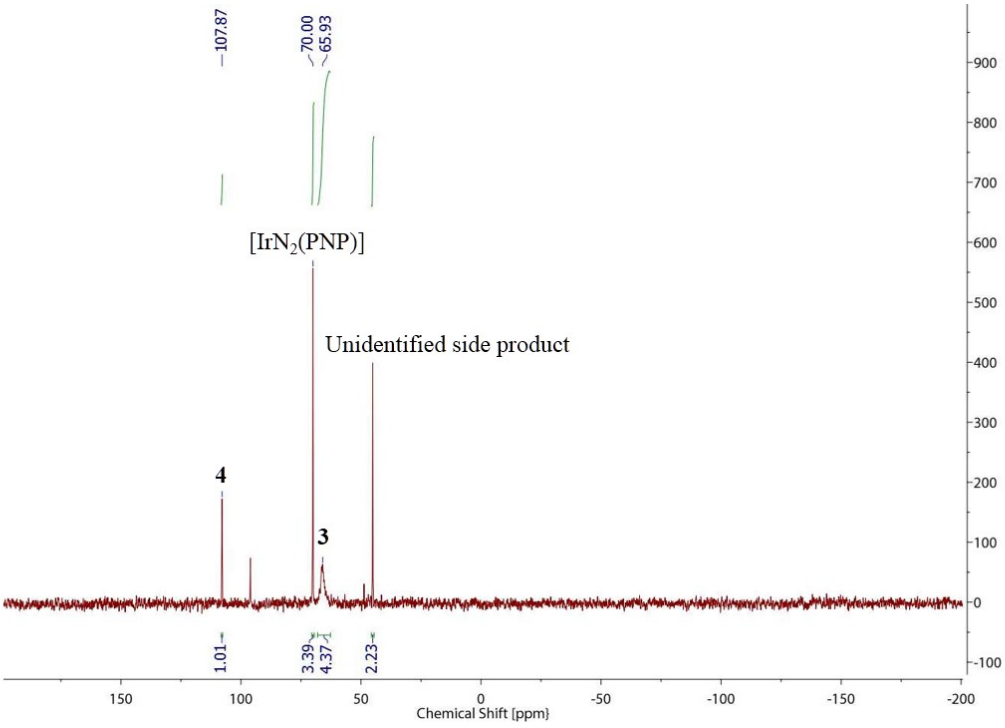

Figure S14. ^{31}P NMR spectrum of the reaction of 1eq. **2** + 0.1 eq. **4** (-70°C, CD_2Cl_2/toluene-d_8 {1:1}).

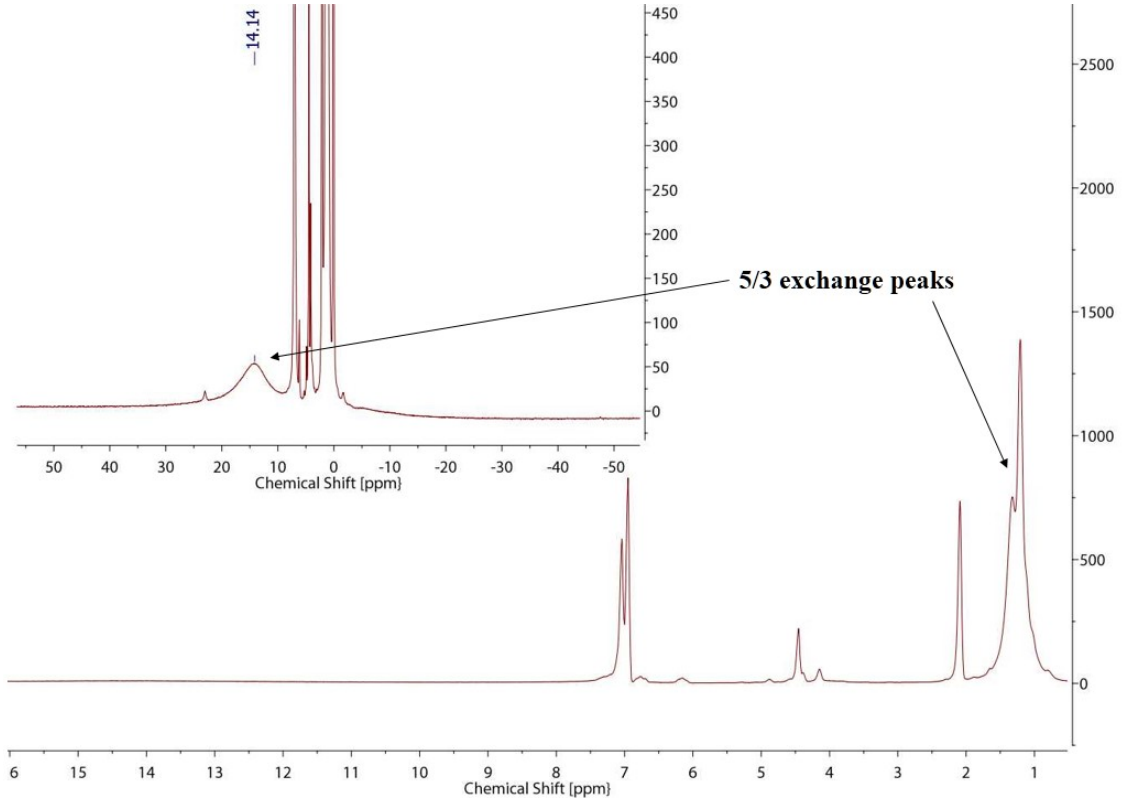

Figure S15. ^{1}H NMR spectrum of the reaction of 1eq. **2** + 0.1 eq. **4** (-70°C, CD_2Cl_2/toluene-d_8 {1:1}).

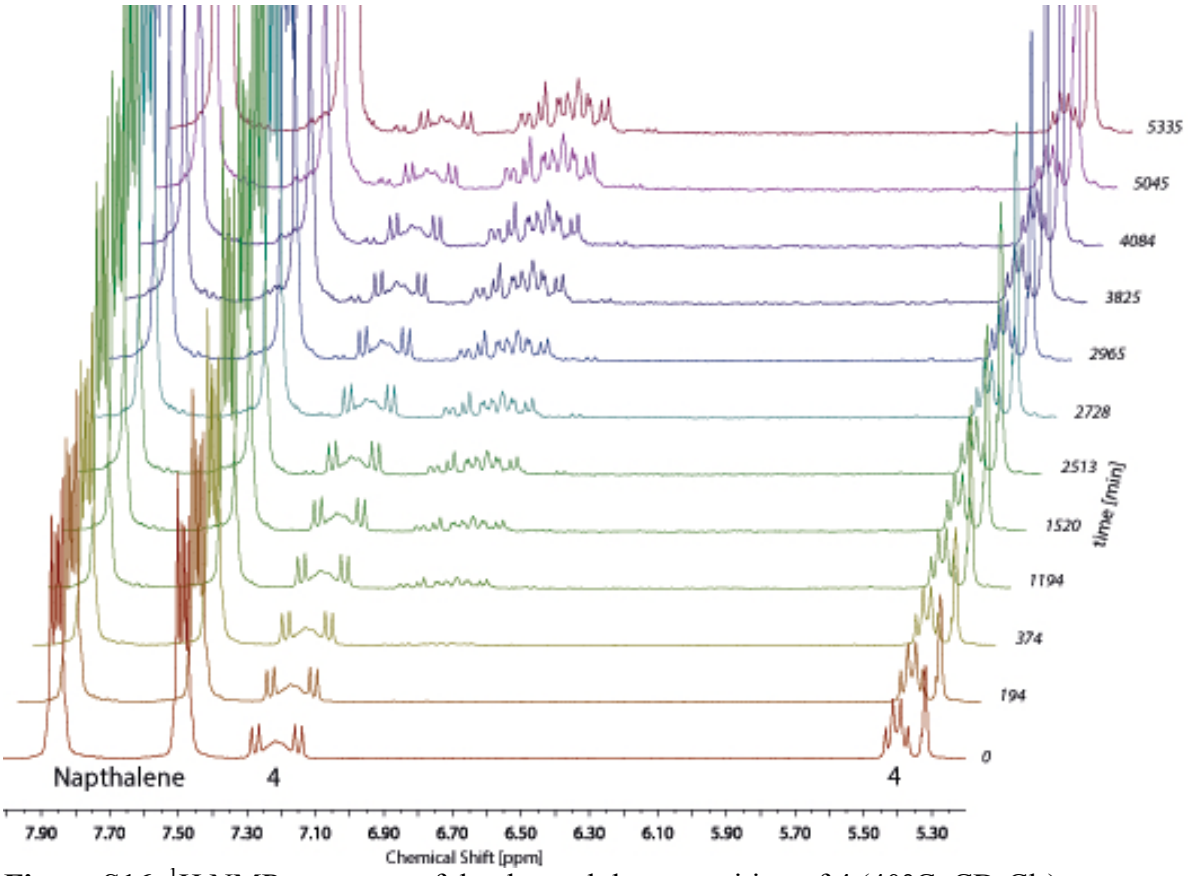

Figure S16. ^{1}H NMR spectrum of the thermal decomposition of **4** (40°C, CD_2Cl_2).

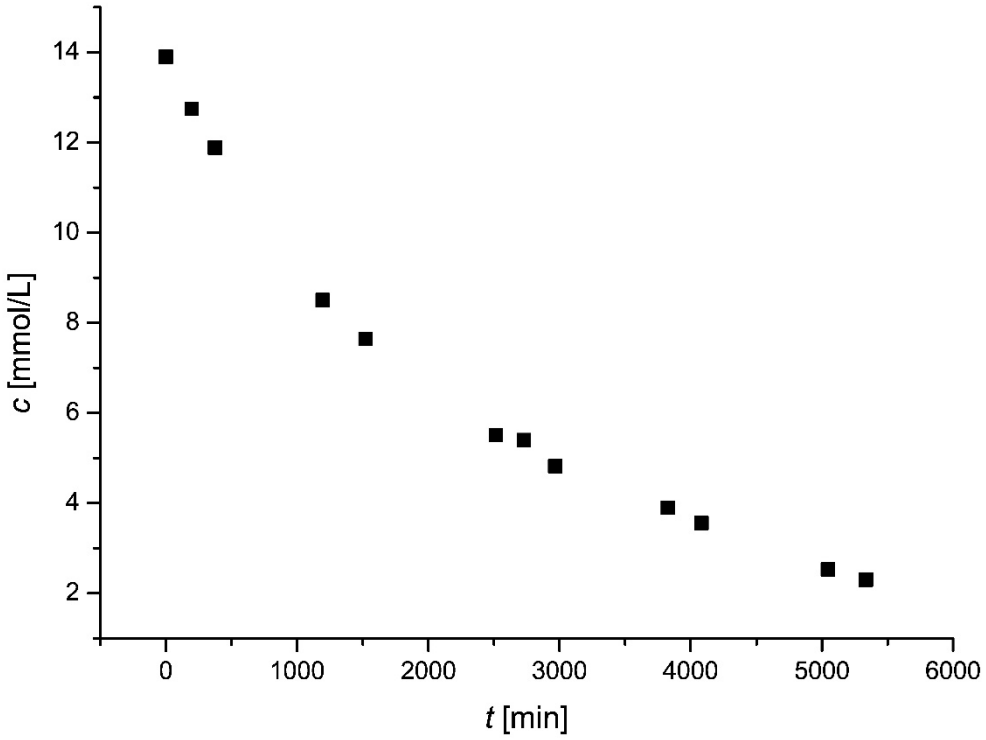

Figure S17. Time/conversion-plot of the decomposition of **4**.

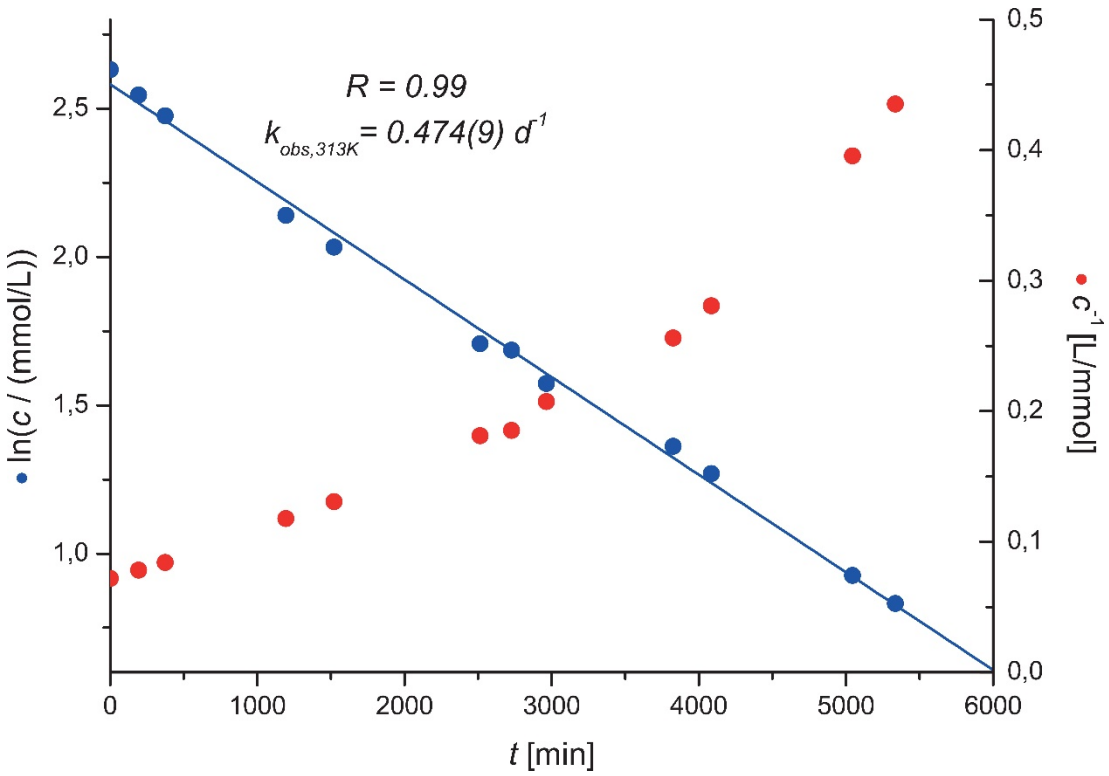

Figure S18. First-order and second-order plot of the decomposition of **4**.

2 Crystallographic Details

2.1 X-ray Single-Crystal Structure Analysis of ***5****.*

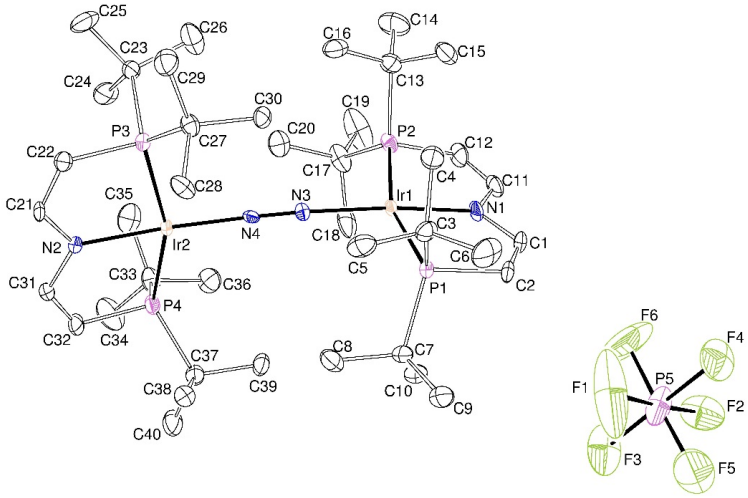

Figure S19. Thermal ellipsoid plot of **5** with the anisotropic displacement parameters drawn at the 50% probability level. The asymmetric unit contains one complex molecule and one PF_6 anion. The structure was refined as an inversion twin using the twin law -100 0-10 00-1 (BASF: 0.014(5). All hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for **5.**

Identification code	mo_CW_JA_270515_0m_a	
Empirical formula	$C_{40}H_{80}F_6Ir_2N_4P_5$	
Formula weight	1270.33	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 13.1762(5) Å	α= 90°
	b = 13.3606(5) Å	β= 90°
	c = 28.3330(11) Å	γ = 90°
Volume	4987.8(3) Å^3	
Z	4	
Density (calculated)	1.692 Mg/m^3	
Absorption coefficient	5.545 mm^{-1}	
F(000)	2524	
Crystal size	0.099 x 0.065 x 0.021 mm^3	
Theta range for data collection	2.095 to 28.327°	
Index ranges	-17<=h<=17, -17<=k<=17, -34<=l<=37	
Reflections collected	78343	
Independent reflections	12410 [R(int) = 0.0589]	

Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.5999	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12410 / 0 / 539	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0291,	wR2 = 0.0431
R indices (all data)	R1 = 0.0407,	wR2 = 0.0454
Absolute structure parameter	0.014(5)	
Largest diff. peak and hole	0.757 and -0.860 e.$Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for **5.**

C(1)-C(2)	1.325(9)	C(22)-C(21)-N(2)	121.7(5)
C(1)-N(1)	1.392(8)	C(21)-C(22)-P(3)	114.6(4)
C(2)-P(1)	1.791(6)	C(25)-C(23)-C(26)	109.8(5)
C(3)-C(5)	1.523(8)	C(25)-C(23)-C(24)	108.2(5)
C(3)-C(4)	1.537(8)	C(26)-C(23)-C(24)	108.5(5)
C(3)-C(6)	1.540(8)	C(25)-C(23)-P(3)	113.7(4)
C(3)-P(1)	1.884(6)	C(26)-C(23)-P(3)	110.9(4)
C(7)-C(9)	1.525(8)	C(24)-C(23)-P(3)	105.5(4)
C(7)-C(8)	1.526(8)	C(30)-C(27)-C(29)	108.4(5)
C(7)-C(10)	1.547(9)	C(30)-C(27)-C(28)	108.0(5)
C(7)-P(1)	1.872(6)	C(29)-C(27)-C(28)	109.0(5)
C(11)-C(12)	1.344(9)	C(30)-C(27)-P(3)	111.3(4)
C(11)-N(1)	1.384(7)	C(29)-C(27)-P(3)	113.7(4)
C(12)-P(2)	1.787(6)	C(28)-C(27)-P(3)	106.3(4)
C(13)-C(16)	1.525(9)	C(32)-C(31)-N(2)	122.2(5)
C(13)-C(15)	1.525(9)	C(31)-C(32)-P(4)	115.0(4)
C(13)-C(14)	1.538(9)	C(34)-C(33)-C(36)	110.2(5)
C(13)-P(2)	1.881(6)	C(34)-C(33)-C(35)	107.7(5)
C(17)-C(19)	1.528(9)	C(36)-C(33)-C(35)	108.2(5)
C(17)-C(20)	1.532(9)	C(34)-C(33)-P(4)	113.1(5)
C(17)-C(18)	1.548(10)	C(36)-C(33)-P(4)	111.8(4)
C(17)-P(2)	1.869(6)	C(35)-C(33)-P(4)	105.6(4)

C(21)-C(22)	1.341(8)	C(39)-C(37)-C(40)	109.8(5)
C(21)-N(2)	1.377(7)	C(39)-C(37)-C(38)	109.3(5)
C(22)-P(3)	1.777(6)	C(40)-C(37)-C(38)	108.8(5)
C(23)-C(25)	1.521(9)	C(39)-C(37)-P(4)	111.3(4)
C(23)-C(26)	1.522(8)	C(40)-C(37)-P(4)	113.3(4)
C(23)-C(24)	1.527(8)	C(38)-C(37)-P(4)	104.2(4)
C(23)-P(3)	1.883(6)	N(1)-Ir(1)-N(3)	172.80(19)
C(27)-C(30)	1.532(8)	N(1)-Ir(1)-P(2)	81.37(14)
C(27)-C(29)	1.540(8)	N(3)-Ir(1)-P(2)	97.60(12)
C(27)-C(28)	1.542(8)	N(1)-Ir(1)-P(1)	81.98(14)
C(27)-P(3)	1.860(6)	N(3)-Ir(1)-P(1)	99.79(13)
C(31)-C(32)	1.328(8)	P(2)-Ir(1)-P(1)	161.91(5)
C(31)-N(2)	1.379(7)	N(4)-Ir(2)-N(2)	173.34(18)
C(32)-P(4)	1.786(6)	N(4)-Ir(2)-P(3)	98.79(13)
C(33)-C(34)	1.522(8)	N(2)-Ir(2)-P(3)	80.58(13)
C(33)-C(36)	1.535(8)	N(4)-Ir(2)-P(4)	100.66(13)
C(33)-C(35)	1.547(9)	N(2)-Ir(2)-P(4)	80.81(13)
C(33)-P(4)	1.897(6)	P(3)-Ir(2)-P(4)	159.57(5)
C(37)-C(39)	1.536(8)	C(11)-N(1)-C(1)	116.1(5)
C(37)-C(40)	1.539(8)	C(11)-N(1)-Ir(1)	122.0(4)
C(37)-C(38)	1.540(9)	C(1)-N(1)-Ir(1)	121.8(4)
C(37)-P(4)	1.871(6)	C(21)-N(2)-C(31)	117.2(5)
F(1)-P(5)	1.571(5)	C(21)-N(2)-Ir(2)	121.3(4)
F(2)-P(5)	1.578(5)	C(31)-N(2)-Ir(2)	121.3(4)
F(3)-P(5)	1.574(5)	N(4)-N(3)-Ir(1)	175.3(4)
F(4)-P(5)	1.592(4)	N(3)-N(4)-Ir(2)	174.6(4)
F(5)-P(5)	1.572(5)	C(2)-P(1)-C(7)	103.8(3)
F(6)-P(5)	1.581(6)	C(2)-P(1)-C(3)	103.7(3)
Ir(1)-N(1)	1.973(4)	C(7)-P(1)-C(3)	112.5(3)
Ir(1)-N(3)	1.984(5)	C(2)-P(1)-Ir(1)	99.2(2)
Ir(1)-P(2)	2.3305(15)	C(7)-P(1)-Ir(1)	118.54(19)
Ir(1)-P(1)	2.3548(15)	C(3)-P(1)-Ir(1)	115.88(18)
Ir(2)-N(4)	1.878(5)	C(12)-P(2)-C(17)	105.1(3)
Ir(2)-N(2)	2.031(4)	C(12)-P(2)-C(13)	103.4(3)

Ir(2)-P(3)	2.3474(15)	C(17)-P(2)-C(13)	113.4(3)
Ir(2)-P(4)	2.3539(15)	C(12)-P(2)-Ir(1)	100.2(2)
N(3)-N(4)	1.136(6)	C(17)-P(2)-Ir(1)	119.2(2)
C(2)-C(1)-N(1)	121.8(5)	C(13)-P(2)-Ir(1)	112.8(2)
C(1)-C(2)-P(1)	115.1(5)	C(22)-P(3)-C(27)	106.0(3)
C(5)-C(3)-C(4)	110.1(5)	C(22)-P(3)-C(23)	103.3(3)
C(5)-C(3)-C(6)	109.1(5)	C(27)-P(3)-C(23)	111.8(3)
C(4)-C(3)-C(6)	107.7(5)	C(22)-P(3)-Ir(2)	100.67(19)
C(5)-C(3)-P(1)	111.6(4)	C(27)-P(3)-Ir(2)	120.36(19)
C(4)-C(3)-P(1)	105.6(4)	C(23)-P(3)-Ir(2)	112.3(2)
C(6)-C(3)-P(1)	112.6(4)	C(32)-P(4)-C(37)	104.9(3)
C(9)-C(7)-C(8)	110.7(5)	C(32)-P(4)-C(33)	102.9(3)
C(9)-C(7)-C(10)	108.9(5)	C(37)-P(4)-C(33)	112.1(3)
C(8)-C(7)-C(10)	109.1(5)	C(32)-P(4)-Ir(2)	100.46(19)
C(9)-C(7)-P(1)	113.2(4)	C(37)-P(4)-Ir(2)	117.70(19)
C(8)-C(7)-P(1)	110.4(4)	C(33)-P(4)-Ir(2)	116.1(2)
C(10)-C(7)-P(1)	104.3(4)	F(1)-P(5)-F(5)	93.0(5)
C(12)-C(11)-N(1)	121.4(5)	F(1)-P(5)-F(3)	90.3(3)
C(11)-C(12)-P(2)	113.5(5)	F(5)-P(5)-F(3)	90.3(3)
C(16)-C(13)-C(15)	108.9(6)	F(1)-P(5)-F(2)	175.6(5)
C(16)-C(13)-C(14)	109.9(5)	F(5)-P(5)-F(2)	91.4(3)
C(15)-C(13)-C(14)	109.2(5)	F(3)-P(5)-F(2)	90.1(3)
C(16)-C(13)-P(2)	108.6(4)	F(1)-P(5)-F(6)	87.9(5)
C(15)-C(13)-P(2)	106.5(4)	F(5)-P(5)-F(6)	178.6(4)
C(14)-C(13)-P(2)	113.6(5)	F(3)-P(5)-F(6)	90.8(3)
C(19)-C(17)-C(20)	110.7(6)	F(2)-P(5)-F(6)	87.7(4)
C(19)-C(17)-C(18)	107.8(6)	F(1)-P(5)-F(4)	90.7(3)
C(20)-C(17)-C(18)	110.2(5)	F(5)-P(5)-F(4)	89.8(3)
C(19)-C(17)-P(2)	113.5(5)	F(3)-P(5)-F(4)	179.0(3)
C(20)-C(17)-P(2)	111.3(4)	F(2)-P(5)-F(4)	88.9(3)
C(18)-C(17)-P(2)	103.0(5)	F(6)-P(5)-F(4)	89.1(3)

Table S3. Torsion angles [°] for **5.**

N(1)-C(1)-C(2)-P(1)	2.1(8)	C(16)-C(13)-P(2)-C(17)	77.8(5)
N(1)-C(11)-C(12)-P(2)	5.2(8)	C(15)-C(13)-P(2)-C(17)	-165.1(4)
N(2)-C(21)-C(22)-P(3)	4.1(7)	C(14)-C(13)-P(2)-C(17)	-44.8(6)
N(2)-C(31)-C(32)-P(4)	-0.8(8)	C(16)-C(13)-P(2)-Ir(1)	-61.6(5)
C(12)-C(11)-N(1)-C(1)	-177.0(6)	C(15)-C(13)-P(2)-Ir(1)	55.5(5)
C(12)-C(11)-N(1)-Ir(1)	5.7(8)	C(14)-C(13)-P(2)-Ir(1)	175.8(4)
C(2)-C(1)-N(1)-C(11)	-178.4(6)	C(21)-C(22)-P(3)-C(27)	-135.4(4)
C(2)-C(1)-N(1)-Ir(1)	-1.2(8)	C(21)-C(22)-P(3)-C(23)	106.8(5)
C(22)-C(21)-N(2)-C(31)	-179.1(5)	C(21)-C(22)-P(3)-Ir(2)	-9.4(5)
C(22)-C(21)-N(2)-Ir(2)	5.3(7)	C(30)-C(27)-P(3)-C(22)	171.8(4)
C(32)-C(31)-N(2)-C(21)	-178.8(5)	C(29)-C(27)-P(3)-C(22)	-65.4(5)
C(32)-C(31)-N(2)-Ir(2)	-3.2(8)	C(28)-C(27)-P(3)-C(22)	54.4(4)
C(1)-C(2)-P(1)-C(7)	120.8(5)	C(30)-C(27)-P(3)-C(23)	-76.4(5)
C(1)-C(2)-P(1)-C(3)	-121.5(5)	C(29)-C(27)-P(3)-C(23)	46.4(5)
C(1)-C(2)-P(1)-Ir(1)	-1.8(5)	C(28)-C(27)-P(3)-C(23)	166.3(4)
C(9)-C(7)-P(1)-C(2)	57.8(5)	C(30)-C(27)-P(3)-Ir(2)	58.8(4)
C(8)-C(7)-P(1)-C(2)	-177.5(4)	C(29)-C(27)-P(3)-Ir(2)	-178.4(3)
C(10)-C(7)-P(1)-C(2)	-60.4(4)	C(28)-C(27)-P(3)-Ir(2)	-58.6(4)
C(9)-C(7)-P(1)-C(3)	-53.7(5)	C(25)-C(23)-P(3)-C(22)	42.2(5)
C(8)-C(7)-P(1)-C(3)	71.0(5)	C(26)-C(23)-P(3)-C(22)	166.5(5)
C(10)-C(7)-P(1)-C(3)	-171.9(4)	C(24)-C(23)-P(3)-C(22)	-76.2(5)
C(9)-C(7)-P(1)-Ir(1)	166.6(4)	C(25)-C(23)-P(3)-C(27)	-71.4(5)
C(8)-C(7)-P(1)-Ir(1)	-68.7(5)	C(26)-C(23)-P(3)-C(27)	53.0(5)
C(10)-C(7)-P(1)-Ir(1)	48.4(4)	C(24)-C(23)-P(3)-C(27)	170.2(4)
C(5)-C(3)-P(1)-C(2)	-159.7(4)	C(25)-C(23)-P(3)-Ir(2)	149.8(4)
C(4)-C(3)-P(1)-C(2)	80.7(4)	C(26)-C(23)-P(3)-Ir(2)	-85.9(5)
C(6)-C(3)-P(1)-C(2)	-36.6(5)	C(24)-C(23)-P(3)-Ir(2)	31.4(4)
C(5)-C(3)-P(1)-C(7)	-48.1(5)	C(31)-C(32)-P(4)-C(37)	126.0(5)
C(4)-C(3)-P(1)-C(7)	-167.8(4)	C(31)-C(32)-P(4)-C(33)	-116.7(5)
C(6)-C(3)-P(1)-C(7)	75.0(5)	C(31)-C(32)-P(4)-Ir(2)	3.4(5)
C(5)-C(3)-P(1)-Ir(1)	92.7(4)	C(39)-C(37)-P(4)-C(32)	-178.7(4)
C(4)-C(3)-P(1)-Ir(1)	-26.9(4)	C(40)-C(37)-P(4)-C(32)	57.0(5)
C(6)-C(3)-P(1)-Ir(1)	-144.2(4)	C(38)-C(37)-P(4)-C(32)	-61.0(4)

C(11)-C(12)-P(2)-C(17)	-135.0(5)	C(39)-C(37)-P(4)-C(33)	70.4(5)
C(11)-C(12)-P(2)-C(13)	105.8(5)	C(40)-C(37)-P(4)-C(33)	-53.9(5)
C(11)-C(12)-P(2)-Ir(1)	-10.8(5)	C(38)-C(37)-P(4)-C(33)	-171.9(4)
C(19)-C(17)-P(2)-C(12)	-48.0(6)	C(39)-C(37)-P(4)-Ir(2)	-68.1(4)
C(20)-C(17)-P(2)-C(12)	-173.8(5)	C(40)-C(37)-P(4)-Ir(2)	167.6(4)
C(18)-C(17)-P(2)-C(12)	68.2(5)	C(38)-C(37)-P(4)-Ir(2)	49.6(4)
C(19)-C(17)-P(2)-C(13)	64.2(6)	C(34)-C(33)-P(4)-C(32)	-36.2(6)
C(20)-C(17)-P(2)-C(13)	-61.5(5)	C(36)-C(33)-P(4)-C(32)	-161.3(5)
C(18)-C(17)-P(2)-C(13)	-179.5(4)	C(35)-C(33)-P(4)-C(32)	81.2(4)
C(19)-C(17)-P(2)-Ir(1)	-159.2(5)	C(34)-C(33)-P(4)-C(37)	75.9(5)
C(20)-C(17)-P(2)-Ir(1)	75.1(5)	C(36)-C(33)-P(4)-C(37)	-49.1(5)
C(18)-C(17)-P(2)-Ir(1)	-42.9(5)	C(35)-C(33)-P(4)-C(37)	-166.6(4)
C(16)-C(13)-P(2)-C(12)	-168.9(4)	C(34)-C(33)-P(4)-Ir(2)	-144.9(4)
C(15)-C(13)-P(2)-C(12)	-51.8(5)	C(36)-C(33)-P(4)-Ir(2)	90.1(5)
C(14)-C(13)-P(2)-C(12)	68.5(5)	C(35)-C(33)-P(4)-Ir(2)	-27.4(4)
P(2)-Ir(1)-N(3)-N(4)	78(5)	P(3)-Ir(2)-N(4)-N(3)	72(4)
P(1)-Ir(1)-N(3)-N(4)	-107(5)	P(4)-Ir(2)-N(4)-N(3)	-114(4)
Ir(1)-N(3)-N(4)-Ir(2)	123(5)		

2.2 X-ray Single-Crystal Structure Analysis of ***6****.*

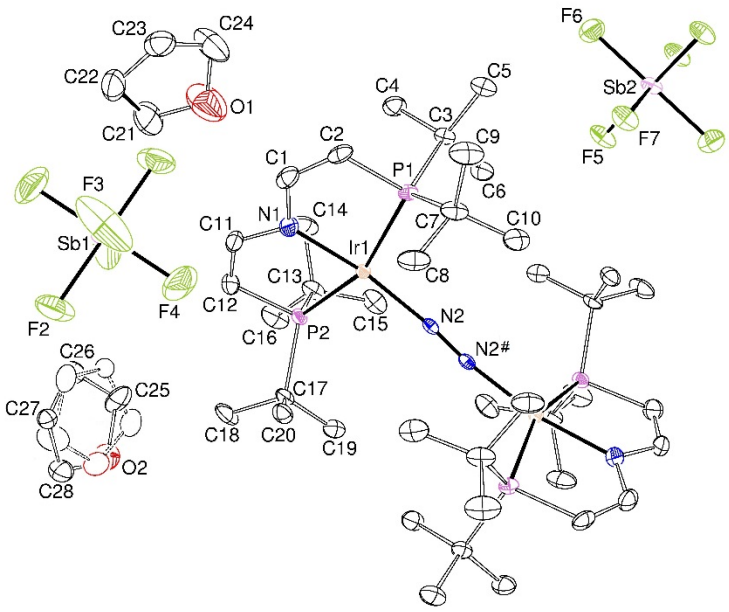

Figure S20. Thermal ellipsoid plot of **6** with the anisotropic displacement parameters drawn at the 50% probability level. The asymmetric unit contains a half complex molecule, two half SbF_6 anions, one THF solvent molecule and a disordered half-occupied THF solvent molecule. The disorder was refined using PART -1 command and some restraints on the distances and anisotropic displacement parameters (SAME, SIMU, RIGU). All hydrogen atoms are omitted for clarity.

Table S4. Crystal data and structure refinement for **6.**

Identification code	cw_ja_230715_3_a	
Empirical formula	$C_{52}H_{104}F_{12}Ir_2N_4O_3P_4Sb_2$	
Formula weight	1813.17	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2/c	
Unit cell dimensions	a = 15.7367(8) Å	α= 90°
	b = 15.1562(7) Å	β= 113.649(2)°
	c = 15.2970(8) Å	γ = 90°
Volume	3342.1(3) Å^3	
Z	2	
Density (calculated)	1.802 Mg/m^3	

Absorption coefficient	4.939 mm^{-1}
F(000)	1784
Crystal size	0.160 x 0.150 x 0.046 mm^3
Theta range for data collection	1.950 to 28.346°
Index ranges	-21<=h<=20, -20<=k<=20, -20<=l<=20
Reflections collected	55887
Independent reflections	8353 [R(int) = 0.0446]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.5410
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8353 / 90 / 393
Goodness-of-fit on F^2	1.229
Final R indices [I>2sigma(I)]	R1 = 0.0266, wR2 = 0.0544
R indices (all data)	R1 = 0.0369, wR2 = 0.0600
Largest diff. peak and hole	1.783 and -1.671 $e.Å^{-3}$

Table S5. Bond lengths [Å] and angles [°] for **6.**

C(1)-C(2)	1.339(6)	C(16)-C(13)-P(2)	113.4(3)
C(1)-N(1)	1.394(5)	C(19)-C(17)-C(20)	110.0(3)
C(2)-P(1)	1.795(4)	C(19)-C(17)-C(18)	109.9(3)
C(3)-C(6)	1.526(5)	C(20)-C(17)-C(18)	107.7(3)
C(3)-C(4)	1.530(5)	C(19)-C(17)-P(2)	110.3(2)
C(3)-C(5)	1.531(5)	C(20)-C(17)-P(2)	104.6(2)
C(3)-P(1)	1.884(4)	C(18)-C(17)-P(2)	114.2(3)
C(7)-C(10)	1.528(6)	C(21)-O(1)-C(24)	107.8(5)
C(7)-C(8)	1.539(6)	O(1)-C(21)-C(22)	111.4(5)
C(7)-C(9)	1.540(5)	C(21)-C(22)-C(23)	104.6(4)
C(7)-P(1)	1.855(4)	C(24)-C(23)-C(22)	103.3(5)
C(11)-C(12)	1.353(6)	O(1)-C(24)-C(23)	104.2(4)
C(11)-N(1)	1.380(5)	C(25)-O(2)-C(28)	109.6(9)
C(12)-P(2)	1.798(4)	O(2)-C(25)-C(26)	108.8(11)
C(13)-C(15)	1.526(6)	C(25)-C(26)-C(27)	103.3(12)
C(13)-C(14)	1.533(6)	C(28)-C(27)-C(26)	104.6(10)
C(13)-C(16)	1.537(5)	O(2)-C(28)-C(27)	106.5(9)

C(13)-P(2)	1.877(4)	C(2)-P(1)-C(7)	103.75(18)
C(17)-C(19)	1.525(5)	C(2)-P(1)-C(3)	105.08(17)
C(17)-C(20)	1.538(5)	C(7)-P(1)-C(3)	114.23(18)
C(17)-C(18)	1.539(5)	C(2)-P(1)-Ir(1)	100.17(14)
C(17)-P(2)	1.863(4)	C(7)-P(1)-Ir(1)	118.99(12)
O(1)-C(21)	1.361(7)	C(3)-P(1)-Ir(1)	112.08(11)
O(1)-C(24)	1.453(7)	C(12)-P(2)-C(17)	103.97(18)
C(21)-C(22)	1.444(9)	C(12)-P(2)-C(13)	105.3(2)
C(22)-C(23)	1.521(8)	C(17)-P(2)-C(13)	113.39(17)
C(23)-C(24)	1.504(7)	C(12)-P(2)-Ir(1)	100.30(14)
O(2)-C(25)	1.416(13)	C(17)-P(2)-Ir(1)	120.49(12)
O(2)-C(28)	1.425(15)	C(13)-P(2)-Ir(1)	111.04(12)
C(25)-C(26)	1.460(16)	F(4)-Sb(1)-F(4)#1	179.0(3)
C(26)-C(27)	1.514(17)	F(4)-Sb(1)-F(3)	90.50(15)
C(27)-C(28)	1.494(13)	F(4)#1-Sb(1)-F(3)	90.49(15)
F(1)-Sb(1)	1.851(4)	F(4)-Sb(1)-F(1)	89.50(15)
F(2)-Sb(1)	1.863(3)	F(4)#1-Sb(1)-F(1)	89.51(15)
F(3)-Sb(1)	1.849(5)	F(3)-Sb(1)-F(1)	180.0
F(4)-Sb(1)	1.848(3)	F(4)-Sb(1)-F(2)#1	89.48(17)
F(5)-Sb(2)	1.877(2)	F(4)#1-Sb(1)-F(2)#1	90.52(17)
F(6)-Sb(2)	1.868(3)	F(3)-Sb(1)-F(2)#1	89.79(11)
F(7)-Sb(2)	1.875(2)	F(1)-Sb(1)-F(2)#1	90.21(11)
P(1)-Ir(1)	2.3489(9)	F(4)-Sb(1)-F(2)	90.53(17)
P(2)-Ir(1)	2.3319(9)	F(4)#1-Sb(1)-F(2)	89.48(17)
Sb(1)-F(4)#1	1.848(3)	F(3)-Sb(1)-F(2)	89.79(11)
Sb(1)-F(2)#1	1.863(3)	F(1)-Sb(1)-F(2)	90.21(11)
Sb(2)-F(6)#2	1.868(3)	F(2)#1-Sb(1)-F(2)	179.6(2)
Sb(2)-F(7)#2	1.875(2)	F(6)-Sb(2)-F(6)#2	179.01(16)
Sb(2)-F(5)#2	1.877(2)	F(6)-Sb(2)-F(7)#2	90.18(11)
Ir(1)-N(2)	1.954(3)	F(6)#2-Sb(2)-F(7)#2	90.52(12)
Ir(1)-N(1)	1.983(3)	F(6)-Sb(2)-F(7)	90.52(12)
N(2)-N(2)#3	1.138(6)	F(6)#2-Sb(2)-F(7)	90.18(11)
C(2)-C(1)-N(1)	120.9(4)	F(7)#2-Sb(2)-F(7)	89.96(14)
C(1)-C(2)-P(1)	114.4(3)	F(6)-Sb(2)-F(5)#2	89.58(12)

C(6)-C(3)-C(4)	108.3(3)	F(6)#2-Sb(2)-F(5)#2	89.73(12)
C(6)-C(3)-C(5)	110.0(3)	F(7)#2-Sb(2)-F(5)#2	89.73(10)
C(4)-C(3)-C(5)	109.0(3)	F(7)-Sb(2)-F(5)#2	179.67(11)
C(6)-C(3)-P(1)	107.8(2)	F(6)-Sb(2)-F(5)	89.73(12)
C(4)-C(3)-P(1)	106.9(3)	F(6)#2-Sb(2)-F(5)	89.58(12)
C(5)-C(3)-P(1)	114.7(3)	F(7)#2-Sb(2)-F(5)	179.67(11)
C(10)-C(7)-C(8)	110.5(3)	F(7)-Sb(2)-F(5)	89.73(10)
C(10)-C(7)-C(9)	110.4(3)	F(5)#2-Sb(2)-F(5)	90.59(14)
C(8)-C(7)-C(9)	107.5(3)	N(2)-Ir(1)-N(1)	168.04(12)
C(10)-C(7)-P(1)	108.9(3)	N(2)-Ir(1)-P(2)	98.49(8)
C(8)-C(7)-P(1)	104.6(3)	N(1)-Ir(1)-P(2)	81.79(10)
C(9)-C(7)-P(1)	114.7(3)	N(2)-Ir(1)-P(1)	100.90(8)
C(12)-C(11)-N(1)	121.5(4)	N(1)-Ir(1)-P(1)	81.12(10)
C(11)-C(12)-P(2)	113.8(3)	P(2)-Ir(1)-P(1)	158.58(3)
C(15)-C(13)-C(14)	108.3(4)	C(11)-N(1)-C(1)	115.1(3)
C(15)-C(13)-C(16)	110.2(4)	C(11)-N(1)-Ir(1)	122.2(3)
C(14)-C(13)-C(16)	109.3(3)	C(1)-N(1)-Ir(1)	122.6(3)
C(15)-C(13)-P(2)	108.5(3)	N(2)#3-N(2)-Ir(1)	172.2(3)
C(14)-C(13)-P(2)	107.0(3)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2 #2 -x,y,-z+3/2 #3 -x,y,-z+1/2

Table S6. Torsion angles [°] for **6**.

N(1)-C(1)-C(2)-P(1)	0.0(5)	C(5)-C(3)-P(1)-C(7)	-32.4(3)
N(1)-C(11)-C(12)-P(2)	-1.0(5)	C(6)-C(3)-P(1)-Ir(1)	-48.7(3)
C(24)-O(1)-C(21)-C(22)	-17.8(9)	C(4)-C(3)-P(1)-Ir(1)	67.6(3)
O(1)-C(21)-C(22)-C(23)	-0.7(8)	C(5)-C(3)-P(1)-Ir(1)	-171.5(2)
C(21)-C(22)-C(23)-C(24)	17.9(7)	C(11)-C(12)-P(2)-C(17)	129.9(3)
C(21)-O(1)-C(24)-C(23)	28.7(8)	C(11)-C(12)-P(2)-C(13)	-110.7(3)
C(22)-C(23)-C(24)-O(1)	-27.9(7)	C(11)-C(12)-P(2)-Ir(1)	4.7(3)
C(28)-O(2)-C(25)-C(26)	-11(4)	C(19)-C(17)-P(2)-C(12)	167.7(3)
O(2)-C(25)-C(26)-C(27)	24(4)	C(20)-C(17)-P(2)-C(12)	-74.0(3)

C(25)-C(26)-C(27)-C(28)	-27(3)	C(18)-C(17)-P(2)-C(12)	43.5(3)
C(25)-O(2)-C(28)-C(27)	-6(4)	C(19)-C(17)-P(2)-C(13)	54.0(3)
C(26)-C(27)-C(28)-O(2)	21(3)	C(20)-C(17)-P(2)-C(13)	172.2(2)
C(1)-C(2)-P(1)-C(7)	-128.8(3)	C(18)-C(17)-P(2)-C(13)	-70.3(3)
C(1)-C(2)-P(1)-C(3)	110.9(3)	C(19)-C(17)-P(2)-Ir(1)	-81.1(3)
C(1)-C(2)-P(1)-Ir(1)	-5.4(3)	C(20)-C(17)-P(2)-Ir(1)	37.1(3)
C(10)-C(7)-P(1)-C(2)	-175.7(3)	C(18)-C(17)-P(2)-Ir(1)	154.6(2)
C(8)-C(7)-P(1)-C(2)	66.1(3)	C(15)-C(13)-P(2)-C(12)	165.0(3)
C(9)-C(7)-P(1)-C(2)	-51.4(4)	C(14)-C(13)-P(2)-C(12)	48.3(3)
C(10)-C(7)-P(1)-C(3)	-61.9(3)	C(16)-C(13)-P(2)-C(12)	-72.2(4)
C(8)-C(7)-P(1)-C(3)	179.9(2)	C(15)-C(13)-P(2)-C(17)	-82.0(3)
C(9)-C(7)-P(1)-C(3)	62.4(4)	C(14)-C(13)-P(2)-C(17)	161.3(3)
C(10)-C(7)-P(1)-Ir(1)	74.2(3)	C(16)-C(13)-P(2)-C(17)	40.8(4)
C(8)-C(7)-P(1)-Ir(1)	-44.0(3)	C(15)-C(13)-P(2)-Ir(1)	57.3(3)
C(9)-C(7)-P(1)-Ir(1)	-161.5(3)	C(14)-C(13)-P(2)-Ir(1)	-59.3(3)
C(6)-C(3)-P(1)-C(2)	-156.5(3)	C(16)-C(13)-P(2)-Ir(1)	-179.9(3)
C(4)-C(3)-P(1)-C(2)	-40.3(3)	C(12)-C(11)-N(1)-C(1)	176.8(4)
C(5)-C(3)-P(1)-C(2)	80.6(3)	C(12)-C(11)-N(1)-Ir(1)	-4.6(5)
C(6)-C(3)-P(1)-C(7)	90.4(3)	C(2)-C(1)-N(1)-C(11)	-173.9(4)
C(4)-C(3)-P(1)-C(7)	-153.3(3)	C(2)-C(1)-N(1)-Ir(1)	7.5(5)
P(2)-Ir(1)-N(2)-N(2)#3	-89.1(18)	P(1)-Ir(1)-N(2)-N(2)#3	100.0(18)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2 #2 -x,y,-z+3/2 #3 -x,y,-z+1/2

3 DFT Computations

3.1 Computational details

The DFT calculations have been performed within the Turbomole 7.0 package[2] applying the PBE0[3] functional and Grimme's dispersion correction with Becke-Johnson damping (D3BJ).[4] The ligand was fully included without truncation of the *tert*-butyl groups to account for the steric bulk of the ligand that constrains possible arrangements of the ligands in respect to each other. Furthermore, we observed that the pure GGA PBE functional[5] does not reproduce the asymmetric structure of the monocationic dimer ^{2}**5** but predicts a rather symmetric structure with an unphysical small HOMO-LUMO gap. Ahlrich's revised basis sets were used (def2-SVP in the structure optimizations and def2-TZVP for single point energies respectively) with a full basis for all elements but Ir for which a Stuttgart-Dresden 60 electron core potential has been used, replacing the inner shell 1s-4f orbitals.[6] No symmetry restrains were imposed and the optimized structures were defined as minima (no negative eigenvalue) or transition states (one negative eigenvalue) by vibrational analyses at the same level of theory. Only in case of **TS$_{4+4}$** a small second vibration of 13 cm^{-1} was observed.

To locate the transition states, the trajectories of the N-N coupling to the dimers have been investigated by relaxed surface scans of the N-N distance between the corresponding nitride monomers. Only if solvent effects are included by the COSMO[7] approximation (ε = 7.6 for tetrahydrofuran), we observe the physically correct behavior that at very long N-N distances (5 Å) the SCF energy approaches the sum of the SCF energies of the monomers. Therefore, we applied COSMO in the single point calculations. The final energies have been obtained by adding the zero vibrational energies or enthalpies from the optimizations to the SCF energies, in short notified as D3BJ-PBE0(COSMO(THF))/def2-TZVP//D3BJ-PBE0/def2-SVP.

The energies of the transition states **TS$_{2+2}$** and **TS$_{2+4}$** are already lower than the sum of the energies of the monomers if entropic corrections are not included. This is probably partially due to the fact that the dispersion interactions are somehow overestimated. We therefore used in table 2 of the manuscript the energy differences to the encounter complexes that are formed before the actual transition states. Formation of the encounter complexes is in all three coupling reactions (**2**+**2**, **2**+**4** and **4**+4) exothermic but endergonic, thus the free energies noted in the aforementioned table are the differences to the sum of the monomers.

The electronic structures of **TS$_{2+2}$** and **6** were evaluated by the broken symmetry protocol and the open shell singlet (OSS) structures (BS1,1) were located. The energies of the (multi-determinant) OSS were estimated from the energy ε_0 of the optimized single-determinant broken symmetry solution and the energy ε_1 from a separate unrestricted triplet (m_s = 1)

calculation at the same geometry with the same functional and basis set, using the approximate spin correction formula proposed by Yamaguchi:[8]

$$\varepsilon_S \approx \frac{S_1^2\varepsilon_0 - S_0^2\varepsilon_1}{S_1^2 - S_0^2}$$

NBO analyses at the D3BJ-PBE0/def2-SV(P)-level have been undertaken with Gaussian 09 RevD.01[9] coupled to NBO6.0[10] using the within Turbomole optimized structures. Visualization of the NBO's and NLMO's failed with larger basis sets but the NBO output regarding the resulting NBO's and NLMO's is essentially equal to the def2-TZVP basis.

3.2 Calculated structures of N-N coupling

3.2.1 Coupling of two Ir(IV) nitrido complexes **2** to dimer **3**

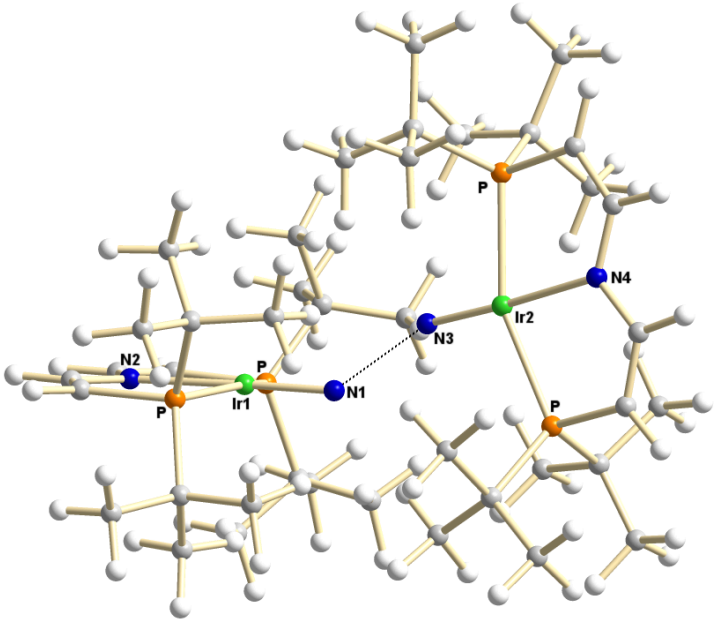

Figure S21. Calculated structure of the $^{BS(1,1)}$**TS$_A$** transition state.

Table S7. Selected computational data for the coupling of two Ir(IV) nitrido complexes **2** to **3** (in pm and deg)

	^{2}**2**	**Encounter complex**[a]	$^{BS(1,1)}$**TS$_{2+2}$**	^{1}**3**	^{1}**3 (exp)**
Ir1 – N1	170.6	170.5	174.0	192.2	193.7
Ir2 – N3		170.6	174.0	192.2	193.3
Ir1 – N2	222.2	222.1	218.8	205.5	204.1
Ir2 – N4		222.2	218.9	205.5	203.5
N1 – N3		345.7	205.7	113.6	113.5
N1 – Ir1 – N2	179.9	175.9	177.2	171.9	173.6
N3 – Ir2 – N4		176.9	177.1	172.0	171.0
Ir1 – N3 – N4		108.3	131.6	172.8	174.6
N3 – N4 – Ir2		137.2	131.7	172.8	172.3
P – Ir1 – N1 – N3		-96.2/90.4	-130.4/ 56.9	-96.9/89.8	-68/72
P – Ir2 – N3 – N1		-166.1/14.3	-130.8/56.5	-96.9/89.8	-96/90
Ir – N – N – Ir		162.5	151.8	92.1	106
Calculated energies: D3BJ-PBE0/def2-TZVP//def2-SVP					
ΔE (kcal mol^{-1})	0.0	-10.3	-4.5	-127.7	-
ΔG (kcal mol^{-1})	0.0	4.7	14.2	-107.4	-
Calculated energies including COSMO (ε=7.6): D3BJ-PBE0/def2-TZVP//def2-SVP					
ΔE (kcal mol^{-1})	**0.0**	**-4.6**	**2.3**	**-121.8**	**-**
ΔG (kcal mol^{-1})	**0.0**	**10.4**	**21.0**	**-101.5**	**-**

(a) Broken Symmetry [1,1]

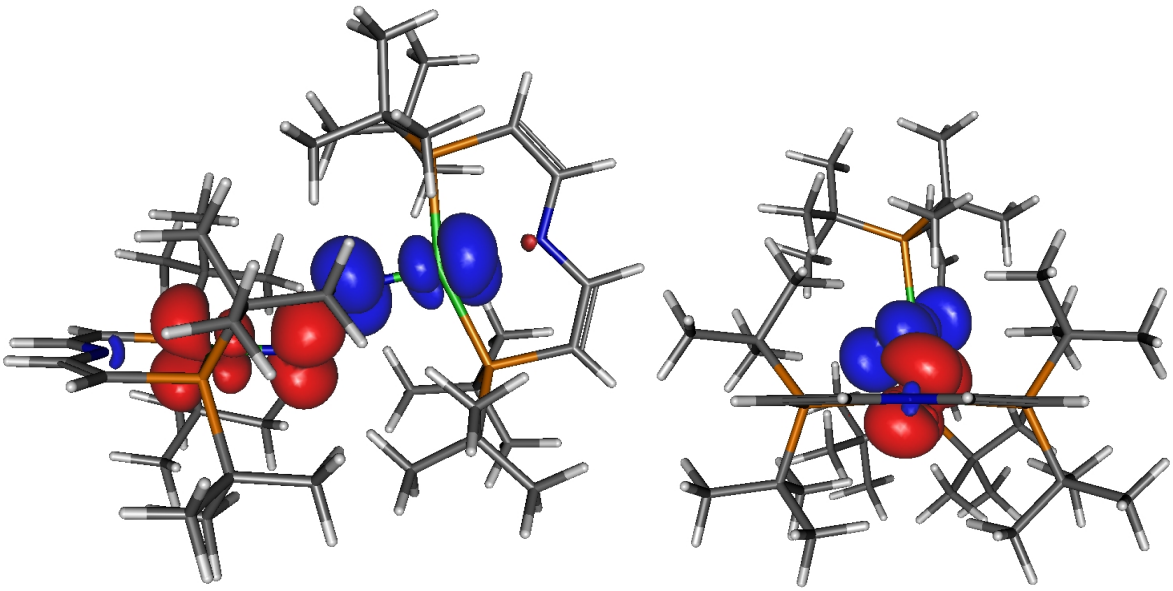

Figure S22. Spin density plot of the $^{BS(1,1)}TS_{2+2}$ transition state (view side-on and end-on).

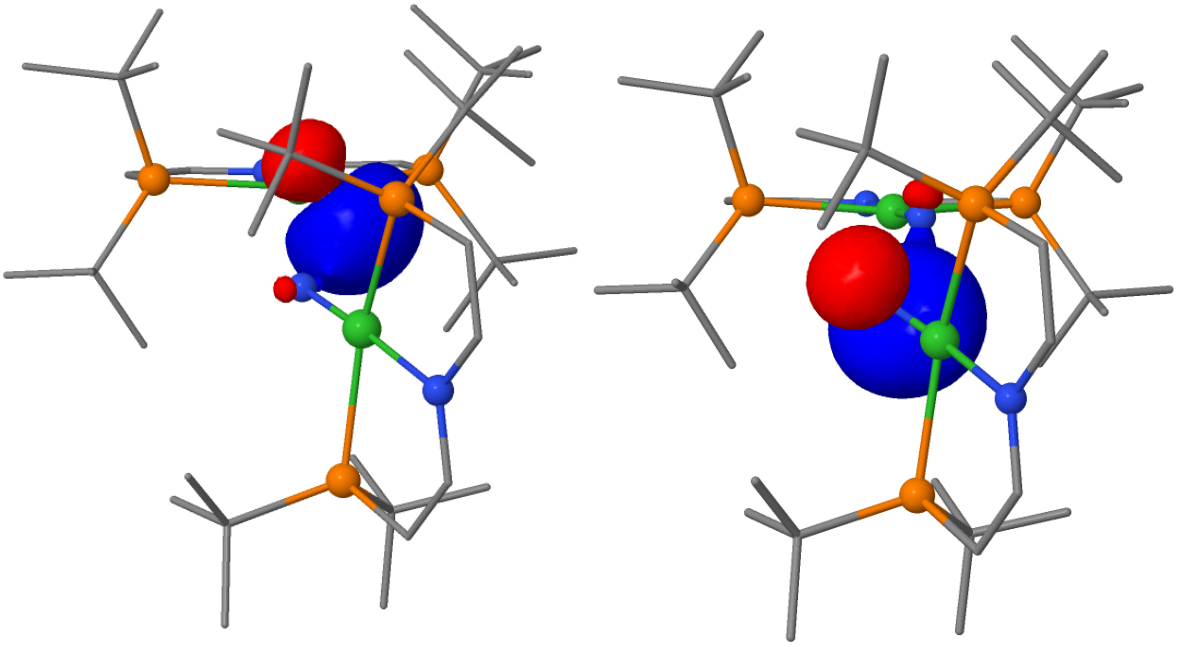

Figure S23. Selected NLMO's of the $^{BS(1,1)}TS_{2+2}$ transition state (view end-on) representing the π-π interaction described in figure 5 of the manuscript , left side: α-spin, right side: β-spin.

3.2.2 Coupling of the Ir(IV) nitrido complex **2** and Ir(V) nitrido complex **4** to dimer **5**

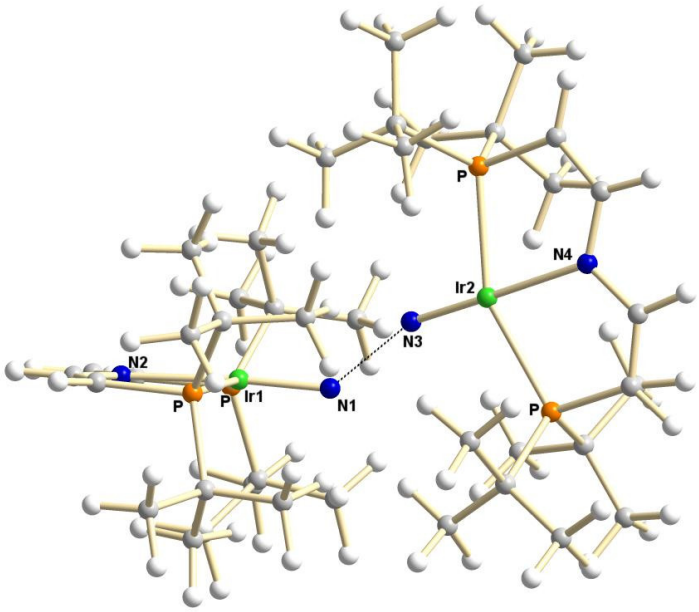

Figure S24. Calculated structure of the ^{2}**TS**$_{2+4}$ transition state.

Table S8. Selected computational data for the coupling of the Ir(IV) nitrido complex **2** and Ir(V) nitrido complex **4** to dimer **5** (in pm and deg)

	^{2}**2**	^{1}**4**	^{1}**4 (exp)**	**Encounter complex**	^{2}**TS**$_{2+4}$	^{2}**5**	^{2}**5 (exp)**
Ir1 – N1	170.6	165.2	167.8	168.2	170.4	198.8	198.4
Ir2 – N3				168.2	170.3	185.5	187.8
Ir1 – N2	222.2	211.0	204.1	217.9	217.4	196.9	197.3
Ir2 – N4				217.9	217.8	205.9	203.1
N1 – N3				246.6	200.3	114.1	113.6
N1 – Ir1 – N2	179.9	165.8	174.5	175.8	176.0	169.8	172.8
N3 – Ir2 – N4				175.8	176.2	171.6	173.3
Ir1 – N1 – N3				127.4	127.9	172.0	175.3
N1 – N3 – Ir2				127.4	127.7	173.2	176.6
P – Ir1 – N1 – N3				-126.5/61.8	-129.0/62.0	-90.5/95.8	-107/78
P – Ir2 – N3 – N1				126.5/61.8	-126.3/64.7	-105.0/82.0	-114/72
Ir – N – N – Ir				143.7	142.1	92.9	123
Calculated energies: D3BJ-PBE0/def2-TZVP//def2-SVP							
ΔE (kcal mol^{-1})	0.0	0.0	-	-20.1	-18.7	-124.5	-
ΔG (kcal mol^{-1})	0.0	0.0	-	-3.7	0.1	-106.1	-
Calculated energies including COSMO (ε=7.6): D3BJ-PBE0/def2-TZVP//def2-SVP							
ΔE (kcal mol^{-1})	**0.0**	**0.0**	**-**	**-9.8**	**-8.6**	**-115.6**	**-**
ΔG (kcal mol^{-1})	**0.0**	**0.0**	**-**	**6.5**	**10.1**	**-97.1**	**-**

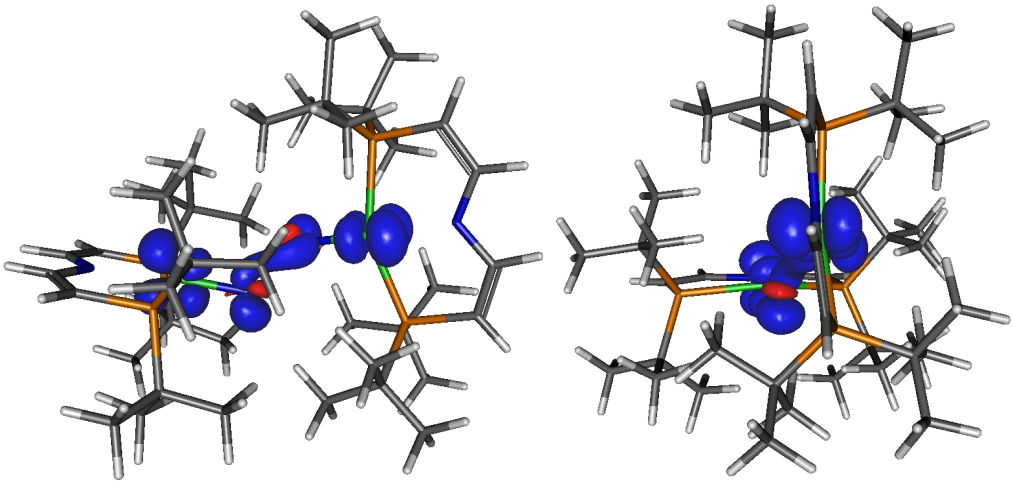

Figure S25. Spin density plot of the ^{2}**TS**$_{2+4}$ transition state (view side-on and end-on).

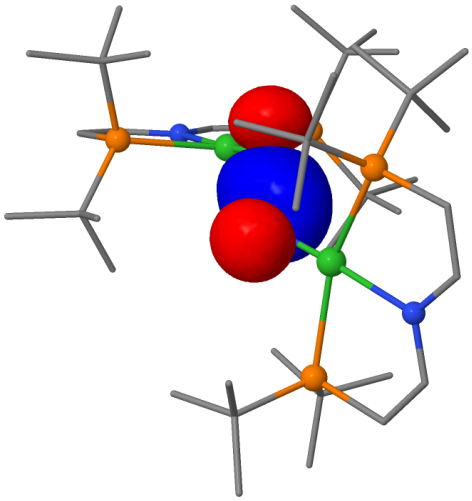

Figure S26. Selected α-spin NLMO of the ^{2}**TS**$_{2+4}$ transition state (view end-on) representing the π-π interaction described in figure 5 of the manuscript.

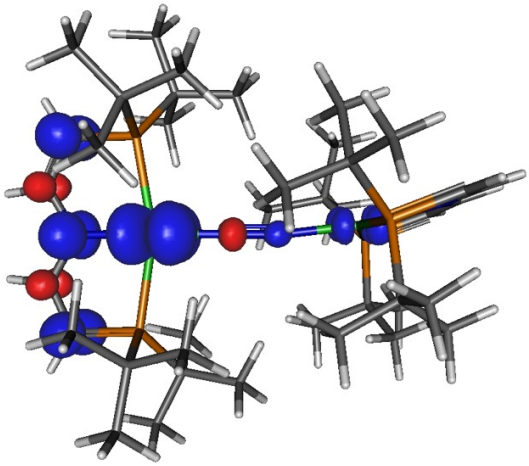

Figure S27. Spin density plot of ^{2}**5**.

3.2.3 Coupling of two Ir(V) nitrido complexes **4** to dimer **6**

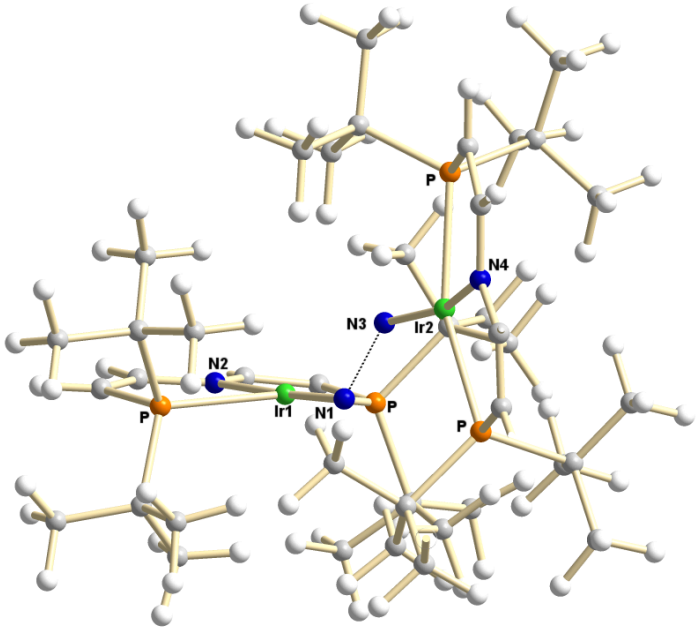

Figure S28. Calculated structure of the ^{1}**TS**$_{4+4}$ transition state.

Table S9. Selected computational data for the coupling of two Ir(V) nitrido complexes **4** to dimer **6** (in pm and deg)

	^{1}**4**	^{1}**4** (exp)	**Encounter Complex**	^{1}**TS**$_{4+4}$*	^{3}**6**	$^{BS(1,1)}$**6**	^{3}**6** (exp)
Ir1 – N1	165.2	167.8	165.4	169.0	192.8	192.9	195.4
Ir2 – N3			165.5	170.5	192.8	192.9	
Ir1 – N2	211.0	204.1	209.7	212.9	199.5	199.5	198.3
Ir2 – N4			211.1	204.8	199.5	199.5	
N1 – N3			313.5	184.1	113.3	113.3	113.8
N1 – Ir1 – N2	165.8	174.5	161.1	176.5	169.0	169.0	168.0
N3 – Ir2 – N4			177.7	159.0	169.0	169.0	
Ir1 – N1 – N3			149.5	130.1	173.2	173.2	172.2
N1 – N3 – Ir2			122.4	141.1	173.2	173.2	
P – Ir1 – N1 – N3			-151.0/31.8	-92.7/97.4	-98.9/87.8	-98.6/88.1	-89/100
P – Ir2 – N3 – N1			-107.1/75.0	-5.6/169.8	-98.9/87.7	-98.6/88.1	
Ir – N – N – Ir			169.8	-177.8	96.2	95.4	-99
Calculated energies: D3BJ-PBE0/def2-TZVP//def2-SVP							
ΔE (kcal mol^{-1})	0.0	-	24.7	39.9	-61.5	-61.2	-
ΔG (kcal mol^{-1})	0.0	-	35.7	58.2	-44.1	-43.6	-
Calculated energies including COSMO (ε=7.6): D3BJ-PBE0/def2-TZVP//def2-SVP							
ΔE (kcal mol^{-1})	**0.0**	**-**	**-2.8**	**11.0**	**-91.3**	**-91.1**	**-**
ΔG (kcal mol^{-1})	**0.0**	**-**	**-8.3**	**29.3**	**-73.9**	**-73.5**	**-**

* Transition state ^{1}**TS**$_{4+4}$ exhibits a second small imaginary vibration (13 cm^{-1}).

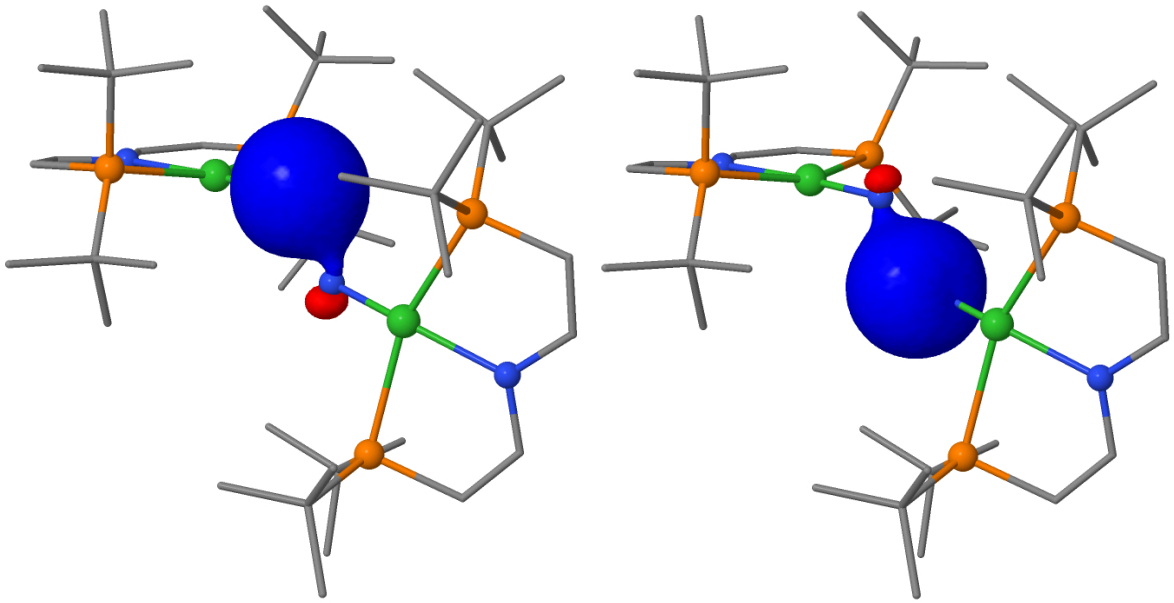

Figure S29. Selected NLMO's of the ^{1}**TS**$_{4+4}$ transition state (view side-on) representing the σ-π interactions described in figure 5 of the manuscript.

3.3 Relaxed surface scans of N-N coupling

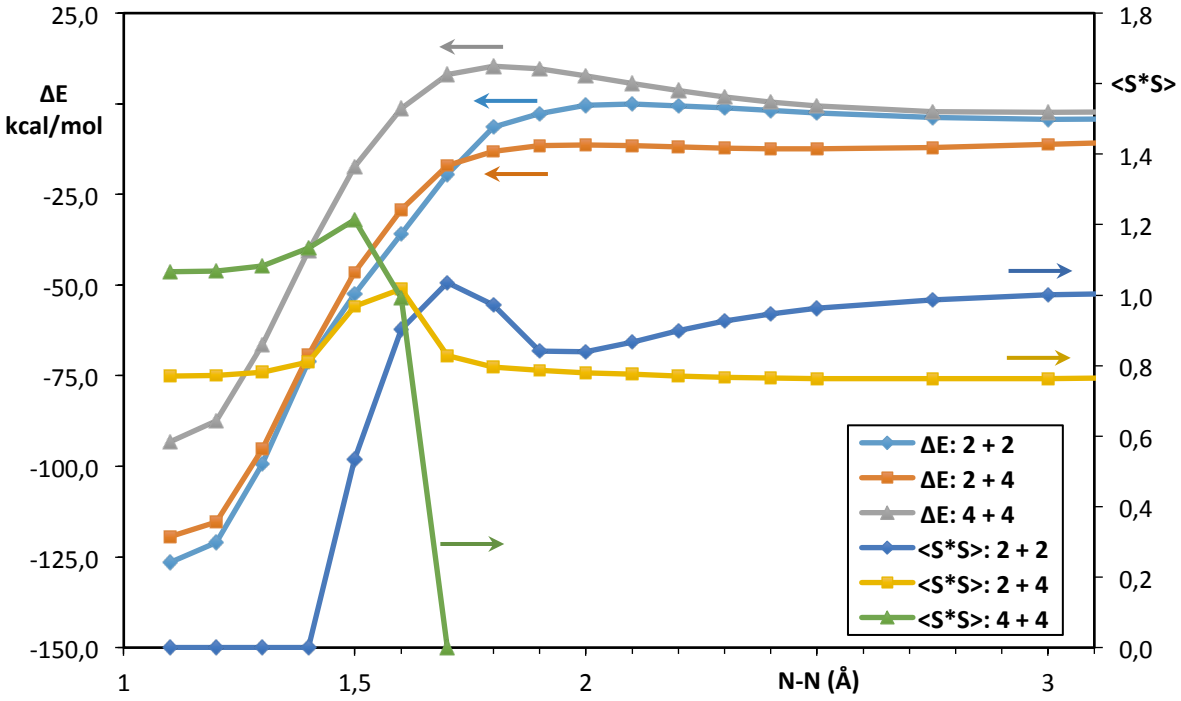

Figure S27. Calculated trajectories (E(SCF) in kcal mol^{-1}, relative to the educts) for the N-N coupling of (a) **2 + 2**, (b) **2 + 4** and (c) **4 + 4** and $<S^2>$ expectation values. The graphs show that - for (a) and (c) - the coupling is accompanied by a change of spin state although the significant change occurs after the transition state: (a) coupling on the open shell singlet surface of two antiferromagnetically coupled ^{2}**2** fragments and then transformation to the closed shell singlet state of dimer ^{1}**3**, (b) coupling at the doublet surface of **2** and **5**, (c) coupling on the closed shell singlet surface and transformation to the open shell singlet surface of $^{BS(1,1)}$**6** which is only slightly higher in energy than the triplet ground state ^{3}**6**. Values are taken from D3BJ-PBE0(Cosmo(THF))/def2-TZVP single point calculations after D3BJ/def2-SVP optimizations.

3.4 Calculated N_2-Vibrations

The calculated N_2 vibrations as obtained from the vibrational analyses at the D3BJ-PBE0/def2-SVP-level of theory have been scaled by an empirical factor of 0.908 which corresponds to the quotient $\nu_{N2}(exp)/\nu_{N2}(calc)$ of the terminal N_2 complex ^{1}[Ir(PNP)(N_2)]. By this procedure, the ν_{N2} of ^{2}**5** is very well reproduced allowing the conclusion that no terminal N_2 complex is formed besides **5** (see table).

Table S10. Calculated IR frequencies (in cm^{-1}) of the N-N vibration in comparison to experiment.

	ν_{N2} (exp. in Nujol)	ν_{N2} (calculated)	ν_{N2} (scaled)
^{1}[Ir(PNP)(N_2)]	2077	2287	2077
^{2}[Ir(PNP)(N_2)]$^+$		2347	2132
^{2}5	1960	2160	1962

3.5 Calculated Structures

^{2}[Ir(PNP)N] (**2**)

Ir	-0.00000	-0.21601	0.00316
P	2.31259	0.25215	0.00436
P	-2.31266	0.25190	-0.00625
N	-0.00002	2.00622	-0.00394
N	0.00001	-1.92150	0.01201
C	1.17622	2.67481	0.01627
H	1.13747	3.77557	0.01822
C	2.37994	2.03532	0.03466
H	3.31647	2.59455	0.03961
C	-1.17630	2.67462	-0.02697
H	-1.13764	3.77537	-0.03372
C	-2.37999	2.03497	-0.04243
H	-3.31654	2.59415	-0.04978
C	3.14385	-0.31080	-1.59503
C	2.89656	-1.80052	-1.83439
H	3.26895	-2.06785	-2.83715
H	1.82377	-2.03967	-1.78737
H	3.41804	-2.43742	-1.10843
C	4.63998	-0.00384	-1.61484
H	5.20277	-0.64425	-0.92105
H	4.85210	1.04841	-1.37044
H	5.03512	-0.19358	-2.62686
C	2.43908	0.48562	-2.69833
H	2.62459	1.56512	-2.60476
H	1.34998	0.32398	-2.66465
H	2.81239	0.14903	-3.67937
C	3.18263	-0.34723	1.56570
C	3.35130	-1.86450	1.53884
H	4.12913	-2.18183	0.82975
H	2.40811	-2.37068	1.27892
H	3.65774	-2.21219	2.53907
C	4.52663	0.34981	1.77859
H	4.40976	1.44253	1.82258
H	5.26132	0.10915	0.99967
H	4.95024	0.02400	2.74322
C	2.23893	0.03802	2.71062
H	2.71233	-0.22255	3.67181
H	1.28011	-0.49435	2.62844
H	2.02716	1.11819	2.71075
C	-3.17694	-0.35181	-1.56922
C	-2.22969	0.03190	-2.71174
H	-2.69933	-0.23164	-3.67395
H	-1.27049	-0.49906	-2.62480
H	-2.01929	1.11232	-2.71375
C	-4.52080	0.34359	-1.78824
H	-4.40485	1.43636	-1.83377
H	-5.25810	0.10364	-1.01155
H	-4.94062	0.01558	-2.75378
C	-3.34439	-1.86915	-1.53972
H	-4.12564	-2.18547	-0.83396
H	-2.40216	-2.37389	-1.27364
H	-3.64539	-2.21945	-2.54070
C	-3.14950	-0.30628	1.59184
C	-4.64456	0.00622	1.60752
H	-5.04283	-0.18028	2.61891
H	-5.20798	-0.63341	0.91353
H	-4.85232	1.05876	1.36071
C	-2.90837	-1.79652	1.83406

H	-3.28144	-2.06022	2.83752
H	-1.83664	-2.04060	1.78726
H	-3.43313	-2.43258	1.10972
C	-2.44437	0.48929	2.69554
H	-2.62300	1.56961	2.59790
H	-1.35615	0.32098	2.66665
H	-2.82367	0.15797	3.67609

^{1}[{Ir(PNP)}$_2$(N$_2$)] (**^{1}3**)

Ir	-0.08774	-2.47297	-0.20281
Ir	-0.08789	2.47320	0.20292
P	1.54321	-2.77755	-1.84877
P	-1.58946	-2.97200	1.54591
P	1.54569	2.77754	1.84588
P	-1.59331	2.97199	-1.54288
N	-0.43484	-4.45043	-0.63924
N	-0.43342	4.45101	0.63901
N	0.07869	-0.56797	-0.00673
N	0.07842	0.56826	0.00712
C	0.20963	-5.05697	-1.67622
H	-0.07806	-6.09608	-1.88846
C	1.16376	-4.43316	-2.41132
H	1.68453	-4.95056	-3.21763
C	-1.35991	-5.16784	0.06079
H	-1.53667	-6.19887	-0.27578
C	-2.03166	-4.65568	1.11944
H	-2.76687	-5.25163	1.66127
C	3.28096	-2.90469	-1.10602
C	4.37250	-3.16301	-2.14052
H	5.32067	-3.38117	-1.62046
H	4.54984	-2.29023	-2.78540
H	4.13993	-4.02872	-2.77881
C	3.21754	-4.08108	-0.12768
H	3.08541	-5.03885	-0.64998
H	2.38072	-3.95925	0.57713
H	4.15699	-4.12299	0.44825
C	3.58260	-1.63561	-0.31693
H	4.55142	-1.73831	0.20095
H	2.80307	-1.45652	0.43766
H	3.64421	-0.74914	-0.95871
C	1.49729	-1.71688	-3.40530
C	2.05400	-0.32338	-3.12003
H	1.86961	0.33467	-3.98380
H	3.14120	-0.34481	-2.95526
H	1.58135	0.14045	-2.24172
C	0.00416	-1.64609	-3.74421
H	-0.57698	-1.20820	-2.91960
H	-0.40069	-2.65297	-3.92787
H	-0.14431	-1.04235	-4.65434
C	2.22918	-2.34009	-4.59441
H	2.05718	-1.71391	-5.48605
H	1.84785	-3.34575	-4.82287
H	3.31376	-2.40524	-4.44388
C	-0.79546	-3.15180	3.26106
C	0.64261	-3.60246	2.99066
H	1.20138	-2.83932	2.42927
H	0.66469	-4.53114	2.40010
H	1.15498	-3.79168	3.94953
C	-1.48503	-4.21723	4.11322
H	-0.97054	-4.28435	5.08673
H	-1.43036	-5.20636	3.63730
H	-2.54017	-3.98847	4.31348
C	-0.77765	-1.81974	3.99917

H	-0.12279	-1.89566	4.88378
H	-1.77543	-1.52752	4.35687
H	-0.38900	-1.01407	3.36529
C	-3.23845	-2.06091	1.64259
C	-4.17294	-2.59364	2.72612
H	-5.16018	-2.11229	2.62192
H	-3.80859	-2.36936	3.73875
H	-4.32771	-3.67988	2.64261
C	-3.00562	-0.56436	1.84296
H	-3.96047	-0.02838	1.72303
H	-2.30040	-0.15533	1.10767
H	-2.62326	-0.32667	2.84334
C	-3.87211	-2.29585	0.26741
H	-4.15935	-3.34824	0.13238
H	-3.17235	-2.03597	-0.54109
H	-4.77489	-1.67052	0.16713
C	0.21363	5.05788	1.67422
H	-0.07286	6.09737	1.88624
C	1.16881	4.43392	2.40785
H	1.69158	4.95151	3.21276
C	-1.35986	5.16840	-0.05928
H	-1.53543	6.19971	0.27710
C	-2.03424	4.65591	-1.11610
H	-2.77046	5.25181	-1.65659
C	3.28247	2.90234	1.10046
C	3.58231	1.63173	0.31312
H	4.54977	1.73358	-0.20746
H	2.80095	1.45109	-0.43920
H	3.64576	0.74649	0.95642
C	4.37566	3.16207	2.13287
H	4.55305	2.29071	2.77967
H	4.14475	4.02959	2.76931
H	5.32334	3.37804	1.61100
C	3.21820	4.07696	0.12006
H	4.15730	4.11803	-0.45653
H	3.08623	5.03566	0.64072
H	2.38092	3.95372	-0.58395
C	1.50117	1.71802	3.40323
C	0.00830	1.64633	3.74295
H	-0.13910	1.04419	4.65432
H	-0.57266	1.20611	2.91948
H	-0.39764	2.65313	3.92476
C	2.05873	0.32462	3.11916
H	3.14602	0.34638	2.95501
H	1.58675	-0.14011	2.24093
H	1.87414	-0.33282	3.98335
C	2.23316	2.34320	4.59122
H	1.84909	3.34768	4.82032
H	3.31730	2.41177	4.43891
H	2.06455	1.71641	5.48310
C	-0.80297	3.15118	-3.25971
C	0.63523	3.60329	-2.99240
H	1.14540	3.79267	-3.95241
H	1.19588	2.84079	-2.43200
H	0.65772	4.53214	-2.40213
C	-1.49509	4.21518	-4.11153
H	-1.44015	5.20489	-3.63684
H	-2.55047	3.98544	-4.30936
H	-0.98267	4.28159	-5.08618
C	-0.78543	1.81833	-3.99643
H	-1.78354	1.52516	-4.35242
H	-0.39549	1.01362	-3.36211
H	-0.13182	1.89352	-4.88202
C	-3.24247	2.06089	-1.63542

C	-4.17945	2.59307	-2.71706
H	-3.81753	2.36792	-3.73036
H	-4.33380	3.67940	-2.63401
H	-5.16653	2.11199	-2.61015
C	-3.01002	0.56427	-1.83566
H	-3.96464	0.02838	-1.71354
H	-2.30327	0.15560	-1.10166
H	-2.62972	0.32611	-2.83671
C	-3.87292	2.29640	-0.25885
H	-4.15979	3.34886	-0.12356
H	-3.17131	2.03674	0.54812
H	-4.77551	1.67116	-0.15623

^{1}[Ir(PNP)N]$^{+}$ (**^{1}4**)

Ir	0.00003	-0.18102	0.13077
P	2.35469	0.24040	-0.05406
P	-2.35462	0.24033	-0.05435
N	0.00006	1.92133	-0.04585
N	-0.00013	-1.74271	0.66951
C	1.18315	2.63018	-0.07209
H	1.10654	3.72503	-0.09609
C	2.39079	2.02567	-0.07932
H	3.31622	2.60164	-0.10624
C	-1.18302	2.63011	-0.07319
H	-1.10644	3.72495	-0.09760
C	-2.39064	2.02557	-0.08094
H	-3.31608	2.60151	-0.10828
C	3.00299	-0.39669	-1.69515
C	2.63388	-1.87215	-1.86367
H	2.99038	-2.21262	-2.84837
H	1.54479	-2.02009	-1.82824
H	3.09434	-2.51776	-1.10536
C	4.51409	-0.19806	-1.81159
H	5.07388	-0.85401	-1.13088
H	4.81550	0.84404	-1.62725
H	4.82477	-0.45247	-2.83740
C	2.28411	0.42712	-2.76821
H	2.55969	1.48983	-2.73102
H	1.18932	0.34894	-2.67494
H	2.56237	0.03571	-3.75903
C	3.27857	-0.31187	1.48503
C	3.44663	-1.82885	1.49625
H	4.16037	-2.17388	0.73549
H	2.49025	-2.35495	1.35213
H	3.84291	-2.13230	2.47785
C	4.63755	0.38990	1.56774
H	4.53138	1.48280	1.61683
H	5.30412	0.13664	0.73421
H	5.13653	0.06887	2.49591
C	2.41429	0.13277	2.67049
H	2.96616	-0.06441	3.60292
H	1.46527	-0.41985	2.71715
H	2.19148	1.20995	2.63503
C	-3.00305	-0.39791	-1.69493
C	-2.28360	0.42454	-2.76863
H	-2.56231	0.03273	-3.75917
H	-1.18887	0.34555	-2.67537
H	-2.55835	1.48751	-2.73216
C	-4.51402	-0.19844	-1.81164
H	-4.81468	0.84418	-1.62900
H	-5.07425	-0.85287	-1.12982
H	-4.82493	-0.45432	-2.83702
C	-2.63480	-1.87374	-1.86218

H	-3.09542	-2.51843	-1.10320
H	-1.54579	-2.02224	-1.82690
H	-2.99174	-2.21489	-2.84649
C	-3.27863	-0.31069	1.48516
C	-4.63670	0.39276	1.56815
H	-5.13624	0.07175	2.49604
H	-5.30350	0.14098	0.73436
H	-4.52900	1.48548	1.61799
C	-3.44848	-1.82747	1.49674
H	-3.84417	-2.13030	2.47877
H	-2.49283	-2.35470	1.35185
H	-4.16333	-2.17178	0.73671
C	-2.41351	0.13311	2.67034
H	-2.18891	1.20990	2.63432
H	-1.46541	-0.42105	2.71716
H	-2.96564	-0.06268	3.60290

^{2}[{Ir(PNP)}$_2$(N$_2$)]$^+$ (**^{2}5**)

C	-0.12978	5.10748	1.45022
H	0.23224	6.12076	1.65692
C	-1.21377	4.60011	2.06549
H	-1.76274	5.18589	2.80398
C	-3.32902	3.16690	0.71291
C	-2.99582	3.62509	-0.70973
H	-2.45125	2.84990	-1.26909
H	-2.38158	4.53879	-0.70898
H	-3.93191	3.84925	-1.24682
C	-4.09366	1.84972	0.65876
H	-4.95795	1.95934	-0.01645
H	-4.48447	1.55303	1.64209
H	-3.47199	1.03337	0.27191
C	-4.17414	4.24504	1.39264
H	-3.69011	5.23074	1.34645
H	-4.39864	4.01633	2.44232
H	-5.13589	4.32589	0.86066
C	-1.80241	1.99765	3.20408
C	-1.99500	0.50600	2.93387
H	-2.97406	0.27995	2.49396
H	-1.93140	-0.04127	3.88675
H	-1.22089	0.10159	2.26855
C	-2.92416	2.51851	4.10024
H	-2.84448	3.59926	4.28890
H	-2.86126	2.01278	5.07739
H	-3.92140	2.30662	3.69046
C	-0.45088	2.22525	3.88994
H	0.38841	1.97286	3.22508
H	-0.38636	1.58531	4.78437
H	-0.32731	3.26974	4.20989
C	1.66286	5.02750	-0.06904
H	1.85940	6.04776	0.27916
C	2.41242	4.44559	-1.02527
H	3.24384	4.97758	-1.48936
C	1.19346	2.96806	-3.22573
C	2.27313	3.21304	-4.27643
H	2.91212	2.33259	-4.43242
H	2.91299	4.07196	-4.02572
H	1.78789	3.43680	-5.24030
C	0.23744	4.16393	-3.18153
H	0.77010	5.11374	-3.03383
H	-0.50577	4.05535	-2.37684
H	-0.30321	4.22264	-4.13953
C	0.39534	1.71098	-3.55823
H	-0.08013	1.82849	-4.54562

H	-0.39931	1.53862	-2.81718
H	1.02449	0.81431	-3.59884
C	3.43487	1.74230	-1.36127
C	3.69996	1.64591	0.14544
H	4.61224	1.05478	0.32164
H	2.86354	1.17299	0.67965
H	3.85434	2.64282	0.58635
C	4.64871	2.39038	-2.02935
H	5.52779	1.74977	-1.85301
H	4.87785	3.37625	-1.60047
H	4.53598	2.49895	-3.11445
C	3.17837	0.36052	-1.96097
H	3.05777	0.40427	-3.05284
H	2.28807	-0.12260	-1.53215
H	4.04055	-0.29204	-1.75622
C	-1.63658	-5.05677	-0.24930
H	-1.85221	-6.09486	0.03524
C	-2.33925	-4.44565	-1.23138
H	-3.12539	-4.96759	-1.77685
C	-0.97988	-2.88725	-3.30343
C	0.00271	-4.05933	-3.22166
H	0.60348	-4.08916	-4.14504
H	-0.51697	-5.02147	-3.11709
H	0.68792	-3.94627	-2.36794
C	-1.98336	-3.14057	-4.42577
H	-1.43414	-3.34017	-5.36058
H	-2.63335	-2.27334	-4.61034
H	-2.61642	-4.01735	-4.22455
C	-0.19282	-1.60770	-3.56801
H	0.34235	-1.69569	-4.52797
H	0.54985	-1.43673	-2.77480
H	-0.83960	-0.72478	-3.63144
C	-3.34267	-1.73122	-1.56644
C	-3.70665	-1.65521	-0.07999
H	-3.86576	-2.66152	0.33612
H	-4.64033	-1.08355	0.04489
H	-2.91018	-1.18033	0.51071
C	-4.51089	-2.37316	-2.31701
H	-4.32984	-2.46650	-3.39463
H	-5.40473	-1.74118	-2.18659
H	-4.75386	-3.36708	-1.91596
C	-3.06036	-0.34006	-2.13024
H	-2.87261	-0.36793	-3.21312
H	-2.19841	0.13816	-1.64163
H	-3.93784	0.30596	-1.97176
C	0.04598	-5.16455	1.37978
H	-0.29995	-6.19376	1.54184
C	1.08164	-4.66098	2.08701
H	1.59778	-5.25801	2.83895
C	3.26042	-3.17346	0.88723
C	4.09713	-4.22977	1.61029
H	3.62574	-5.22077	1.55811
H	4.27744	-3.98656	2.66548
H	5.07999	-4.30207	1.11632
C	3.01163	-3.64446	-0.54833
H	3.97789	-3.85242	-1.03697
H	2.47387	-2.88407	-1.13380
H	2.41537	-4.56937	-0.56952
C	3.99747	-1.84079	0.86569
H	4.89668	-1.92949	0.23371
H	4.33278	-1.53226	1.86615
H	3.37171	-1.04363	0.44673
C	1.57966	-2.05606	3.29396
C	0.19116	-2.29243	3.89728

H	-0.60554	-2.04574	3.17951
H	0.06840	-1.65860	4.79081
H	0.05534	-3.34076	4.19708
C	1.78151	-0.56188	3.05020
H	2.78053	-0.32880	2.66160
H	1.66906	-0.02250	4.00375
H	1.03914	-0.15821	2.34886
C	2.64661	-2.57795	4.25436
H	2.56609	-3.66302	4.41521
H	2.51609	-2.09220	5.23557
H	3.66569	-2.34933	3.91239
Ir	0.16588	2.49534	0.11060
Ir	-0.17920	-2.45760	0.09844
N	0.58999	4.37436	0.51906
N	-0.62355	-4.44049	0.43145
N	-0.00221	0.52302	-0.07578
N	-0.00054	-0.61757	-0.05673
P	-1.66192	2.92349	1.57437
P	1.87916	2.78617	-1.47829
P	-1.78796	-2.78982	-1.59924
P	1.54132	-2.98867	1.65944

^{3}[{Ir(PNP)}$_2$(N$_2$)]$^{2+}$ (**^{3}6**)

Ir	-0.08215	-2.47712	-0.21558
Ir	-0.08251	2.47765	0.21499
P	1.57447	-2.73324	-1.87888
P	-1.59957	-2.97828	1.55269
P	1.57345	2.73384	1.87874
P	-1.60013	2.97806	-1.55329
N	-0.47853	-4.36676	-0.71576
N	-0.47784	4.36800	0.71356
N	0.07073	-0.56604	-0.01020
N	0.07045	0.56659	0.01035
C	0.15492	-4.99662	-1.77073
H	-0.17783	-6.01231	-2.00941
C	1.14691	-4.38801	-2.45685
H	1.65290	-4.90077	-3.27689
C	-1.43221	-5.12046	-0.05876
H	-1.63132	-6.12158	-0.45577
C	-2.07769	-4.63834	1.02467
H	-2.83355	-5.23958	1.53335
C	3.29732	-2.92676	-1.13921
C	4.38313	-3.14324	-2.19008
H	5.33153	-3.36840	-1.67671
H	4.55433	-2.25090	-2.80801
H	4.16381	-3.99344	-2.85211
C	3.22237	-4.14277	-0.21085
H	3.10323	-5.08315	-0.76719
H	2.39200	-4.05500	0.50673
H	4.16006	-4.21011	0.36263
C	3.59406	-1.68289	-0.30570
H	4.56562	-1.80761	0.19875
H	2.82759	-1.53211	0.46977
H	3.65387	-0.77479	-0.91738
C	1.49034	-1.67092	-3.42569
C	2.08233	-0.29292	-3.13162
H	1.90612	0.36806	-3.99377
H	3.16961	-0.33657	-2.97652
H	1.62331	0.17940	-2.25021
C	-0.00754	-1.56840	-3.73325
H	-0.56663	-1.10068	-2.90998
H	-0.44974	-2.56040	-3.91299
H	-0.15310	-0.97119	-4.64690

C	2.19696	-2.30334	-4.62634
H	2.06020	-1.64319	-5.49763
H	1.76583	-3.27789	-4.89512
H	3.27590	-2.42650	-4.47736
C	-0.77798	-3.28944	3.22738
C	0.64924	-3.74288	2.90876
H	1.22133	-2.95671	2.39283
H	0.66094	-4.64447	2.27707
H	1.16758	-3.99030	3.84900
C	-1.48614	-4.39166	4.01669
H	-0.97696	-4.51019	4.98648
H	-1.43272	-5.36234	3.50359
H	-2.53878	-4.16445	4.22708
C	-0.73671	-1.99659	4.03444
H	-0.09029	-2.14339	4.91462
H	-1.72837	-1.70259	4.40534
H	-0.32005	-1.16557	3.45126
C	-3.23908	-2.06631	1.66719
C	-4.15768	-2.62146	2.75417
H	-5.13567	-2.11952	2.68020
H	-3.77447	-2.43372	3.76643
H	-4.34153	-3.69987	2.64266
C	-2.97691	-0.58037	1.90845
H	-3.93444	-0.03928	1.86542
H	-2.31780	-0.14865	1.14331
H	-2.53698	-0.38399	2.89410
C	-3.88810	-2.25947	0.29229
H	-4.21101	-3.29852	0.13416
H	-3.20232	-1.98832	-0.52448
H	-4.78133	-1.61883	0.22135
C	0.15618	4.99850	1.76778
H	-0.17555	6.01482	2.00521
C	1.14741	4.38967	2.45480
H	1.65384	4.90292	3.27426
C	-1.43141	5.12154	0.05627
H	-1.62984	6.12314	0.45238
C	-2.07772	4.63861	-1.02632
H	-2.83359	5.23967	-1.53520
C	3.29706	2.92492	1.14029
C	3.59388	1.67944	0.30924
H	4.56602	1.80270	-0.19446
H	2.82811	1.52790	-0.46675
H	3.65251	0.77230	0.92243
C	4.38189	3.14268	2.19194
H	4.55153	2.25159	2.81210
H	4.16261	3.99458	2.85179
H	5.33112	3.36579	1.67919
C	3.22376	4.13928	0.20965
H	4.16215	4.20515	-0.36283
H	3.10440	5.08075	0.76412
H	2.39418	4.05057	-0.50871
C	1.48740	1.67300	3.42650
C	-0.01090	1.56933	3.73159
H	-0.15740	0.97358	4.64606
H	-0.56796	1.09947	2.90820
H	-0.45459	2.56113	3.90870
C	2.08115	0.29519	3.13514
H	3.16875	0.33949	2.98259
H	1.62454	-0.17836	2.25310
H	1.90337	-0.36507	3.99753
C	2.19131	2.30762	4.62758
H	1.75783	3.28148	4.89508
H	3.27019	2.43292	4.47978
H	2.05486	1.64783	5.49919

C	-0.77923	3.28811	-3.22853
C	0.64822	3.74154	-2.91088
H	1.16610	3.98830	-3.85154
H	1.22040	2.95557	-2.39479
H	0.66043	4.64349	-2.27973
C	-1.48765	4.38984	-4.01830
H	-1.43341	5.36101	-3.50620
H	-2.54056	4.16284	-4.22755
H	-0.97927	4.50723	-4.98864
C	-0.73851	1.99469	-4.03467
H	-1.73040	1.70055	-4.40488
H	-0.32169	1.16409	-3.45104
H	-0.09249	2.14071	-4.91527
C	-3.23978	2.06620	-1.66648
C	-4.15902	2.62091	-2.75314
H	-3.77656	2.43246	-3.76555
H	-4.34254	3.69943	-2.64216
H	-5.13708	2.11925	-2.67819
C	-2.97793	0.58010	-1.90718
H	-3.93551	0.03918	-1.86307
H	-2.31823	0.14873	-1.14236
H	-2.53887	0.38310	-2.89309
C	-3.88792	2.26003	-0.29124
H	-4.21028	3.29927	-0.13323
H	-3.20178	1.98882	0.52519
H	-4.78140	1.61981	-0.21959

$^{BS(1,1)}$[{Ir(PNP)}$_2$(N$_2$)]$^{2+}$ (**$^{BS(1,1)}$6**)

Ir	-0.08348	-2.47745	-0.21351
Ir	-0.08256	2.47820	0.21348
P	1.56884	-2.73502	-1.87996
P	-1.59624	-2.97535	1.55884
P	1.57430	2.73544	1.87513
P	-1.60081	2.97563	-1.55430
N	-0.48178	-4.36775	-0.71102
N	-0.47750	4.36950	0.71010
N	0.07090	-0.56590	-0.00985
N	0.07081	0.56659	0.01038
C	0.14773	-4.99803	-1.76787
H	-0.18639	-6.01347	-2.00579
C	1.13868	-4.39003	-2.45638
H	1.64255	-4.90373	-3.27716
C	-1.43282	-5.12081	-0.05010
H	-1.63310	-6.12259	-0.44486
C	-2.07531	-4.63666	1.03449
H	-2.82981	-5.23717	1.54609
C	3.29317	-2.92962	-1.14364
C	4.37641	-3.14978	-2.19640
H	5.32572	-3.37497	-1.68475
H	4.54724	-2.25893	-2.81653
H	4.15459	-4.00101	-2.85628
C	3.21841	-4.14354	-0.21259
H	3.08528	-5.08398	-0.76574
H	2.39678	-4.04736	0.51383
H	4.16186	-4.21788	0.35046
C	3.59374	-1.68478	-0.31280
H	4.56288	-1.81336	0.19534
H	2.82554	-1.52763	0.45964
H	3.66071	-0.77871	-0.92681
C	1.48343	-1.67439	-3.42796
C	2.07422	-0.29573	-3.13458
H	1.89922	0.36420	-3.99780
H	3.16124	-0.33884	-2.97773

H	1.61366	0.17735	-2.25442
C	-0.01464	-1.57369	-3.73527
H	-0.57460	-1.10950	-2.91055
H	-0.45497	-2.56597	-3.91801
H	-0.16131	-0.97411	-4.64717
C	2.19067	-2.30617	-4.62857
H	2.04390	-1.65156	-5.50239
H	1.76802	-3.28609	-4.89114
H	3.27135	-2.41820	-4.48354
C	-0.77185	-3.28445	3.23274
C	0.65625	-3.73394	2.91258
H	1.22597	-2.94568	2.39730
H	0.66975	-4.63463	2.27964
H	1.17590	-3.98142	3.85209
C	-1.47620	-4.38864	4.02273
H	-0.96562	-4.50608	4.99191
H	-1.42089	-5.35913	3.50942
H	-2.52921	-4.16416	4.23432
C	-0.73338	-1.99166	4.04005
H	-0.08637	-2.13725	4.92000
H	-1.72558	-1.70009	4.41137
H	-0.31886	-1.15949	3.45705
C	-3.23644	-2.06477	1.67583
C	-4.15304	-2.62001	2.76442
H	-5.13066	-2.11693	2.69350
H	-3.76722	-2.43399	3.77601
H	-4.33836	-3.69810	2.65208
C	-2.97499	-0.57842	1.91567
H	-3.93254	-0.03754	1.87031
H	-2.31464	-0.14751	1.15112
H	-2.53683	-0.38072	2.90183
C	-3.88746	-2.25890	0.30202
H	-4.20750	-3.29881	0.14356
H	-3.20396	-1.98500	-0.51571
H	-4.78282	-1.62100	0.23326
C	0.15645	5.00057	1.76381
H	-0.17528	6.01693	2.00110
C	1.14866	4.39213	2.45013
H	1.65605	4.90639	3.26840
C	-1.43019	5.12266	0.05169
H	-1.62801	6.12517	0.44584
C	-2.07710	4.63771	-1.02992
H	-2.83288	5.23822	-1.53962
C	3.29723	2.92612	1.13452
C	3.59278	1.68023	0.30343
H	4.56173	1.80561	-0.20589
H	2.82316	1.52540	-0.46805
H	3.65755	0.77404	0.91747
C	4.38376	3.14431	2.18428
H	4.55417	2.25353	2.80464
H	4.16569	3.99658	2.84408
H	5.33224	3.36695	1.66996
C	3.22268	4.13988	0.20319
H	4.16291	4.20917	-0.36588
H	3.09772	5.08125	0.75665
H	2.39602	4.04746	-0.51806
C	1.49093	1.67677	3.42459
C	-0.00663	1.57622	3.73427
H	-0.15170	0.97971	4.64846
H	-0.56731	1.10871	2.91196
H	-0.44746	2.56883	3.91404
C	2.08128	0.29770	3.13220
H	3.16792	0.34055	2.97260
H	1.61857	-0.17706	2.25405

H	1.90845	-0.36060	3.99707
C	2.19992	2.31048	4.62312
H	1.77450	3.28883	4.88716
H	3.27974	2.42644	4.47473
H	2.05828	1.65516	5.49726
C	-0.78189	3.28332	-3.23114
C	0.64746	3.73251	-2.91625
H	1.16442	3.97748	-3.85791
H	1.21819	2.94507	-2.40085
H	0.66344	4.63462	-2.28541
C	-1.48854	4.38706	-4.01972
H	-1.42930	5.35840	-3.50848
H	-2.54293	4.16379	-4.22569
H	-0.98261	4.50190	-4.99164
C	-0.74672	1.98970	-4.03724
H	-1.74040	1.69780	-4.40434
H	-0.33006	1.15823	-3.45477
H	-0.10311	2.13409	-4.91989
C	-3.24174	2.06562	-1.66496
C	-4.16201	2.62022	-2.75078
H	-3.77967	2.43346	-3.76355
H	-4.34689	3.69839	-2.63853
H	-5.13943	2.11725	-2.67619
C	-2.98174	0.57896	-1.90441
H	-3.93936	0.03857	-1.85492
H	-2.31867	0.14853	-1.14193
H	-2.54743	0.38004	-2.89203
C	-3.88776	2.26115	-0.28898
H	-4.20650	3.30141	-0.13010
H	-3.20156	1.98729	0.52652
H	-4.78333	1.62394	-0.21659

$^{BS(1,1)}$[{Ir(PNP)}$_2$(N$_2$)]$^{\#}$ (**$^{BS(1,1)}$TS$_{2+2}$**)

Ir	0.05311	-2.51546	0.18639
P	1.59639	-3.24312	-1.46077
P	-1.50390	-2.73262	1.95630
N	0.50148	-4.53918	0.88836
N	-0.26661	-0.92682	-0.44674
C	1.42822	-5.29259	0.24704
H	1.65141	-6.28563	0.66716
C	2.06159	-4.86686	-0.87830
H	2.80939	-5.48651	-1.37455
C	-0.13961	-5.03537	1.97604
H	0.14523	-6.04413	2.31251
C	-1.09772	-4.33568	2.63938
H	-1.60823	-4.76195	3.50357
C	3.17970	-2.22382	-1.50662
C	2.85826	-0.75602	-1.78364
H	3.76775	-0.15465	-1.62779
H	2.07348	-0.37690	-1.11128
H	2.52972	-0.58677	-2.81680
C	4.19346	-2.74983	-2.52024
H	3.86412	-2.58986	-3.55689
H	4.40437	-3.82103	-2.37992
H	5.14495	-2.20633	-2.39434
C	3.75354	-2.35198	-0.09203
H	4.05671	-3.38468	0.13144
H	3.01191	-2.04568	0.66155
H	4.63751	-1.69930	-0.00102
C	0.85458	-3.53384	-3.17364
C	0.72015	-2.21886	-3.93133
H	1.69034	-1.83995	-4.28340
H	0.25093	-1.44738	-3.30681

H	0.08335	-2.36858	-4.81944
C	1.65831	-4.54958	-3.98564
H	1.71185	-5.52026	-3.47226
H	2.68109	-4.21233	-4.19987
H	1.15507	-4.71242	-4.95350
C	-0.54015	-4.10823	-2.90631
H	-1.00948	-4.38616	-3.86498
H	-1.17883	-3.37286	-2.39577
H	-0.49102	-5.00802	-2.27363
C	-1.40497	-1.53874	3.40840
C	0.10025	-1.33601	3.60913
H	0.27294	-0.70973	4.49983
H	0.55133	-0.84880	2.73348
H	0.61286	-2.29866	3.76177
C	-1.99821	-2.12656	4.68982
H	-1.47987	-3.04793	4.99182
H	-3.07124	-2.34254	4.60531
H	-1.87131	-1.39457	5.50495
C	-2.07366	-0.20836	3.07024
H	-3.16690	-0.30363	2.99918
H	-1.68313	0.20938	2.12856
H	-1.86429	0.51481	3.87522
C	-3.25147	-2.90122	1.25519
C	-4.29742	-3.12302	2.34527
H	-5.26938	-3.34482	1.87350
H	-4.43737	-2.23283	2.97526
H	-4.04333	-3.97547	2.99345
C	-3.59726	-1.67369	0.41689
H	-4.55547	-1.84499	-0.10209
H	-2.81963	-1.48051	-0.33591
H	-3.70560	-0.76764	1.02399
C	-3.20336	-4.12532	0.33648
H	-3.00878	-5.04975	0.89845
H	-2.41299	-4.01503	-0.42179
H	-4.17250	-4.22610	-0.17937
Ir	0.05162	2.51539	-0.18702
P	1.59662	3.24548	1.45741
P	-1.50948	2.73075	-1.95374
N	0.49478	4.54070	-0.88899
N	-0.26224	0.92604	0.44714
C	1.42138	5.29541	-0.24914
H	1.64193	6.28909	-0.66915
C	2.05786	4.87015	0.87463
H	2.80550	5.49090	1.36973
C	-0.14938	5.03604	-1.97516
H	0.13285	6.04547	-2.31186
C	-1.10749	4.33476	-2.63686
H	-1.62050	4.76036	-3.49991
C	3.18184	2.22905	1.50080
C	2.86365	0.76057	1.77791
H	3.77426	0.16112	1.62130
H	2.07920	0.38001	1.10601
H	2.53616	0.59041	2.81123
C	4.19608	2.75676	2.51305
H	3.86872	2.59556	3.55013
H	4.40445	3.82849	2.37296
H	5.14854	2.21540	2.38538
C	3.75339	2.35855	0.08540
H	4.05402	3.39193	-0.13848
H	3.01128	2.05071	-0.66715
H	4.63865	1.70779	-0.00695
C	0.85674	3.53417	3.17146
C	0.72518	2.21851	3.92847
H	1.69631	1.84100	4.27943

H	0.25664	1.44668	3.30388
H	0.08895	2.36661	4.81727
C	1.66012	4.55057	3.98294
H	1.71248	5.52133	3.46956
H	2.68332	4.21418	4.19648
H	1.15738	4.71293	4.95115
C	-0.53918	4.10671	2.90640
H	-1.00778	4.38288	3.86594
H	-1.17732	3.37086	2.39583
H	-0.49220	5.00725	2.27457
C	-1.41160	1.53776	-3.40665
C	0.09345	1.33630	-3.60969
H	0.26535	0.71088	-4.50117
H	0.54616	0.84872	-2.73507
H	0.60519	2.29947	-3.76221
C	-2.00711	2.12606	-4.68680
H	-1.48909	3.04739	-4.98947
H	-3.07994	2.34232	-4.60024
H	-1.88193	1.39424	-5.50235
C	-2.07881	0.20664	-3.06847
H	-3.17203	0.30099	-2.99586
H	-1.68673	-0.21138	-2.12755
H	-1.86998	-0.51582	-3.87424
C	-3.25592	2.89580	-1.24906
C	-4.30446	3.11606	-2.33693
H	-5.27606	3.33512	-1.86313
H	-4.44350	2.22615	-2.96751
H	-4.05359	3.96972	-2.98478
C	-3.59770	1.66733	-0.41049
H	-4.55480	1.83694	0.11109
H	-2.81784	1.47489	0.34021
H	-3.70630	0.76143	-1.01777
C	-3.20821	4.11966	-0.33002
H	-3.01627	5.04465	-0.89204
H	-2.41616	4.01049	0.42672
H	-4.17655	4.21859	0.18771

$^{BS(1,1)}$[Ir(PNP)N]·[Ir(PNP)N] (Encounter complex)

Ir	-0.42661	-3.00455	0.01271
P	1.35797	-3.59963	-1.40876
P	-1.73104	-3.03485	1.97971
N	0.40719	-4.77521	1.06284
N	-1.12779	-1.72161	-0.86420
C	1.44235	-5.45322	0.51623
H	1.80742	-6.34468	1.05046
C	2.03100	-5.06829	-0.65130
H	2.87458	-5.61998	-1.06841
C	-0.15664	-5.18882	2.22179
H	0.24748	-6.10130	2.68785
C	-1.18377	-4.51732	2.81354
H	-1.62383	-4.86981	3.74744
C	2.71459	-2.28707	-1.39622
C	2.13879	-0.91346	-1.73955
H	2.93756	-0.15878	-1.64517
H	1.32578	-0.62762	-1.05518
H	1.75777	-0.85950	-2.76724
C	3.87135	-2.63430	-2.33063
H	3.58968	-2.54237	-3.38939
H	4.25733	-3.65064	-2.15727
H	4.70156	-1.93029	-2.15313
C	3.21384	-2.26110	0.05188
H	3.68889	-3.21038	0.33790
H	2.38433	-2.06824	0.74977

H	3.95255	-1.45115	0.16120
C	0.80159	-4.10631	-3.13750
C	0.37060	-2.88145	-3.93796
H	1.22473	-2.25362	-4.22981
H	-0.34007	-2.26488	-3.36726
H	-0.13036	-3.20938	-4.86390
C	1.87597	-4.89865	-3.88267
H	2.18224	-5.79173	-3.31806
H	2.77036	-4.30240	-4.10311
H	1.46330	-5.24346	-4.84529
C	-0.41179	-5.01381	-2.90779
H	-0.77077	-5.39121	-3.88004
H	-1.22801	-4.46770	-2.41224
H	-0.15247	-5.87658	-2.27568
C	-1.35894	-1.61362	3.16221
C	0.16393	-1.44484	3.09737
H	0.47952	-0.73401	3.87821
H	0.47239	-1.05271	2.11739
H	0.68461	-2.39899	3.27342
C	-1.76181	-1.95455	4.59753
H	-1.24149	-2.85360	4.95909
H	-2.84291	-2.10748	4.71400
H	-1.47430	-1.11716	5.25510
C	-2.02831	-0.32320	2.70035
H	-3.12098	-0.35469	2.81932
H	-1.77606	-0.09611	1.65427
H	-1.65607	0.51485	3.31161
C	-3.56812	-3.24879	1.60510
C	-4.41299	-3.30116	2.87679
H	-5.44795	-3.57646	2.61308
H	-4.45411	-2.32738	3.38525
H	-4.04379	-4.05431	3.58967
C	-4.06260	-2.13896	0.67709
H	-5.09814	-2.36409	0.37218
H	-3.44263	-2.07128	-0.22944
H	-4.06523	-1.15337	1.15933
C	-3.66326	-4.58643	0.86391
H	-3.35855	-5.42868	1.50149
H	-3.01805	-4.58600	-0.02878
H	-4.70587	-4.74803	0.54385
Ir	0.22763	2.87657	-0.12829
P	1.80203	3.63593	1.45684
P	-1.27369	3.02472	-1.95500
N	0.43904	5.01401	-0.69786
N	0.12320	1.25137	0.37988
C	1.30317	5.80496	-0.02344
H	1.38927	6.85548	-0.34332
C	2.05116	5.34677	1.02047
H	2.74591	6.00090	1.54871
C	-0.30780	5.51433	-1.71079
H	-0.18981	6.58272	-1.95085
C	-1.17865	4.74701	-2.42168
H	-1.77557	5.17308	-3.22917
C	3.46409	2.76231	1.27705
C	3.31418	1.25446	1.47215
H	4.25902	0.76486	1.18373
H	2.50773	0.84321	0.84657
H	3.10975	0.98041	2.51464
C	4.52077	3.32346	2.22676
H	4.32537	3.04692	3.27231
H	4.59817	4.41950	2.16217
H	5.50598	2.90649	1.95884
C	3.88081	3.02956	-0.17351
H	4.02308	4.10280	-0.36607

H	3.11675	2.65834	-0.87439
H	4.83058	2.50797	-0.37740
C	1.12942	3.63474	3.21926
C	1.04781	2.20953	3.75827
H	2.03466	1.81265	4.03522
H	0.59058	1.53040	3.02300
H	0.42340	2.19782	4.66706
C	1.94592	4.53013	4.15058
H	1.99457	5.56273	3.77498
H	2.97053	4.16607	4.30139
H	1.45804	4.55992	5.13893
C	-0.28637	4.20805	3.09354
H	-0.72988	4.30045	4.09907
H	-0.92342	3.55474	2.47902
H	-0.27671	5.20444	2.62640
C	-0.74450	2.05398	-3.48244
C	0.77942	2.20265	-3.53526
H	1.15981	1.71491	-4.44866
H	1.25318	1.73749	-2.65923
H	1.07986	3.26172	-3.55893
C	-1.34030	2.64488	-4.76154
H	-1.02973	3.68965	-4.90593
H	-2.43719	2.60103	-4.78168
H	-0.97115	2.06536	-5.62397
C	-1.11122	0.58013	-3.35022
H	-2.19303	0.40966	-3.44868
H	-0.78984	0.14342	-2.39256
H	-0.62021	0.01816	-4.16155
C	-3.05481	2.68046	-1.44253
C	-4.02057	2.74741	-2.62383
H	-5.05489	2.67925	-2.24732
H	-3.87372	1.91495	-3.32605
H	-3.93412	3.69474	-3.17801
C	-3.14797	1.32558	-0.74089
H	-4.18672	1.16842	-0.40516
H	-2.49266	1.30049	0.14090
H	-2.86649	0.47778	-1.37789
C	-3.39930	3.77957	-0.43242
H	-3.41487	4.77507	-0.89854
H	-2.66635	3.80044	0.38986
H	-4.39529	3.57601	-0.00546

^{2}[{Ir(PNP)}$_2$(N$_2$)]$^{+\#}$ (**^{2}TS$_{2+4}$**)

N	-0.46733	0.88715	-0.36181
Ir	0.18966	2.40230	0.05965
N	0.89363	4.39734	0.56194
P	-1.46726	3.12995	1.63653
P	1.93308	2.73467	-1.56833
C	0.27434	5.13561	1.52749
H	0.71467	6.11276	1.77082
C	-0.83584	4.70519	2.17134
H	-1.31006	5.29749	2.95410
C	-3.09886	3.51102	0.76725
C	-2.71970	4.12492	-0.58313
H	-2.23293	3.38546	-1.23470
H	-2.03922	4.98216	-0.46600
H	-3.63337	4.48411	-1.08350
C	-3.89893	2.23538	0.53748
H	-4.74346	2.45492	-0.13572
H	-4.32004	1.83242	1.46929
H	-3.28515	1.45870	0.06270
C	-3.91598	4.53323	1.55992
H	-3.37262	5.48151	1.67523

H	-4.20800	4.17374	2.55440
H	-4.84243	4.74787	1.00307
C	-1.64890	2.07374	3.17642
C	-1.94724	0.62511	2.79983
H	-2.93391	0.50928	2.33604
H	-1.94179	0.01214	3.71407
H	-1.19602	0.21549	2.10884
C	-2.72962	2.60624	4.11746
H	-2.58875	3.66999	4.35959
H	-2.68056	2.04561	5.06480
H	-3.74124	2.46839	3.71098
C	-0.28281	2.15910	3.86388
H	0.53139	1.89788	3.17225
H	-0.25912	1.45152	4.70852
H	-0.08565	3.16725	4.25322
C	1.95936	4.94866	-0.08780
H	2.28856	5.94210	0.24698
C	2.59094	4.32634	-1.11010
H	3.43321	4.78834	-1.62466
C	1.19739	2.93243	-3.29100
C	2.28353	3.15127	-4.34383
H	2.89724	2.25421	-4.50655
H	2.94680	3.99066	-4.08786
H	1.80237	3.39592	-5.30453
C	0.30053	4.17097	-3.21653
H	0.88135	5.08728	-3.04330
H	-0.44395	4.08124	-2.41159
H	-0.23953	4.27871	-4.17063
C	0.34398	1.71699	-3.64460
H	-0.11741	1.87666	-4.63266
H	-0.46069	1.56878	-2.91077
H	0.92997	0.79208	-3.69684
C	3.39287	1.55371	-1.48269
C	3.60635	1.33103	0.01677
H	4.50986	0.72013	0.17198
H	2.74720	0.81748	0.46821
H	3.74850	2.28599	0.54595
C	4.65715	2.18320	-2.07293
H	5.48155	1.45825	-1.97638
H	4.95438	3.09051	-1.52910
H	4.55944	2.42826	-3.13790
C	3.07977	0.23530	-2.18510
H	2.99414	0.35800	-3.27402
H	2.15647	-0.21975	-1.79828
H	3.90697	-0.46926	-2.00461
N	0.45425	-0.89152	-0.37831
Ir	-0.19024	-2.40174	0.07522
N	-0.89913	-4.39381	0.59558
P	-1.92072	-2.75458	-1.56090
P	1.45083	-3.11219	1.67696
C	-1.96040	-4.95111	-0.05544
H	-2.29284	-5.94077	0.28738
C	-2.58518	-4.33863	-1.08808
H	-3.42436	-4.80517	-1.60358
C	-1.16706	-2.97636	-3.27314
C	-0.27360	-4.21557	-3.17337
H	0.27610	-4.33671	-4.12036
H	-0.85809	-5.12842	-2.99427
H	0.46267	-4.11656	-2.36192
C	-2.24357	-3.20708	-4.33339
H	-1.75362	-3.46539	-5.28602
H	-2.85390	-2.31110	-4.51383
H	-2.91097	-4.04174	-4.07267
C	-0.30764	-1.76762	-3.63494

H	0.15682	-1.93872	-4.61967
H	0.49462	-1.61527	-2.89935
H	-0.88972	-0.84095	-3.69840
C	-3.37729	-1.56838	-1.50481
C	-3.60436	-1.32602	-0.01038
H	-3.75347	-2.27377	0.52979
H	-4.50806	-0.71146	0.12827
H	-2.74827	-0.80801	0.44189
C	-4.63730	-2.20210	-2.09955
H	-4.53018	-2.45950	-3.16069
H	-5.46110	-1.47450	-2.01898
H	-4.94145	-3.10252	-1.54810
C	-3.05345	-0.25955	-2.21995
H	-2.95744	-0.39508	-3.30647
H	-2.13319	0.19755	-1.82847
H	-3.88006	0.44966	-2.05554
C	-0.28744	-5.12103	1.57386
H	-0.72917	-6.09575	1.82455
C	0.81792	-4.68331	2.22127
H	1.28691	-5.26693	3.01363
C	3.09493	-3.49594	0.83331
C	3.90439	-4.50766	1.64715
H	3.36218	-5.45624	1.76523
H	4.18257	-4.13703	2.64161
H	4.83863	-4.72543	1.10473
C	2.73515	-4.12438	-0.51568
H	3.65646	-4.48396	-1.00155
H	2.25269	-3.39361	-1.18030
H	2.05728	-4.98376	-0.39844
C	3.89470	-2.22047	0.60192
H	4.74896	-2.44429	-0.05750
H	4.30196	-1.80733	1.53540
H	3.28585	-1.44999	0.11105
C	1.60724	-2.03784	3.20713
C	0.23193	-2.12003	3.87637
H	-0.57359	-1.86988	3.17063
H	0.19402	-1.40255	4.71211
H	0.03307	-3.12428	4.27491
C	1.90677	-0.59271	2.81857
H	2.89980	-0.47928	2.36797
H	1.88675	0.03025	3.72582
H	1.16435	-0.19275	2.11247
C	2.67631	-2.55683	4.16886
H	2.53553	-3.61851	4.41998
H	2.61205	-1.98663	5.10959
H	3.69313	-2.41962	3.77533

^{2}[Ir(PNP)N]·[Ir(PNP)N]$^{+}$ (Encounter complex)

N	-0.53694	1.10933	-0.38176
Ir	0.16143	2.58164	0.03348
N	0.92256	4.55691	0.55164
P	-1.43467	3.30048	1.66394
P	1.92864	2.85031	-1.57073
C	0.31365	5.30397	1.51653
H	0.75981	6.28026	1.75390
C	-0.79838	4.88468	2.16855
H	-1.26378	5.48714	2.94901
C	-3.10985	3.63328	0.86809
C	-2.80149	4.29671	-0.47787
H	-2.30565	3.59575	-1.16449
H	-2.15424	5.17933	-0.35994
H	-3.74589	4.62856	-0.93844
C	-3.86478	2.32946	0.63198

H	-4.73535	2.53010	-0.01350
H	-4.24527	1.89372	1.56642
H	-3.23545	1.58393	0.12528
C	-3.93824	4.59981	1.71712
H	-3.42659	5.56416	1.84563
H	-4.18433	4.19923	2.70863
H	-4.88976	4.79745	1.19762
C	-1.49836	2.21601	3.19532
C	-1.80378	0.76758	2.81988
H	-2.82030	0.63957	2.42860
H	-1.72008	0.14334	3.72263
H	-1.09780	0.37975	2.07093
C	-2.51799	2.72590	4.21372
H	-2.37270	3.78901	4.45658
H	-2.40077	2.15666	5.15003
H	-3.55277	2.58034	3.87392
C	-0.08829	2.30319	3.78788
H	0.67560	2.01974	3.04784
H	-0.01552	1.61116	4.64232
H	0.14275	3.31637	4.14464
C	1.99381	5.08369	-0.10948
H	2.34303	6.07552	0.21033
C	2.61234	4.43625	-1.12603
H	3.46232	4.87780	-1.64631
C	1.21369	3.02602	-3.30431
C	2.31786	3.21909	-4.34361
H	2.93076	2.31664	-4.47726
H	2.98045	4.06067	-4.09274
H	1.85483	3.44624	-5.31741
C	0.32700	4.27369	-3.25839
H	0.91213	5.18601	-3.07800
H	-0.43697	4.19572	-2.46963
H	-0.19003	4.38005	-4.22527
C	0.35025	1.81407	-3.65218
H	-0.09593	1.96848	-4.64798
H	-0.46695	1.68633	-2.92813
H	0.92319	0.87988	-3.68587
C	3.34850	1.62397	-1.43931
C	3.50773	1.37463	0.06354
H	4.39637	0.74606	0.23549
H	2.62773	0.86275	0.47676
H	3.64814	2.31750	0.61464
C	4.64494	2.22787	-1.98517
H	5.44759	1.47999	-1.88106
H	4.95022	3.11840	-1.41839
H	4.58026	2.49403	-3.04814
C	3.02548	0.31784	-2.15947
H	2.98327	0.44415	-3.25039
H	2.08107	-0.11818	-1.80364
H	3.82806	-0.40737	-1.94997
N	0.53718	-1.11068	-0.38198
Ir	-0.16054	-2.58247	0.03611
N	-0.92091	-4.55711	0.55772
P	-1.93056	-2.85268	-1.56469
P	1.43826	-3.29961	1.66471
C	-1.99334	-5.08452	-0.10099
H	-2.34208	-6.07599	0.22046
C	-2.61361	-4.43810	-1.11713
H	-3.46453	-4.88011	-1.63546
C	-1.21865	-3.03027	-3.29933
C	-0.33181	-4.27783	-3.25361
H	0.18332	-4.38537	-4.22138
H	-0.91653	-5.18997	-3.07095
H	0.43372	-4.19882	-2.46647

C	-2.32471	-3.22459	-4.33640
H	-1.86345	-3.45277	-5.31079
H	-2.93794	-2.32235	-4.46993
H	-2.98676	-4.06597	-4.08340
C	-0.35593	-1.81867	-3.65012
H	0.08847	-1.97419	-4.64656
H	0.46255	-1.69006	-2.92769
H	-0.92899	-0.88456	-3.68387
C	-3.35006	-1.62608	-1.43202
C	-3.50663	-1.37519	0.07084
H	-3.64614	-2.31747	0.62315
H	-4.39494	-0.74638	0.24370
H	-2.62588	-0.86292	0.48199
C	-4.64752	-2.23042	-1.97497
H	-4.58468	-2.49790	-3.03772
H	-5.44987	-1.48229	-1.87041
H	-4.95196	-3.12021	-1.40658
C	-3.02815	-0.32073	-2.15409
H	-2.98793	-0.44816	-3.24495
H	-2.08304	0.11550	-1.80041
H	-3.83024	0.40481	-1.94388
C	-0.31038	-5.30320	1.52235
H	-0.75618	-6.27920	1.76151
C	0.80277	-4.88327	2.17205
H	1.26947	-5.48491	2.95235
C	3.11214	-3.63327	0.86652
C	3.94189	-4.59895	1.71520
H	3.43045	-5.56317	1.84552
H	4.18957	-4.19736	2.70592
H	4.89256	-4.79712	1.19437
C	2.80161	-4.29808	-0.47826
H	3.74525	-4.63047	-0.93999
H	2.30472	-3.59780	-1.16482
H	2.15448	-5.18052	-0.35837
C	3.86671	-2.32971	0.62787
H	4.73626	-2.53103	-0.01877
H	4.24865	-1.89300	1.56127
H	3.23659	-1.58469	0.12139
C	1.50444	-2.21350	3.19481
C	0.09529	-2.29993	3.78967
H	-0.66972	-2.01712	3.05056
H	0.02394	-1.60707	4.64356
H	-0.13530	-3.31274	4.14778
C	1.80939	-0.76550	2.81737
H	2.82541	-0.63794	2.42463
H	1.72687	-0.14026	3.71954
H	1.10246	-0.37849	2.06889
C	2.52562	-2.72239	4.21217
H	2.38062	-3.78524	4.45638
H	2.40991	-2.15215	5.14805
H	3.55988	-2.57728	3.87058

$^{1}[\{Ir(PNP)\}_{2}(N_{2})]^{2+\#}$ (^{1}**TS**$_{4+4}$)

N	0.34340	-0.86558	0.39492
Ir	-0.02972	-2.41622	-0.16414
P	1.76663	-2.73285	-1.74124
P	-1.76483	-3.20026	1.33096
N	-0.49761	-4.32258	-0.98816
C	0.21685	-4.85409	-2.03778
H	-0.13794	-5.80825	-2.44652
C	1.30843	-4.24958	-2.54730
H	1.87249	-4.68010	-3.37495
C	-1.54282	-5.08536	-0.51401

H	-1.76437	-6.01499	-1.05332
C	-2.25969	-4.72977	0.56909
H	-3.08402	-5.33900	0.94085
C	3.37311	-3.04985	-0.81623
C	4.54133	-3.19167	-1.79299
H	5.42578	-3.52976	-1.23012
H	4.80657	-2.23913	-2.27216
H	4.34808	-3.94137	-2.57386
C	3.16773	-4.36591	-0.06068
H	3.06870	-5.22147	-0.74213
H	2.27752	-4.33344	0.58481
H	4.04358	-4.54281	0.58272
C	3.64394	-1.92651	0.18206
H	4.59063	-2.13712	0.70379
H	2.84912	-1.85967	0.93840
H	3.74325	-0.94809	-0.30306
C	1.82347	-1.42516	-3.08495
C	2.39947	-0.12019	-2.54689
H	2.32017	0.65425	-3.32606
H	3.46385	-0.20939	-2.29020
H	1.84776	0.23567	-1.66379
C	0.36354	-1.23806	-3.50734
H	-0.23563	-0.79009	-2.70292
H	-0.10226	-2.19292	-3.79515
H	0.32534	-0.57401	-4.38453
C	2.63096	-1.91833	-4.28979
H	2.59186	-1.14100	-5.06970
H	2.20493	-2.83285	-4.72445
H	3.68806	-2.09551	-4.05938
C	-1.06153	-3.65157	3.01610
C	0.29793	-4.29946	2.73660
H	1.02000	-3.56907	2.34292
H	0.21749	-5.13411	2.02309
H	0.70016	-4.70483	3.67809
C	-1.96523	-4.67089	3.71549
H	-1.50985	-4.92750	4.68505
H	-2.05229	-5.60228	3.13913
H	-2.97236	-4.28733	3.92079
C	-0.87339	-2.40757	3.87638
H	-0.29848	-2.68066	4.77559
H	-1.82930	-1.98665	4.21754
H	-0.31154	-1.62734	3.34459
C	-3.28673	-2.09893	1.33955
C	-4.36056	-2.67770	2.26357
H	-5.28663	-2.09747	2.12447
H	-4.08601	-2.59891	3.32421
H	-4.59750	-3.72663	2.03461
C	-2.93550	-0.67772	1.76490
H	-3.84315	-0.05850	1.69595
H	-2.17403	-0.23081	1.10967
H	-2.58390	-0.62321	2.80196
C	-3.78669	-2.09863	-0.10804
H	-4.13897	-3.09020	-0.42289
H	-3.00335	-1.77266	-0.80850
H	-4.63132	-1.39629	-0.19065
N	-0.32886	0.77081	-0.11391
Ir	-0.14727	2.43608	0.20122
P	1.41257	2.67469	2.03663
P	-1.52790	3.17067	-1.65792
N	-0.62098	4.32439	0.83594
C	-0.08891	4.86702	1.99692
H	-0.47671	5.84575	2.30265
C	0.86272	4.23934	2.70948
H	1.27420	4.67890	3.61827

C	-1.58430	5.08692	0.19042
H	-1.87276	6.02657	0.67610
C	-2.12916	4.71385	-0.98064
H	-2.88417	5.32649	-1.47487
C	3.15567	2.96642	1.39103
C	3.55372	1.79781	0.49351
H	4.56053	1.98368	0.08676
H	2.85844	1.69417	-0.35144
H	3.58397	0.84480	1.03520
C	4.15759	3.14320	2.53089
H	4.31237	2.21939	3.10518
H	3.86661	3.94661	3.22291
H	5.13155	3.42363	2.09939
C	3.09586	4.24984	0.55808
H	4.06886	4.39536	0.06353
H	2.89631	5.13495	1.17679
H	2.32897	4.19555	-0.22904
C	1.27416	1.45817	3.46144
C	-0.22806	1.20618	3.61495
H	-0.40060	0.58378	4.50683
H	-0.64326	0.68645	2.74203
H	-0.78494	2.14548	3.75356
C	2.01289	0.16026	3.14331
H	3.10177	0.30116	3.09984
H	1.67344	-0.27890	2.19509
H	1.81510	-0.56613	3.94702
C	1.80729	2.06816	4.76105
H	1.22806	2.94760	5.07395
H	2.86721	2.34386	4.70796
H	1.70436	1.31512	5.55857
C	-0.52736	3.64913	-3.17852
C	0.79095	4.21452	-2.64234
H	1.37230	4.62992	-3.48057
H	1.39695	3.43311	-2.16011
H	0.62499	5.02918	-1.92048
C	-1.24405	4.73275	-3.98706
H	-1.37492	5.65624	-3.40598
H	-2.22323	4.41308	-4.36364
H	-0.62189	4.98159	-4.86142
C	-0.24728	2.42122	-4.03814
H	-1.14540	2.06253	-4.56017
H	0.16855	1.59691	-3.44267
H	0.49286	2.68797	-4.80889
C	-3.05650	2.12987	-1.98744
C	-3.91979	2.75837	-3.08289
H	-3.44403	2.70708	-4.07163
H	-4.18140	3.80469	-2.86956
H	-4.86396	2.19470	-3.14712
C	-2.66746	0.70604	-2.37315
H	-3.58414	0.10114	-2.44925
H	-2.01873	0.24202	-1.61553
H	-2.16107	0.65660	-3.34424
C	-3.82519	2.11625	-0.66241
H	-4.19908	3.11314	-0.39183
H	-3.20360	1.74486	0.16537
H	-4.69388	1.44636	-0.76272

^{1}[Ir(PNP)N]$^{+}$·[Ir(PNP)N]$^{+}$ (Encounter complex)

N	-0.04116	-1.24836	0.08786
Ir	-0.05546	-2.86744	-0.24907
P	1.74719	-3.07617	-1.83099
P	-1.78133	-3.63789	1.24016

N	-0.53377	-4.70397	-1.14188
C	0.14221	-5.14989	-2.26089
H	-0.23470	-6.06399	-2.73655
C	1.22581	-4.51304	-2.75144
H	1.75569	-4.88345	-3.62963
C	-1.59899	-5.45825	-0.69178
H	-1.84624	-6.36070	-1.26525
C	-2.30782	-5.12569	0.40716
H	-3.15168	-5.72908	0.74422
C	3.34247	-3.50160	-0.93294
C	4.52237	-3.58437	-1.90101
H	5.40222	-3.95585	-1.35211
H	4.79202	-2.60646	-2.32331
H	4.33504	-4.28694	-2.72639
C	3.10481	-4.87303	-0.29246
H	2.98714	-5.66529	-1.04400
H	2.21503	-4.87737	0.35568
H	3.97406	-5.12553	0.33438
C	3.60640	-2.47114	0.16717
H	4.51330	-2.76785	0.71711
H	2.77262	-2.42777	0.88385
H	3.77430	-1.46081	-0.22737
C	1.85046	-1.64234	-3.04033
C	2.57893	-0.46103	-2.40668
H	2.48746	0.40906	-3.07599
H	3.65105	-0.65773	-2.26879
H	2.13169	-0.17049	-1.44525
C	0.40649	-1.25241	-3.37477
H	-0.09400	-0.77502	-2.52070
H	-0.18892	-2.11977	-3.69966
H	0.42159	-0.52975	-4.20652
C	2.55784	-2.09865	-4.32060
H	2.62929	-1.23605	-5.00208
H	1.99067	-2.88086	-4.84380
H	3.57874	-2.46066	-4.14499
C	-1.08722	-4.14415	2.90804
C	0.22149	-4.87742	2.59595
H	0.98216	-4.18955	2.19724
H	0.07313	-5.69853	1.87762
H	0.61623	-5.31762	3.52499
C	-2.04153	-5.10253	3.62485
H	-1.58139	-5.40452	4.57887
H	-2.21451	-6.01780	3.04122
H	-3.01167	-4.64782	3.86089
C	-0.79811	-2.91257	3.76329
H	-0.21430	-3.22274	4.64424
H	-1.71709	-2.43830	4.13359
H	-0.20766	-2.16231	3.21452
C	-3.25096	-2.46429	1.26309
C	-4.36987	-3.03483	2.13815
H	-5.27035	-2.41513	2.00250
H	-4.11682	-3.00868	3.20653
H	-4.63963	-4.06466	1.86291
C	-2.84992	-1.07579	1.75457
H	-3.72633	-0.41417	1.67593
H	-2.04690	-0.63904	1.14323
H	-2.53073	-1.07109	2.80363
C	-3.72028	-2.37615	-0.19314
H	-4.06426	-3.34640	-0.57661
H	-2.92543	-2.00349	-0.85773
H	-4.56704	-1.67371	-0.24754
N	0.48488	1.70009	-0.83884
Ir	0.03103	3.00895	0.06704
P	1.67725	3.00704	1.81987

P	-1.81899	3.76139	-1.26358
N	-0.55200	4.72397	1.15204
C	0.12368	5.11599	2.29090
H	-0.23878	6.01749	2.80138
C	1.18664	4.43616	2.76971
H	1.71697	4.76419	3.66466
C	-1.61083	5.50673	0.73509
H	-1.85315	6.38594	1.34582
C	-2.32781	5.22131	-0.37220
H	-3.16591	5.84553	-0.68507
C	3.38904	3.33696	1.11864
C	3.73546	2.31536	0.03398
H	4.73253	2.55773	-0.36607
H	3.02203	2.35187	-0.80196
H	3.77395	1.28612	0.41268
C	4.44022	3.32140	2.22947
H	4.60241	2.31418	2.63779
H	4.18801	4.00225	3.05564
H	5.40018	3.66169	1.81022
C	3.31212	4.73237	0.48957
H	4.26989	4.94816	-0.00907
H	3.13678	5.51586	1.23928
H	2.51735	4.79556	-0.27084
C	1.51919	1.51322	2.94612
C	0.01279	1.28460	3.11388
H	-0.14634	0.50161	3.87274
H	-0.45081	0.95382	2.17306
H	-0.50349	2.19287	3.46159
C	2.16134	0.28565	2.30542
H	3.25730	0.35684	2.27213
H	1.78071	0.10518	1.28848
H	1.91253	-0.59944	2.91270
C	2.14155	1.80507	4.31411
H	1.63751	2.63972	4.82104
H	3.21541	2.02374	4.26059
H	2.01907	0.91422	4.95029
C	-1.24891	4.30745	-2.96605
C	0.05305	5.08242	-2.73357
H	0.37440	5.53136	-3.68639
H	0.86011	4.42523	-2.37771
H	-0.07923	5.89995	-2.00855
C	-2.28142	5.24183	-3.60306
H	-2.43987	6.14718	-3.00029
H	-3.25148	4.75911	-3.77508
H	-1.89850	5.56577	-4.58346
C	-0.98456	3.09587	-3.85756
H	-1.91292	2.59188	-4.16018
H	-0.32280	2.36074	-3.37289
H	-0.48669	3.43835	-4.77824
C	-3.23252	2.52735	-1.21080
C	-4.40563	3.00801	-2.06648
H	-4.18025	2.97093	-3.14104
H	-4.72484	4.02815	-1.80759
H	-5.26651	2.34310	-1.89182
C	-2.76143	1.14669	-1.67066
H	-3.60948	0.44848	-1.59308
H	-1.94676	0.76126	-1.04004
H	-2.42499	1.13631	-2.71468
C	-3.65331	2.45273	0.26045
H	-4.04368	3.41076	0.62995
H	-2.81637	2.14544	0.90741
H	-4.45309	1.70183	0.36016

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