List of Electronic Supplementary Information

A New Method for the Conversion of Allyl Alcohol into π-Allyl Species Promoted by Nucleophilic Interaction with a CO Ligand

Christian Dubs, Toshiki Yamamoto, Akiko Inagaki and Munetaka Akita *

Chemical Resources Laboratory, Tokyo Institute of Technology, R1-27, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Experimental procedures for X-ray crystallography.

Single crystals of **4b**, **5**·BF_4, and **6**·BF_4·(CH_2Cl_2) were obtained by recrystallization from CH_2Cl_2-ether. Diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with Mo Kα radiation (λ= 0.71069 Å) at –60°C. Indexing was performed from 3 oscillation images, which were exposed for 3 min. The crystal-to-detector distance was 110 mm ($2\theta_{max}$= 55°). In the reduction of data, Lorentz and polarization corrections and empirical absorption corrections were made.[1] The crystallographic data are summarized in Table S1.

The structural analysis was performed on an IRIS O2 computer using teXsan structure solving program system obtained from the Rigaku Corp., Tokyo, Japan.[2] Neutral scattering factors were obtained from the standard source.[3]

The structures were solved by a combination of the direct methods (SHELXS-86)[4] and Fourier synthesis (DIRDIF94).[5] Least-squares refinements were carried out using SHELXL-97 [4] (refined on F^2) linked to teXsan. Unless otherwise stated, all non-hydrogen atoms were refined anisotropically, methyl hydrogen atoms were refined using riding models, and other hydrogen atoms were fixed at the calculated positions. **4b**: H1-4 in the allyl ligand were refined isotropically. **6**·BF_4: The disordered central carbon atom was refined taking into account the minor component (C05 : C05a= 0.80 : 0.20). H1-5 in the allyl ligand were refined isotropically, and the hydrogen atom attached to C05a was not included in the refinement.

(1) Higashi, T. *Program for absorption correction*, Rigaku Corp., Tokyo, Japan, 1995.

(2) *teXsan; Crystal Structure Analysis Package, ver. 1. 11*, Rigaku Corp., Tokyo, Japan, 2000.

(3) *International Tables for X-ray Crystallography*; Kynoch Press, Birmingham, 1975, Vol. 4.

(4) (a) Sheldrick, G. M. *SHELXS-86: Program for crystal structure determination*, University of Göttingen, Göttingen, Germany, 1986. (b) Sheldrick, G. M. *SHELXL-97: Program for crystal structure refinement*, University of Göttingen: Göttingen, Germany, 1997.

(5) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system, Technical Report of the Crystallography Laboratory*, University of Nijmegen, Nijmegen, The Netherland, 1992.

Table S1. Crystallographic data.

complex	**4b**	**5**·BF_4	**6**·BF_4
solvate	-	-	CH_2Cl_2
formula	$C_{29}H_{25}NO_3PIr$	$C_{26}H_{26}NO_3BF_4PIr$	$C_{26}H_{28}NO_2BF_4PCl_2Ir$
formula weight	658.72	710.49	767.42
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	C2/c	$P\bar{1}$
a / Å	10.4334(8)	33.60(1)	9.9562(9)
b / Å	14.1368(9)	10.959(2)	11.5147(7)
c / Å	16.992(1)	15.568(5)	12.548(1)
α / deg	-	-	91.706(5)
β / deg	94.627(4)	112.406(8)	103.789(3)
γ / deg	-	-	91.982(5)
V/ $Å^3$	2498.0(3)	5298(2)	1395.2(2)
Z	4	8	2
d_{calcd} / $g \cdot cm^{-3}$	1.751	1.781	1.827
μ / mm^{-1}	0.5455	0.5171	0.5099
no of diffractions collected	19880	18920	11539
no of variable	332	334	368
R1 for data	0.0346	0.0633	0.0494
with $I > 2\sigma(I)$	(for 4960 data)	(for 4549 data)	(for 5644 data)
wR2	0.1172	0.1710	0.1471
	(for all 5571 data)	(for all 5997 data)	(for all 5828 data)

Table S2. Interatomic distances (Å) and bond angles (deg) for **4b**.

ATOM	ATOM	DISTANCE	ATOM	ATOM	DISTANCE
Ir(1)	P(1)	2.321(1)	C(06)	C(07)	1.40(1)
Ir(1)	N(1)	2.182(4)	C(07)	C(08)	1.37(1)
Ir(1)	C(1)	2.009(5)	C(08)	C(09)	1.390(8)
Ir(1)	C(2)	1.893(5)	C(11)	C(12)	1.402(6)
Ir(1)	C(02)	2.110(4)	C(11)	C(16)	1.500(7)
Ir(1)	C(03)	2.174(4)	C(12)	C(13)	1.375(8)
P(1)	C(16)	1.832(5)	C(13)	C(14)	1.371(8)
P(1)	C(21)	1.826(5)	C(14)	C(15)	1.382(7)
P(1)	C(31)	1.824(4)	C(21)	C(22)	1.386(7)
O(1)	C(1)	1.219(6)	C(21)	C(26)	1.395(7)
O(2)	C(2)	1.140(6)	C(22)	C(23)	1.395(8)
O(3)	C(1)	1.385(6)	C(23)	C(24)	1.389(9)
O(3)	C(01)	1.444(7)	C(24)	C(25)	1.366(8)
N(1)	C(11)	1.343(6)	C(25)	C(26)	1.387(8)
N(1)	C(15)	1.350(6)	C(31)	C(32)	1.399(7)
C(01)	C(02)	1.506(7)	C(31)	C(36)	1.403(7)
C(02)	C(03)	1.449(7)	C(32)	C(33)	1.392(7)
C(03)	C(04)	1.476(7)	C(33)	C(34)	1.382(8)
C(04)	C(05)	1.421(9)	C(34)	C(35)	1.389(8)
C(04)	C(09)	1.393(7)	C(35)	C(36)	1.375(7)
C(05)	C(06)	1.36(1)			

Table S2. Interatomic distances (Å) and bond angles (deg) for **4b**. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
P(1)	Ir(1)	C(1)	99.2(1)	C(05)	C(04)	C(09)	116.3(5)
P(1)	Ir(1)	C(2)	101.7(2)	C(04)	C(05)	C(06)	122.2(6)
P(1)	Ir(1)	C(02)	142.9(1)	C(05)	C(06)	C(07)	120.0(7)
P(1)	Ir(1)	C(03)	103.4(1)	C(06)	C(07)	C(08)	119.1(6)
N(1)	Ir(1)	C(1)	177.6(2)	C(07)	C(08)	C(09)	121.0(6)
N(1)	Ir(1)	C(2)	91.1(2)	C(04)	C(09)	C(08)	121.4(5)
N(1)	Ir(1)	C(02)	97.7(2)	N(1)	C(11)	C(12)	120.7(4)
N(1)	Ir(1)	C(03)	92.7(2)	N(1)	C(11)	C(16)	118.3(4)
C(1)	Ir(1)	C(2)	91.1(2)	C(12)	C(11)	C(16)	121.0(4)
C(1)	Ir(1)	C(02)	80.8(2)	C(11)	C(12)	C(13)	119.4(5)
C(1)	Ir(1)	C(03)	85.0(2)	C(12)	C(13)	C(14)	119.5(5)
C(2)	Ir(1)	C(02)	115.4(2)	C(13)	C(14)	C(15)	119.1(5)
C(2)	Ir(1)	C(03)	154.9(2)	N(1)	C(15)	C(14)	121.8(5)
C(02)	Ir(1)	C(03)	39.5(2)	P(1)	C(16)	C(11)	111.5(3)
Ir(1)	P(1)	C(16)	100.9(2)	P(1)	C(21)	C(22)	120.2(4)
Ir(1)	P(1)	C(21)	124.1(2)	P(1)	C(21)	C(26)	121.0(4)
Ir(1)	P(1)	C(31)	116.1(2)	C(22)	C(21)	C(26)	118.8(4)
C(16)	P(1)	C(21)	102.5(2)	C(21)	C(22)	C(23)	120.6(5)
C(16)	P(1)	C(31)	108.0(2)	C(22)	C(23)	C(24)	119.3(5)
C(21)	P(1)	C(31)	103.5(2)	C(23)	C(24)	C(25)	120.6(5)
C(1)	O(3)	C(01)	116.4(4)	C(24)	C(25)	C(26)	120.1(5)
Ir(1)	N(1)	C(11)	120.6(3)	C(21)	C(26)	C(25)	120.6(5)
Ir(1)	N(1)	C(15)	119.7(3)	P(1)	C(31)	C(32)	116.3(3)
C(11)	N(1)	C(15)	119.4(4)	P(1)	C(31)	C(36)	125.2(4)
Ir(1)	C(1)	O(1)	129.4(4)	C(32)	C(31)	C(36)	118.4(4)
O(1)	C(1)	O(3)	114.6(4)	C(31)	C(32)	C(33)	120.8(5)
O(3)	C(01)	C(02)	111.5(4)	C(32)	C(33)	C(34)	119.7(5)
Ir(1)	C(2)	O(2)	179.0(5)	C(33)	C(34)	C(35)	120.0(5)
Ir(1)	C(02)	C(01)	108.4(3)	C(34)	C(35)	C(36)	120.7(5)
Ir(1)	C(02)	C(03)	72.6(3)	C(31)	C(36)	C(35)	120.3(5)
C(01)	C(02)	C(03)	117.1(4)				
Ir(1)	C(03)	C(02)	67.9(2)				
Ir(1)	C(03)	C(04)	121.2(3)				
C(02)	C(03)	C(04)	124.2(4)				
C(03)	C(04)	C(05)	119.3(5)				
C(03)	C(04)	C(09)	124.2(5)				

Table S3. Interatomic distances (Å) and bond angles (deg) for **5**·BF_4.

ATOM	ATOM	DISTANCE	ATOM	ATOM	DISTANCE
Ir(1)	P(1)	2.304(2)	C(02)	C(03)	1.35(2)
Ir(1)	N(1)	2.195(5)	C(04)	C(05)	1.40(2)
Ir(1)	C(1)	2.059(8)	C(05)	C(06)	1.33(2)
Ir(1)	C(2)	1.89(1)	C(11)	C(12)	1.40(1)
Ir(1)	C(04)	2.21(1)	C(11)	C(16)	1.50(1)
Ir(1)	C(05)	2.217(9)	C(12)	C(13)	1.36(1)
Ir(1)	C(06)	2.26(1)	C(13)	C(14)	1.39(1)
P(1)	C(16)	1.806(7)	C(14)	C(15)	1.34(1)
P(1)	C(21)	1.820(7)	C(21)	C(22)	1.39(1)
P(1)	C(31)	1.821(8)	C(21)	C(26)	1.38(1)
F(1)	B(1)	1.40(2)	C(22)	C(23)	1.37(1)
F(2)	B(1)	1.41(2)	C(23)	C(24)	1.38(1)
F(3)	B(1)	1.31(1)	C(24)	C(25)	1.40(2)
F(4)	B(1)	1.34(1)	C(25)	C(26)	1.37(1)
O(1)	C(1)	1.19(1)	C(31)	C(32)	1.40(1)
O(2)	C(2)	1.15(1)	C(31)	C(36)	1.39(1)
O(3)	C(1)	1.34(1)	C(32)	C(33)	1.33(1)
O(3)	C(01)	1.45(1)	C(33)	C(34)	1.40(1)
N(1)	C(11)	1.36(1)	C(34)	C(35)	1.37(1)
N(1)	C(15)	1.34(1)	C(35)	C(36)	1.40(1)
C(01)	C(02)	1.36(3)			

Table S3. Interatomic distances (Å) and bond angles (deg) for **5**·BF_4. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
P(1)	Ir(1)	N(1)	80.4(2)	C(01)	C(02)	C(03)	129(2)
P(1)	Ir(1)	C(1)	93.5(3)	Ir(1)	C(04)	C(05)	71.8(6)
P(1)	Ir(1)	C(2)	98.0(2)	Ir(1)	C(05)	C(04)	71.3(5)
P(1)	Ir(1)	C(04)	98.6(3)	Ir(1)	C(05)	C(06)	74.4(6)
P(1)	Ir(1)	C(05)	131.4(3)	C(04)	C(05)	C(06)	126.8(8)
P(1)	Ir(1)	C(06)	164.9(4)	Ir(1)	C(06)	C(05)	70.9(6)
N(1)	Ir(1)	C(1)	173.7(3)	N(1)	C(11)	C(12)	120.2(6)
N(1)	Ir(1)	C(2)	94.5(3)	N(1)	C(11)	C(16)	117.8(6)
N(1)	Ir(1)	C(04)	91.5(3)	C(12)	C(11)	C(16)	122.1(7)
N(1)	Ir(1)	C(05)	82.4(3)	C(11)	C(12)	C(13)	118.5(8)
N(1)	Ir(1)	C(06)	99.2(3)	C(12)	C(13)	C(14)	120.4(7)
C(1)	Ir(1)	C(2)	87.9(4)	C(13)	C(14)	C(15)	118.8(7)
C(1)	Ir(1)	C(04)	87.8(4)	N(1)	C(15)	C(14)	122.8(8)
C(1)	Ir(1)	C(05)	100.7(3)	P(1)	C(16)	C(11)	111.5(6)
C(1)	Ir(1)	C(06)	86.3(3)	P(1)	C(21)	C(22)	118.9(6)
C(2)	Ir(1)	C(04)	163.0(4)	P(1)	C(21)	C(26)	122.1(6)
C(2)	Ir(1)	C(05)	128.5(4)	C(22)	C(21)	C(26)	119.0(7)
C(2)	Ir(1)	C(06)	97.0(4)	C(21)	C(22)	C(23)	120.4(8)
C(04)	Ir(1)	C(05)	36.9(4)	C(22)	C(23)	C(24)	120.6(8)
C(04)	Ir(1)	C(06)	66.3(4)	C(23)	C(24)	C(25)	119.6(9)
C(05)	Ir(1)	C(06)	34.6(5)	C(24)	C(25)	C(26)	118.7(8)
Ir(1)	P(1)	C(16)	99.4(2)	C(21)	C(26)	C(25)	121.8(8)
Ir(1)	P(1)	C(21)	115.8(3)	P(1)	C(31)	C(32)	120.0(5)
Ir(1)	P(1)	C(31)	120.9(2)	P(1)	C(31)	C(36)	121.1(6)
C(16)	P(1)	C(21)	106.9(3)	C(32)	C(31)	C(36)	118.7(8)
C(16)	P(1)	C(31)	105.3(4)	C(31)	C(32)	C(33)	122.0(8)
C(21)	P(1)	C(31)	106.9(3)	C(32)	C(33)	C(34)	120.5(9)
C(1)	O(3)	C(01)	116.3(8)	C(33)	C(34)	C(35)	119(1)
Ir(1)	N(1)	C(11)	118.0(4)	C(34)	C(35)	C(36)	120.9(8)
Ir(1)	N(1)	C(15)	122.6(5)	C(31)	C(36)	C(35)	118.8(8)
C(11)	N(1)	C(15)	119.3(6)	F(1)	B(1)	F(2)	99(1)
Ir(1)	C(1)	O(1)	127.0(6)	F(1)	B(1)	F(3)	106(1)
Ir(1)	C(1)	O(3)	112.3(6)	F(1)	B(1)	F(4)	113(1)
O(1)	C(1)	O(3)	120.7(8)	F(2)	B(1)	F(3)	110(1)
O(3)	C(01)	C(02)	115(1)	F(2)	B(1)	F(4)	108(1)
Ir(1)	C(2)	O(2)	177.5(7)	F(3)	B(1)	F(4)	119(1)

Table S4. Interatomic distances (Å) and bond angles (deg) for **6**·BF_4.

ATOM	ATOM	DISTANCE	ATOM	ATOM	DISTANCE
Ir(1)	P(1)	2.313(1)	C(01)	C(02)	1.52(1)
Ir(1)	N(1)	2.213(5)	C(02)	C(03)	1.40(1)
Ir(1)	C(1)	2.029(8)	C(04)	C(05)	1.40(1)
Ir(1)	C(02)	2.180(7)	C(04)	C(05A)	1.31(3)
Ir(1)	C(03)	2.204(6)	C(05)	C(06)	1.34(1)
Ir(1)	C(04)	2.261(7)	C(05A)	C(06)	1.44(3)
Ir(1)	C(05)	2.212(9)	C(11)	C(12)	1.396(9)
Ir(1)	C(05A)	2.27(3)	C(11)	C(16)	1.512(8)
Ir(1)	C(06)	2.188(8)	C(12)	C(13)	1.37(1)
Cl(1)	C(41)	1.73(1)	C(13)	C(14)	1.393(9)
Cl(2)	C(41)	1.81(1)	C(14)	C(15)	1.356(9)
P(1)	C(16)	1.834(6)	C(21)	C(22)	1.385(9)
P(1)	C(21)	1.816(7)	C(21)	C(26)	1.41(1)
P(1)	C(31)	1.810(6)	C(22)	C(23)	1.38(1)
F(1)	B(1)	1.387(8)	C(23)	C(24)	1.38(2)
F(2)	B(1)	1.37(1)	C(24)	C(25)	1.36(1)
F(3)	B(1)	1.380(9)	C(25)	C(26)	1.40(1)
F(4)	B(1)	1.38(1)	C(31)	C(32)	1.365(8)
O(1)	C(1)	1.222(9)	C(31)	C(36)	1.395(7)
O(3)	C(1)	1.37(1)	C(32)	C(33)	1.40(1)
O(3)	C(01)	1.42(1)	C(33)	C(34)	1.39(1)
N(1)	C(11)	1.339(7)	C(34)	C(35)	1.39(1)
N(1)	C(15)	1.351(8)	C(35)	C(36)	1.41(1)

Table S4. Interatomic distances (Å) and bond angles (deg) for **6**·BF_4. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
P(1)	Ir(1)	N(1)	80.5(2)	Ir(1)	P(1)	C(21)	119.7(2)
P(1)	Ir(1)	C(1)	97.2(2)	Ir(1)	P(1)	C(31)	122.3(2)
P(1)	Ir(1)	C(02)	89.3(2)	C(16)	P(1)	C(21)	103.2(3)
P(1)	Ir(1)	C(03)	125.2(2)	C(16)	P(1)	C(31)	104.9(3)
P(1)	Ir(1)	C(04)	154.2(2)	C(21)	P(1)	C(31)	104.1(3)
P(1)	Ir(1)	C(05)	118.5(2)	C(1)	O(3)	C(01)	117.6(6)
P(1)	Ir(1)	C(05A)	123.3(8)	Ir(1)	N(1)	C(11)	119.5(4)
P(1)	Ir(1)	C(06)	87.9(2)	Ir(1)	N(1)	C(15)	122.2(4)
N(1)	Ir(1)	C(1)	175.8(3)	C(11)	N(1)	C(15)	118.2(5)
N(1)	Ir(1)	C(02)	96.2(2)	Ir(1)	C(1)	O(1)	129.3(6)
N(1)	Ir(1)	C(03)	92.0(2)	Ir(1)	C(1)	O(3)	116.2(5)
N(1)	Ir(1)	C(04)	96.8(3)	O(1)	C(1)	O(3)	114.4(7)
N(1)	Ir(1)	C(05)	82.1(3)	O(3)	C(01)	C(02)	113.2(6)
N(1)	Ir(1)	C(05A)	110.2(9)	Ir(1)	C(02)	C(01)	105.7(4)
N(1)	Ir(1)	C(06)	93.8(3)	Ir(1)	C(02)	C(03)	72.3(4)
C(1)	Ir(1)	C(02)	80.2(3)	C(01)	C(02)	C(03)	119.8(6)
C(1)	Ir(1)	C(03)	86.4(2)	Ir(1)	C(03)	C(02)	70.4(4)
C(1)	Ir(1)	C(04)	86.8(3)	Ir(1)	C(04)	C(05)	69.9(5)
C(1)	Ir(1)	C(05)	102.1(3)	Ir(1)	C(04)	C(05A)	73(2)
C(1)	Ir(1)	C(05A)	74.0(9)	C(05)	C(04)	C(05A)	47(1)
C(1)	Ir(1)	C(06)	89.6(3)	Ir(1)	C(05)	C(04)	73.7(5)
C(02)	Ir(1)	C(03)	37.3(3)	Ir(1)	C(05)	C(06)	71.3(5)
C(02)	Ir(1)	C(04)	116.4(3)	C(04)	C(05)	C(06)	126.4(8)
C(02)	Ir(1)	C(05)	151.1(3)	Ir(1)	C(05A)	C(04)	73(1)
C(02)	Ir(1)	C(05A)	140.1(8)	Ir(1)	C(05A)	C(06)	68(1)
C(02)	Ir(1)	C(06)	169.1(3)	C(04)	C(05A)	C(06)	125(2)
C(03)	Ir(1)	C(04)	80.3(3)	Ir(1)	C(06)	C(05)	73.3(5)
C(03)	Ir(1)	C(05)	113.9(3)	Ir(1)	C(06)	C(05A)	74(1)
C(03)	Ir(1)	C(05A)	110.2(8)	N(1)	C(11)	C(12)	122.5(5)
C(03)	Ir(1)	C(06)	146.8(3)	N(1)	C(11)	C(16)	117.3(5)
C(04)	Ir(1)	C(05)	36.4(3)	C(12)	C(11)	C(16)	120.1(5)
C(04)	Ir(1)	C(05A)	33.7(8)	C(11)	C(12)	C(13)	118.1(6)
C(04)	Ir(1)	C(06)	66.6(3)	C(12)	C(13)	C(14)	119.4(6)
C(05)	Ir(1)	C(06)	35.4(3)	C(13)	C(14)	C(15)	119.2(6)
C(05A)	Ir(1)	C(06)	37.7(8)	N(1)	C(15)	C(14)	122.5(5)
Ir(1)	P(1)	C(16)	99.7(2)	P(1)	C(16)	C(11)	110.6(4)

Table S4. Interatomic distances (Å) and bond angles (deg) for **6**·BF_4. (cont'd.)

ATOM	ATOM	ATOM	ANGLE	ATOM	ATOM	ATOM	ANGLE
P(1)	C(21)	C(22)	120.7(6)				
P(1)	C(21)	C(26)	120.3(5)				
C(22)	C(21)	C(26)	119.0(7)				
C(21)	C(22)	C(23)	119.5(8)				
C(22)	C(23)	C(24)	122.3(9)				
C(23)	C(24)	C(25)	118.7(9)				
C(24)	C(25)	C(26)	121.2(8)				
C(21)	C(26)	C(25)	119.3(6)				
P(1)	C(31)	C(32)	121.9(4)				
P(1)	C(31)	C(36)	118.2(4)				
C(32)	C(31)	C(36)	119.9(5)				
C(31)	C(32)	C(33)	121.5(6)				
C(32)	C(33)	C(34)	119.1(7)				
C(33)	C(34)	C(35)	119.8(6)				
C(34)	C(35)	C(36)	120.4(6)				
C(31)	C(36)	C(35)	119.4(6)				
Cl(1)	C(41)	Cl(2)	110.4(6)				
F(1)	B(1)	F(2)	108.2(6)				
F(1)	B(1)	F(3)	108.1(5)				
F(1)	B(1)	F(4)	108.1(6)				
F(2)	B(1)	F(3)	112.2(7)				
F(2)	B(1)	F(4)	109.9(6)				
F(3)	B(1)	F(4)	110.2(6)				

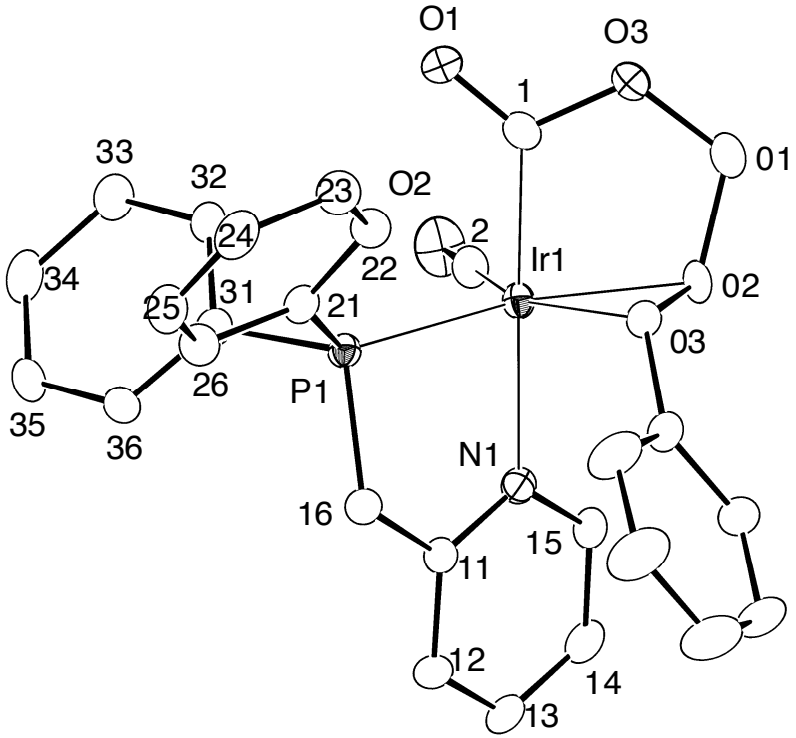

Figure S1. Atomic numbering scheme for **4b**.
Labels without atom names are for carbon atoms.

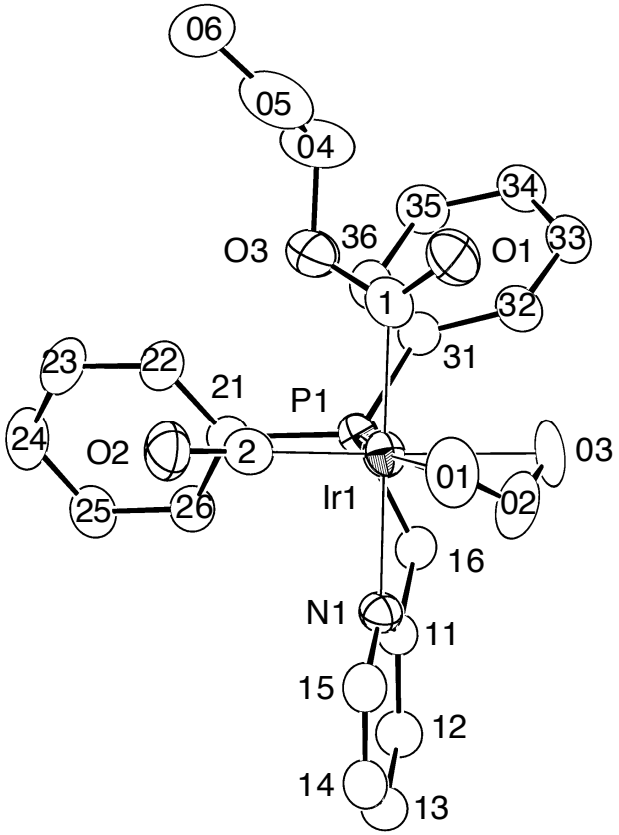

Figure S2. Atomic numbering scheme for **5**·BF_4. Labels without atom names are for carbon atoms.

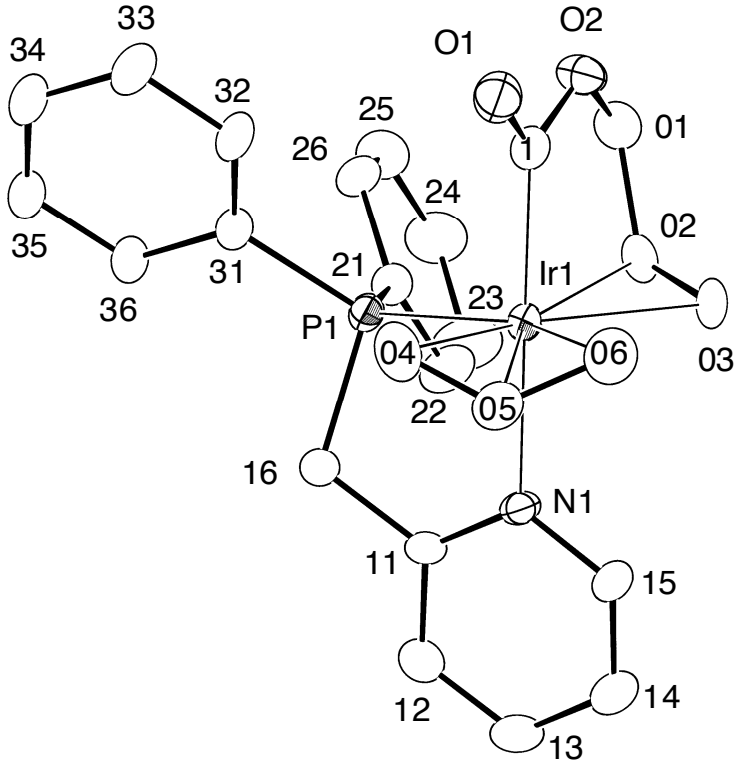

Figure S3. Atomic numbering scheme for **6**·BF_4. Labels without atom names are for carbon atoms.