Supporting Information

X-ray Structure Report for $IrCl(COD)(dppp)\bullet CHCl_3$

Experimental

Data Collection

A yellow prismatic crystal of $C_{35}H_{39}Cl_4IrP_2$ having approximate dimensions of 0.20 x 0.20 x 0.40 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo-K_ radiation and a rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $22.81 < 2\_ < 24.98^o$ corresponded to a primitive monoclinic cell with dimensions:

a = 11.32(1) Å
b = 20.90(1) Å _ = 91.89(4)^o
c = 14.682(5) Å
V = 3471(3) Å^3

For Z = 4 and F.W. = 855.67, the calculated density is 1.64 g/cm^3. The systematic absences of:

h0l: h+l ± 2n
0k0: k ± 2n

uniquely determine the space group to be:

$P2_1/n$ (#14)

The data were collected at a temperature of 20 ± 1^{o}C using the _-2_ scan technique to a maximum 2_ value of 55.0^o. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.17^o with a take-off angle of 6.0^o. Scans of (1.31 + 0.30 tan _)^o were made at a speed of 6.0^o/min (in _). The weak reflections (I < 10.0_(I)) were

rescanned (maximum of 3 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 258 mm, and the detector aperture was 9.0 x 13.0 mm (horizontal x vertical).

Data Reduction

Of the 9417 reflections which were collected, 8189 were unique (R_{int} = 0.105); equivalent reflections were merged. The intensities of three representative reflections were measured after every 97 reflections. No decay correction was applied.

The linear absorption coefficient, _, for Mo-K_ radiation is 42.8 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.87 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 1.58652e-007).

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement[3] on F was based on 4357 observed reflections (I > 2.00_(I)) and 389 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of:

$$R = \_ ||Fo| - |Fc|| / \_ |Fo| = 0.059$$

$$R_w = [\_ w (|Fo| - |Fc|)^2 / \_ w Fo^2]^{1/2} = 0.046$$

The standard deviation of an observation of unit weight[4] was 1.38. The weighting scheme was based on counting statistics and included a factor (p = 0.010) to downweight the intense reflections. Plots of _ w $(|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, sin _/_ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the

final difference Fourier map corresponded to 1.73 and -1.27 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for _f' and _f" were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1) SIR97: Altomare, A., Cascarano, M., Giacovazzo, C., Guagliardi, A. (1993). J. Appl. Cryst., 26, 343.

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least Squares function minimized:

$$\_w(|F_o|-|F_c|)^2 \text{ where}$$

$w = 1/[\_^2(Fo)] = [\_^2_c(Fo) + p^2Fo^2/4]^{-1}$
$\__c(Fo)$ = e.s.d. based on counting statistics
p = p-factor

(4) Standard deviation of an observation of unit weight:

$$[\_w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$$

where: N_o = number of observations
N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The

Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan for Windows: Crystal Structure Analysis Package, Molecular Structure Corporation (1997).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{35}H_{39}Cl_4IrP_2$
Formula Weight	855.67
Crystal Color, Habit	yellow, prismatic
Crystal Dimensions	0.20 X 0.20 X 0.40 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2_ range)	25 (22.8 - 25.0^o)
Omega Scan Peak Width at Half-height	0.17^o
Lattice Parameters	a = 11.32(1) Å b = 20.90(1) Å c = 14.682(5) Å _ = 91.89(4) Å V = 3471(3) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.637 g/cm^3

F_{000}	1696.00
(MoK)	42.81 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC5R
Radiation	MoK_ (_ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factors = 1.00, 3.42, 12.12, 41.81)
Take-off Angle	6.0^{o}
Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	258 mm
Voltage, Current	50 kV, 200 mA
Temperature	20.0^{o}C
Scan Type	_-2_
Scan Rate	6.0^{o}/min (in _) (up to 3 scans)
Scan Width	$(1.31 + 0.30 \tan \_)^{o}$
2_{max}	55.0^{o}
No. of Reflections Measured	Total: 9417

	Unique: 8189 (R_{int} = 0.105)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.8665 - 1.0000) Secondary Extinction (coefficient: 1.58652e-007)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F
Function Minimized	_ w (|Fo| - |Fc|)^2
Least Squares Weights	1/_^{2}(Fo) = 4Fo^2/_^{2}(Fo^2)
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>2.00_(I))	4357
No. Variables	389
Reflection/Parameter Ratio	11.20
Residuals: R; Rw	0.059 ; 0.046
Goodness of Fit Indicator	1.38
Max Shift/Error in Final Cycle	0.01

Maximum peak in Final Diff. Map 1.73 $e^-/Å^3$

Minimum peak in Final Diff. Map -1.27 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Ir(1)	0.94876(4)	0.17883(2)	0.43096(3)	2.368(7)
Cl(1)	0.7879(2)	0.1693(1)	0.3026(2)	3.29(6)
Cl(2)	0.5090(3)	0.0568(2)	0.1919(2)	6.2(1)
Cl(3)	0.5233(4)	-0.0001(2)	0.3682(3)	8.6(1)
Cl(4)	0.7068(3)	-0.0220(2)	0.2411(3)	8.1(1)
P(1)	0.9497(2)	0.2875(1)	0.3994(2)	2.43(6)
P(2)	1.0960(2)	0.1655(1)	0.3256(2)	2.54(6)
C(1)	0.8142(8)	0.3293(4)	0.4352(6)	2.5(2)
C(2)	0.7114(9)	0.3224(5)	0.3832(7)	3.5(2)
C(3)	0.6061(9)	0.3502(5)	0.4120(9)	4.5(3)
C(4)	0.606(1)	0.3860(5)	0.4898(8)	4.1(3)
C(5)	0.706(1)	0.3927(5)	0.5417(6)	3.3(3)
C(6)	0.8093(9)	0.3646(5)	0.5145(6)	3.1(3)
C(7)	1.0667(8)	0.3375(5)	0.4515(6)	2.9(2)
C(8)	1.0684(9)	0.4031(5)	0.4340(7)	3.5(3)
C(9)	1.156(1)	0.4413(6)	0.4709(9)	4.9(4)
C(10)	1.247(1)	0.4144(7)	0.528(1)	5.5(4)
C(11)	1.246(1)	0.3513(7)	0.5423(8)	5.4(4)
C(12)	1.156(1)	0.3110(5)	0.5075(7)	4.0(3)
C(13)	0.9589(9)	0.3084(5)	0.2800(6)	3.2(3)
C(14)	1.070(1)	0.2842(5)	0.2347(7)	3.5(3)
C(15)	1.0769(9)	0.2123(5)	0.2196(7)	3.3(3)
C(16)	1.2508(8)	0.1794(5)	0.3617(6)	2.9(2)
C(17)	1.2855(9)	0.1698(6)	0.4473(8)	4.8(3)
C(18)	1.405(1)	0.1730(8)	0.4801(9)	6.4(4)
C(19)	1.486(1)	0.1890(7)	0.415(1)	6.4(4)
C(20)	1.453(1)	0.2003(6)	0.326(1)	5.6(4)
C(21)	1.3363(9)	0.1971(5)	0.3010(8)	3.9(3)
C(22)	1.1070(9)	0.0838(5)	0.2760(6)	3.0(2)
C(23)	1.2091(8)	0.0480(5)	0.2856(6)	2.6(2)

C(24)	1.2139(9)	-0.0108(5)	0.2421(7)	3.5(3)
C(25)	1.119(1)	-0.0332(5)	0.1913(7)	3.6(3)
C(26)	1.0176(9)	0.0018(5)	0.1834(7)	3.5(3)
C(27)	1.0115(8)	0.0604(5)	0.2264(7)	3.1(3)
C(28)	0.941(1)	0.2050(5)	0.5708(7)	3.4(3)
C(29)	0.829(1)	0.1861(5)	0.5421(7)	3.7(3)
C(30)	0.772(1)	0.1235(6)	0.5688(7)	4.2(3)
C(31)	0.797(1)	0.0700(6)	0.5048(8)	4.4(3)
C(32)	0.909(1)	0.0771(5)	0.4559(7)	3.5(3)
C(33)	1.020(1)	0.0911(5)	0.4966(8)	4.4(3)
C(34)	1.036(1)	0.0970(6)	0.5981(7)	4.6(3)
C(35)	1.020(1)	0.1641(6)	0.6336(8)	5.1(3)
C(36)	0.604(1)	0.0337(6)	0.2815(9)	5.2(4)
H(27)	0.9484	0.2497	0.5815	4.049
H(28)	0.7747	0.2206	0.5357	4.440
H(29)	0.8001	0.1119	0.6281	5.088
H(30)	0.6883	0.1296	0.5695	5.088
H(31)	0.7338	0.0675	0.4607	5.318
H(32)	0.8009	0.0313	0.5387	5.318
H(33)	0.9135	0.0511	0.4030	4.255
H(34)	0.9808	0.0698	0.6259	5.556
H(35)	1.0848	0.0726	0.4669	5.232
H(36)	1.1142	0.0833	0.6146	5.556
H(37)	0.9848	0.1616	0.6914	6.054
H(38)	1.0950	0.1840	0.6399	6.054
H(39)	0.6447	0.0702	0.3046	6.255
H(1)	0.7117	0.2987	0.3280	4.254
H(2)	0.5348	0.3441	0.3772	5.477
H(3)	0.5346	0.4063	0.5075	4.888
H(4)	0.7051	0.4167	0.5967	3.918
H(5)	0.8791	0.3695	0.5515	3.718
H(6)	1.0081	0.4215	0.3959	4.157
H(7)	1.1555	0.4860	0.4586	5.846
H(8)	1.3076	0.4405	0.5543	6.642
H(9)	1.3086	0.3328	0.5779	6.532
H(10)	1.1559	0.2667	0.5218	4.853
H(17)	1.2267	0.1601	0.4899	5.779
H(18)	1.4282	0.1646	0.5418	7.672

H(19)	1.5670	0.1924	0.4332	7.708
H(20)	1.5106	0.2102	0.2831	6.696
H(21)	1.3128	0.2073	0.2400	4.606
H(22)	1.2747	0.0633	0.3214	3.153
H(23)	1.2838	-0.0357	0.2476	4.197
H(24)	1.1240	-0.0735	0.1616	4.325
H(25)	0.9516	-0.0140	0.1485	4.205
H(26)	0.9406	0.0848	0.2217	3.715
H(11)	0.8920	0.2908	0.2482	3.883
H(12)	0.9571	0.3537	0.2751	3.883
H(13)	1.0738	0.3045	0.1769	4.255
H(14)	1.1363	0.2965	0.2718	4.255
H(15)	1.1422	0.2037	0.1824	3.976
H(16)	1.0060	0.1987	0.1891	3.976

$B_{eq} = 8/3\ \_^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\ \_ + 2U_{13}(aa^*cc^*)\cos\ \_ + 2U_{23}(bb^*cc^*)\cos\ \_)$

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir(1)	0.0329(2)	0.0300(2)	0.0273(2)	0.0040(3)	0.0035(1)	0.0006(2)
Cl(1)	0.033(1)	0.045(2)	0.047(2)	-0.001(1)	-0.003(1)	-0.004(1)
Cl(2)	0.063(2)	0.090(3)	0.082(3)	0.008(2)	-0.003(2)	-0.001(2)
Cl(3)	0.097(3)	0.140(4)	0.089(3)	-0.028(3)	0.002(2)	0.030(3)
Cl(4)	0.059(2)	0.085(3)	0.165(4)	0.011(2)	0.001(3)	0.021(3)
P(1)	0.029(1)	0.032(1)	0.031(1)	0.001(1)	-0.001(1)	-0.002(1)
P(2)	0.031(1)	0.036(2)	0.030(1)	0.001(1)	0.004(1)	-0.002(1)
C(1)	0.040(6)	0.016(5)	0.037(5)	-0.000(5)	-0.003(4)	0.011(5)
C(2)	0.042(6)	0.037(6)	0.054(7)	-0.000(6)	-0.010(5)	-0.009(6)
C(3)	0.032(7)	0.050(8)	0.09(1)	0.014(6)	-0.009(7)	-0.002(7)
C(4)	0.051(8)	0.039(7)	0.067(8)	0.009(6)	0.015(7)	-0.008(6)
C(5)	0.061(8)	0.039(7)	0.024(5)	0.004(6)	0.010(5)	-0.009(5)
C(6)	0.048(7)	0.045(7)	0.025(5)	-0.012(6)	0.010(5)	0.002(5)
C(7)	0.031(6)	0.045(7)	0.035(6)	-0.003(5)	0.006(5)	-0.010(5)
C(8)	0.052(7)	0.043(7)	0.037(6)	-0.011(6)	-0.001(5)	0.003(5)
C(9)	0.064(9)	0.053(9)	0.070(9)	-0.017(7)	0.017(7)	-0.023(7)
C(10)	0.058(9)	0.06(1)	0.09(1)	-0.023(8)	0.014(8)	-0.025(9)

C(11)	0.028(7)	0.12(1)	0.060(9)	0.009(8)	-0.011(6)	-0.013(9)
C(12)	0.058(8)	0.041(8)	0.053(7)	0.008(6)	-0.003(6)	0.005(6)
C(13)	0.045(6)	0.042(7)	0.036(6)	0.000(5)	0.003(5)	0.005(5)
C(14)	0.050(7)	0.043(7)	0.042(7)	0.002(6)	0.002(6)	0.014(5)
C(15)	0.038(6)	0.051(7)	0.038(6)	-0.005(5)	0.015(5)	0.004(5)
C(16)	0.034(5)	0.034(6)	0.042(6)	-0.004(6)	-0.006(5)	-0.005(6)
C(17)	0.023(6)	0.071(9)	0.088(9)	-0.001(6)	0.001(6)	-0.011(8)
C(18)	0.050(8)	0.11(1)	0.08(1)	-0.01(1)	-0.023(7)	-0.02(1)
C(19)	0.025(6)	0.07(1)	0.15(2)	-0.010(7)	0.001(8)	-0.02(1)
C(20)	0.043(8)	0.064(9)	0.11(1)	-0.012(7)	0.002(8)	0.028(8)
C(21)	0.031(6)	0.039(7)	0.077(9)	-0.001(5)	-0.001(6)	0.001(6)
C(22)	0.042(6)	0.043(7)	0.030(6)	0.007(5)	0.015(5)	-0.006(5)
C(23)	0.036(6)	0.033(6)	0.030(6)	0.001(5)	-0.001(5)	0.010(5)
C(24)	0.055(8)	0.037(7)	0.042(7)	0.005(6)	0.019(6)	0.005(5)
C(25)	0.053(8)	0.036(7)	0.050(7)	0.003(6)	0.021(6)	-0.010(6)
C(26)	0.040(7)	0.053(7)	0.041(7)	-0.014(6)	0.005(5)	-0.017(6)
C(27)	0.028(6)	0.048(7)	0.042(6)	0.005(5)	-0.007(5)	-0.002(5)
C(28)	0.059(8)	0.034(6)	0.036(6)	0.001(6)	0.006(6)	-0.001(5)
C(29)	0.066(8)	0.039(7)	0.037(6)	0.012(6)	0.023(5)	0.005(6)
C(30)	0.051(8)	0.059(8)	0.053(7)	0.012(6)	0.029(6)	0.006(6)
C(31)	0.052(8)	0.049(8)	0.069(9)	-0.001(6)	0.027(7)	0.008(7)
C(32)	0.069(8)	0.026(6)	0.041(7)	0.010(6)	0.011(6)	0.007(5)
C(33)	0.077(9)	0.043(7)	0.046(7)	0.023(7)	0.008(7)	0.011(6)
C(34)	0.08(1)	0.050(8)	0.043(7)	0.020(7)	0.005(7)	0.013(6)
C(35)	0.080(9)	0.059(9)	0.052(8)	-0.007(7)	-0.015(7)	0.005(7)
C(36)	0.058(8)	0.051(8)	0.09(1)	-0.023(7)	-0.010(7)	-0.003(7)

The general temperature factor expression:

$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
IR1	CL1	2.584(3)	IR1	P1	2.318(3)
IR1	P2	2.327(3)	IR1	C28	2.13(1)
IR1	C29	2.16(1)	IR1	C32	2.20(1)
IR1	C33	2.21(1)	CL2	C36	1.74(1)
CL3	C36	1.74(1)	CL4	C36	1.76(2)
P1	C1	1.86(1)	P1	C7	1.83(1)
P1	C13	1.81(1)	P2	C15	1.84(1)
P2	C16	1.84(1)	P2	C22	1.86(1)
C1	C2	1.38(1)	C1	C6	1.38(1)
C2	C3	1.40(2)	C3	C4	1.37(2)
C4	C5	1.35(2)	C5	C6	1.38(2)
C7	C8	1.40(2)	C7	C12	1.40(2)
C8	C9	1.37(2)	C9	C10	1.42(2)
C10	C11	1.34(2)	C11	C12	1.40(2)
C13	C14	1.53(2)	C14	C15	1.52(2)
C16	C17	1.32(2)	C16	C21	1.39(2)
C17	C18	1.43(2)	C18	C19	1.38(2)

C19	C20	1.36(2)	C20	C21	1.36(2)
C22	C23	1.38(1)	C22	C27	1.37(1)
C23	C24	1.39(2)	C24	C25	1.37(2)
C25	C26	1.36(2)	C26	C27	1.38(2)
C28	C29	1.38(2)	C28	C35	1.52(2)
C29	C30	1.52(2)	C30	C31	1.50(2)
C31	C32	1.49(2)	C32	C33	1.40(2)
C33	C34	1.50(2)	C34	C35	1.51(2)
C2	H1	0.95	C3	H2	0.95
C4	H3	0.95	C5	H4	0.95
C6	H5	0.95	C8	H6	0.95
C9	H7	0.95	C10	H8	0.95
C11	H9	0.95	C12	H10	0.95
C13	H11	0.95	C13	H12	0.95
C14	H13	0.95	C14	H14	0.95
C15	H15	0.95	C15	H16	0.95
C17	H17	0.95	C18	H18	0.95
C19	H19	0.95	C20	H20	0.95
C21	H21	0.95	C23	H22	0.95

C24	H23	0.95	C25	H24	0.95
C26	H25	0.95	C27	H26	0.95
C28	H27	0.95	C29	H28	0.95
C30	H29	0.95	C30	H30	0.95
C31	H31	0.95	C31	H32	0.95
C32	H33	0.95	C33	H35	0.95
C34	H34	0.95	C34	H36	0.95
C35	H37	0.95	C35	H38	0.95
C36	H39	0.95			

Table 5. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
CL1	IR1	P1	86.4(1)	CL1	IR1	P2	90.5(1)
CL1	IR1	C28	132.3(4)	CL1	IR1	C29	96.4(4)
CL1	IR1	C32	84.6(4)	CL1	IR1	C33	119.4(4)
P1	IR1	P2	88.6(1)	P1	IR1	C28	86.7(3)
P1	IR1	C29	95.1(4)	P1	IR1	C32	168.5(4)
P1	IR1	C33	153.6(4)	P2	IR1	C28	136.4(4)
P2	IR1	C29	172.3(3)	P2	IR1	C32	98.5(3)
P2	IR1	C33	86.2(4)	C28	IR1	C29	37.5(4)

C28	IR1	C32	94.2(4)	C28	IR1	C33	79.5(5)
C29	IR1	C32	78.9(5)	C29	IR1	C33	87.6(5)
C32	IR1	C33	36.9(4)	IR1	P1	C1	113.3(4)
IR1	P1	C7	118.9(4)	IR1	P1	C13	115.5(4)
C1	P1	C7	101.9(5)	C1	P1	C13	103.6(5)
C7	P1	C13	101.7(5)	IR1	P2	C15	115.6(4)
IR1	P2	C16	119.1(4)	IR1	P2	C22	115.3(4)
C15	P2	C16	104.1(5)	C15	P2	C22	99.4(5)
C16	P2	C22	100.5(6)	P1	C1	C2	118.9(9)
P1	C1	C6	123.1(9)	C2	C1	C6	118(1)
C1	C2	C3	120(1)	C2	C3	C4	120(1)
C3	C4	C5	120(1)	C4	C5	C6	120(1)
C1	C6	C5	122(1)	P1	C7	C8	119.9(9)
P1	C7	C12	121(1)	C8	C7	C12	119(1)
C7	C8	C9	121(1)	C8	C9	C10	120(1)
C9	C10	C11	118(1)	C10	C11	C12	123(1)
C7	C12	C11	119(1)	P1	C13	C14	114.6(8)
C13	C14	C15	116(1)	P2	C15	C14	114.0(8)
P2	C16	C17	120(1)	P2	C16	C21	122.4(9)

C17	C16	C21	117(1)	C16	C17	C18	124(1)
C17	C18	C19	115(1)	C18	C19	C20	122(1)
C19	C20	C21	119(2)	C16	C21	C20	122(1)
P2	C22	C23	121.6(9)	P2	C22	C27	118.1(9)
C23	C22	C27	120(1)	C22	C23	C24	119(1)
C23	C24	C25	121(1)	C24	C25	C26	120(1)
C25	C26	C27	119(1)	C22	C27	C26	121(1)
IR1	C28	C29	72.5(7)	IR1	C28	C35	113.4(9)
C29	C28	C35	123(1)	IR1	C29	C28	70.0(7)
IR1	C29	C30	114.8(8)	C28	C29	C30	124(1)
C29	C30	C31	113(1)	C30	C31	C32	114(1)
IR1	C32	C31	110.9(8)	IR1	C32	C33	71.7(8)
C31	C32	C33	125(1)	IR1	C33	C32	71.4(7)
IR1	C33	C34	113.4(9)	C32	C33	C34	122(1)
C33	C34	C35	114(1)	C28	C35	C34	113(1)
CL2	C36	CL3	110.0(8)	CL2	C36	CL4	109.1(8)
CL3	C36	CL4	110.2(8)				

Table 6. Bond Angles(^{o})

atom	atom	atom	angle	atom	atom	atom	angle

C1	C2	H1	120.0	C3	C2	H1	120.1
C2	C3	H2	119.7	C4	C3	H2	119.8
C3	C4	H3	120.0	C5	C4	H3	120.0
C4	C5	H4	120.1	C6	C5	H4	120.1
C1	C6	H5	119.0	C5	C6	H5	119.1
C7	C8	H6	119.5	C9	C8	H6	119.5
C8	C9	H7	119.9	C10	C9	H7	120.0
C9	C10	H8	120.9	C11	C10	H8	120.7
C10	C11	H9	118.6	C12	C11	H9	118.4
C7	C12	H10	120.7	C11	C12	H10	120.8
P1	C13	H11	108.2	P1	C13	H12	108.2
C14	C13	H11	108.1	C14	C13	H12	108.1
H11	C13	H12	109.4	C13	C14	H13	107.9
C13	C14	H14	107.9	C15	C14	H13	107.8
C15	C14	H14	107.8	H13	C14	H14	109.4
P2	C15	H15	108.3	P2	C15	H16	108.3
C14	C15	H15	108.4	C14	C15	H16	108.4
H15	C15	H16	109.5	C16	C17	H17	117.8
C18	C17	H17	117.9	C17	C18	H18	122.5

C19	C18	H18	122.6	C18	C19	H19	118.7
C20	C19	H19	118.9	C19	C20	H20	120.4
C21	C20	H20	120.5	C16	C21	H21	119.1
C20	C21	H21	119.1	C22	C23	H22	120.7
C24	C23	H22	120.7	C23	C24	H23	119.6
C25	C24	H23	119.6	C24	C25	H24	119.8
C26	C25	H24	119.9	C25	C26	H25	120.3
C27	C26	H25	120.3	C22	C27	H26	119.7
C26	C27	H26	119.8	IR1	C28	H27	113.9
C29	C28	H27	113.9	C35	C28	H27	113.9
IR1	C29	H28	113.5	C28	C29	H28	113.5
C30	C29	H28	113.5	C29	C30	H29	108.7
C29	C30	H30	108.7	C31	C30	H29	108.6
C31	C30	H30	108.5	H29	C30	H30	109.4
C30	C31	H31	108.3	C30	C31	H32	108.3
C32	C31	H31	108.2	C32	C31	H32	108.2
H31	C31	H32	109.4	IR1	C32	H33	113.7
C31	C32	H33	113.7	C33	C32	H33	113.7
IR1	C33	H35	114.5	C32	C33	H35	114.4

C34	C33	H35	114.4	C33	C34	H34	108.3
C33	C34	H36	108.3	C35	C34	H34	108.4
C35	C34	H36	108.5	H34	C34	H36	109.5
C28	C35	H37	108.7	C28	C35	H38	108.6
C34	C35	H37	108.6	C34	C35	H38	108.5
H37	C35	H38	109.5	CL2	C36	H39	109.2
CL3	C36	H39	109.0	CL4	C36	H39	109.2

Table 7. Torsion Angles(º)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
IR1	P1	C1	C2	-76(1)	IR1	P1	C1	C6	100(1)
IR1	P1	C7	C8	-179.5(8)	IR1	P1	C7	C12	2(1)
IR1	P1	C13	C14	-60(1)	IR1	P2	C15	C14	58(1)
IR1	P2	C16	C17	29(1)	IR1	P2	C16	C21	-154.3(9)
IR1	P2	C22	C23	-120.3(9)	IR1	P2	C22	C27	62(1)
IR1	C28	C29	C30	107(1)	IR1	C28	C35	C34	-29(2)
IR1	C29	C28	C35	-107(1)	IR1	C29	C30	C31	-7(2)
IR1	C32	C31	C30	-32(2)	IR1	C32	C33	C34	107(1)
IR1	C33	C32	C31	-103(1)	IR1	C33	C34	C35	-9(2)
CL1	IR1	P1	C1	70.8(4)	CL1	IR1	P1	C7	-169.6(4)

CL1	IR1	P1	C13	-48.4(4)	CL1	IR1	P2	C15	45.0(5)
CL1	IR1	P2	C16	170.1(5)	CL1	IR1	P2	C22	-70.3(4)
CL1	IR1	C28	C29	20.7(9)	CL1	IR1	C28	C35	139.2(8)
CL1	IR1	C29	C28	-164.7(7)	CL1	IR1	C29	C30	75.7(9)
CL1	IR1	C32	C31	-76.6(9)	CL1	IR1	C32	C33	161.5(8)
CL1	IR1	C33	C32	-21.3(9)	CL1	IR1	C33	C34	-138.4(9)
P1	IR1	P2	C15	-41.4(5)	P1	IR1	P2	C16	83.7(5)
P1	IR1	P2	C22	-156.7(4)	P1	IR1	C28	C29	102.8(7)
P1	IR1	C28	C35	-138.7(9)	P1	IR1	C29	C28	-77.7(7)
P1	IR1	C29	C30	162.7(9)	P1	IR1	C32	C31	-38(2)
P1	IR1	C32	C33	-160(1)	P1	IR1	C33	C32	171.3(6)
P1	IR1	C33	C34	54(2)	P1	C1	C2	C3	176(1)
P1	C1	C6	C5	-176.9(9)	P1	C7	C8	C9	-179(1)
P1	C7	C12	C11	177(1)	P1	C13	C14	C15	70(1)
P2	IR1	P1	C1	161.4(4)	P2	IR1	P1	C7	-79.1(4)
P2	IR1	P1	C13	42.2(4)	P2	IR1	C28	C29	-172.7(6)
P2	IR1	C28	C35	-54(1)	P2	IR1	C29	C28	41(3)
P2	IR1	C29	C30	-79(3)	P2	IR1	C32	C31	-166.3(9)
P2	IR1	C32	C33	71.8(8)	P2	IR1	C33	C32	-109.7(7)

P2	IR1	C33	C34	133(1)	P2	C15	C14	C13	-69(1)
P2	C16	C17	C18	173(1)	P2	C16	C21	C20	-172(1)
P2	C22	C23	C24	-175.9(8)	P2	C22	C27	C26	175.9(9)
C1	P1	IR1	C28	-61.9(5)	C1	P1	IR1	C29	-25.3(5)
C1	P1	IR1	C32	33(2)	C1	P1	IR1	C33	-120.1(9)
C1	P1	C7	C8	-54(1)	C1	P1	C7	C12	127(1)
C1	P1	C13	C14	175.2(9)	C1	C2	C3	C4	2(2)
C1	C6	C5	C4	-0(2)	C2	C1	P1	C7	155(1)
C2	C1	P1	C13	50(1)	C2	C1	C6	C5	-0(2)
C2	C3	C4	C5	-3(2)	C3	C2	C1	C6	-1(2)
C3	C4	C5	C6	2(2)	C6	C1	P1	C7	-29(1)
C6	C1	P1	C13	-134(1)	C7	P1	IR1	C28	57.6(5)
C7	P1	IR1	C29	94.2(6)	C7	P1	IR1	C32	152(2)
C7	P1	IR1	C33	-0.6(9)	C7	P1	C13	C14	70(1)
C7	C8	C9	C10	0(2)	C7	C12	C11	C10	3(2)
C8	C7	P1	C13	53(1)	C8	C7	C12	C11	-2(2)
C8	C9	C10	C11	1(3)	C9	C8	C7	C12	0(2)
C9	C10	C11	C12	-3(3)	C12	C7	P1	C13	-126(1)
C13	P1	IR1	C28	178.9(6)	C13	P1	IR1	C29	-144.6(6)

C13	P1	IR1	C32	-87(2)	C13	P1	IR1	C33	120.7(9)
C14	C15	P2	C16	-74(1)	C14	C15	P2	C22	-177.5(9)
C15	P2	IR1	C28	-125.1(6)	C15	P2	IR1	C29	-161(3)
C15	P2	IR1	C32	129.6(6)	C15	P2	IR1	C33	164.4(6)
C15	P2	C16	C17	159(1)	C15	P2	C16	C21	-24(1)
C15	P2	C22	C23	116(1)	C15	P2	C22	C27	-62(1)
C16	P2	IR1	C28	-0.0(7)	C16	P2	IR1	C29	-35(3)
C16	P2	IR1	C32	-105.3(6)	C16	P2	IR1	C33	-70.5(6)
C16	P2	C22	C23	9(1)	C16	P2	C22	C27	-169(1)
C16	C17	C18	C19	2(3)	C16	C21	C20	C19	-4(2)
C17	C16	P2	C22	-98(1)	C17	C16	C21	C20	4(2)
C17	C18	C19	C20	-1(3)	C18	C17	C16	C21	-4(2)
C18	C19	C20	C21	2(3)	C21	C16	P2	C22	79(1)
C22	P2	IR1	C28	119.6(6)	C22	P2	IR1	C29	84(3)
C22	P2	IR1	C32	14.3(6)	C22	P2	IR1	C33	49.1(6)
C22	C23	C24	C25	-1(2)	C22	C27	C26	C25	1(2)
C23	C22	C27	C26	-2(2)	C23	C24	C25	C26	-1(2)
C24	C23	C22	C27	2(2)	C24	C25	C26	C27	0(2)
C28	IR1	C29	C30	-120(1)	C28	IR1	C32	C31	55(1)

C28	IR1	C32	C33	-66.4(8)	C28	IR1	C33	C32	111.6(8)
C28	IR1	C33	C34	-5(1)	C28	C29	IR1	C32	112.1(8)
C28	C29	IR1	C33	76.0(8)	C28	C29	C30	C31	-89(2)
C28	C35	C34	C33	25(2)	C29	IR1	C28	C35	119(1)
C29	IR1	C32	C31	21.0(9)	C29	IR1	C32	C33	-100.9(8)
C29	IR1	C33	C32	74.7(8)	C29	IR1	C33	C34	-42(1)
C29	C28	IR1	C32	-65.7(8)	C29	C28	IR1	C33	-99.7(8)
C29	C28	C35	C34	54(2)	C29	C30	C31	C32	26(2)
C30	C29	IR1	C32	-7(1)	C30	C29	IR1	C33	-44(1)
C30	C29	C28	C35	-0(2)	C30	C31	C32	C33	50(2)
C31	C32	IR1	C33	122(1)	C31	C32	C33	C34	4(2)
C32	IR1	C28	C35	53(1)	C32	IR1	C33	C34	-117(1)
C32	C33	C34	C35	-91(2)	C33	IR1	C28	C35	19(1)

Table 8. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
CL1	C36	3.53(1)	1	C9	C25	3.58(2)	75502

The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number shown in the table is a composite of three one-digit numbers and one two-digit number: TA (first digit) + TB (second digit) + TC (third digit) + SN (last two digits). TA, TB and TC are the crystal

lattice translation digits along cell edges a, b and c. A translation digit of 5 indicates the origin unit cell. If TA = 4, this indicates a translation of one unit cell length along the a-axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus ±4 lattice translations from the origin (TA=5, TB=5, TC=5) can be represented.

The SN, or symmetry operator number, refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of symmetry operators relevant to this structure is given below.

For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always 55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of the atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through symmetry operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis.

An ADC of 1 indicates an intermolecular contact between two fragments (eg. cation and anion) that reside in the same asymmetric unit.

Symmetry Operators:

(1)	+X,	+Y,	+Z	(2)	1/2-X,	1/2+Y,	1/2-Z
(3)	-X,	-Y,	-Z	(4)	1/2+X,	1/2-Y,	1/2+Z

General. IR spectra were recorded with Horiba FT210 spectrophotometer. ^{1}H NMR spectra (200 MHz) were measured with Varian VXR-200 spectrometer using tetramethylsilane as an internal standard and $CDCl_3$ was used as solvent. Xylene was dried over molecular sieves 4A (MS 4A) and degassed prior to use. All reaction was performed using CO balloon.

2,4-Bis(triphenylsilyl)-7-oxabicyclo[3.3.0]octa-1,4-dien-3-one (2a). Yellow solid. Mp. 211.5-212°C. IR (neat) 1693 cm^{-1}; ^{1}H NMR δ= 3.69 (s, 4H), 7.31-7.43 (m, 18H), 7.54 (m, 12H).

1-Oxo-2,5-bis(triphenylsilyl)cyclopenta-1,4-dieno[3,4-a]acenaphthene (2b). Red solid. Mp. >300°C. IR (neat) 1672 cm^{-1}; ^{1}H NMR δ= 6.00 (d, *J*= 7.3 Hz, 2H), 7.06 (dd, *J*= 7.3 Hz, 8.2 Hz, 2H), 7.26-7.46 (m, 20H), 7.63-7.67 (m, 12H).

2,4-Diphenyl-7,7-bis(benzoxycarbonyl)bicyclo[3.3.0]octa-1,4-dien-3-one (3a). Violet solid. Mp. 133°C. IR (neat) 1732, 1712 cm^{-1}; ^{1}H NMR δ= 3.51 (s, 4H), 5.15 (s, 4H), 7.18-7.41 (m, 16H), 7.60-7.64 (m, 4H).

2,4-Diphenyl-7,7-bis(ethoxycarbonyl)bicyclo[3.3.0]octa-1,4-dien-3-one (3b). Reddish violet solid. Mp. 137°C. IR (neat) 1727 cm^{-1}; ^{1}H NMR δ= 1.28 (t, *J*= 7.1 Hz, 6H), 3.52 (s, 4H), 4.24 (q, *J*= 7.1 Hz, 4H), 7.24-7.44 (m, 6H), 7.65-7.69 (m, 4H).

2,4-Diphenyl-7,7-bis(*t*-butoxycarbonyl)bicyclo[3.3.0]octa-1,4-dien-3-one (3c). Reddish violet solid. Mp. 190°C. IR (neat) 1717 cm^{-1}; ^{1}H NMR δ= 1.47 (s, 18H), 3.40 (s, 4H), 7.24-7.43 (m, 6H), 7.65-7.69 (m, 4H).

2,4-Bis(4-methoxyphenyl)-7,7-bis(benzoxycarbonyl)bicyclo[3.3.0]octa-1,4-dien-3-one (3d). Reddish violet solid. Mp. 136°C. IR (neat) 1737, 1716 cm^{-1}; ^{1}H NMR δ= 3.46 (s, 4H), 3.82 (s, 6H), 5.14 (s, 4H), 6.90 (d, *J*= 6.8 Hz, 4H), 7.18-7.32 (m, 10H), 7.55-7.59 (m, 4H).

2,4-Bis(4-chlorophenyl)-7,7-bis(benzoxycarbonyl)bicyclo[3.3.0]octa-1,4-dien-3-one (3e). Dark violet solid. Mp. 177°C. IR (neat) 1720 cm^{-1}; ^{1}H NMR δ= 3.47 (s, 4H), 5.15 (s, 4H), 7.18-7.36 (m, 14H), 7.53-7.57 (m, 4H).

2,4-Bis(4-methoxycarbonylphenyl)-7,7-bis(benzoxycarbonyl)bicyclo[3.3.0]octa-1,5-dien-3-one (4f). Pale yellow oil. IR (neat) 1717 cm^{-1}; ^{1}H NMR δ= 3.85 (s, 2H), 3.92 (s, 3H), 3.93 (s, 3H), 4.27 (s, 1H), 5.20 (s, 4H), 6.32 (s, 1H), 7.23-7.36 (m, 12H), 7.88 (d, *J*=8.4 Hz, 2H), 7.95 (d, *J*=8.4 Hz, 2H), 8.07 (d, *J*=8.4 Hz, 2H).

2,4-diphenylbicyclo[3.3.0]octa-1,4-dien-3-one (3g). Red oil. IR (neat) 1707 cm^{-1}; ^{1}H NMR δ=

2.18 (quint, *J*= 7.3 Hz, 2H), 2.85 (t, *J*= 7.3 Hz, 4H), 7.24-7.42 (m, 6H), 7.66- 7.70 (m, 4H).

2,4-Diphenyl-7-oxabicyclo[3.3.0]octa-1,4-dien-3-one (3h). Violet solid. Mp. 66-67°C. IR (neat) 1715 cm^{-1}; ^{1}H NMR δ= 4.98 (s, 4H), 7.26-7.48 (m, 6H), 7.58-7.61 (m, 4H).