N-Heterocyclic Carbenes of Iridium(I): Ligand Effects on the Catalytic Activity in Transfer Hydrogenation

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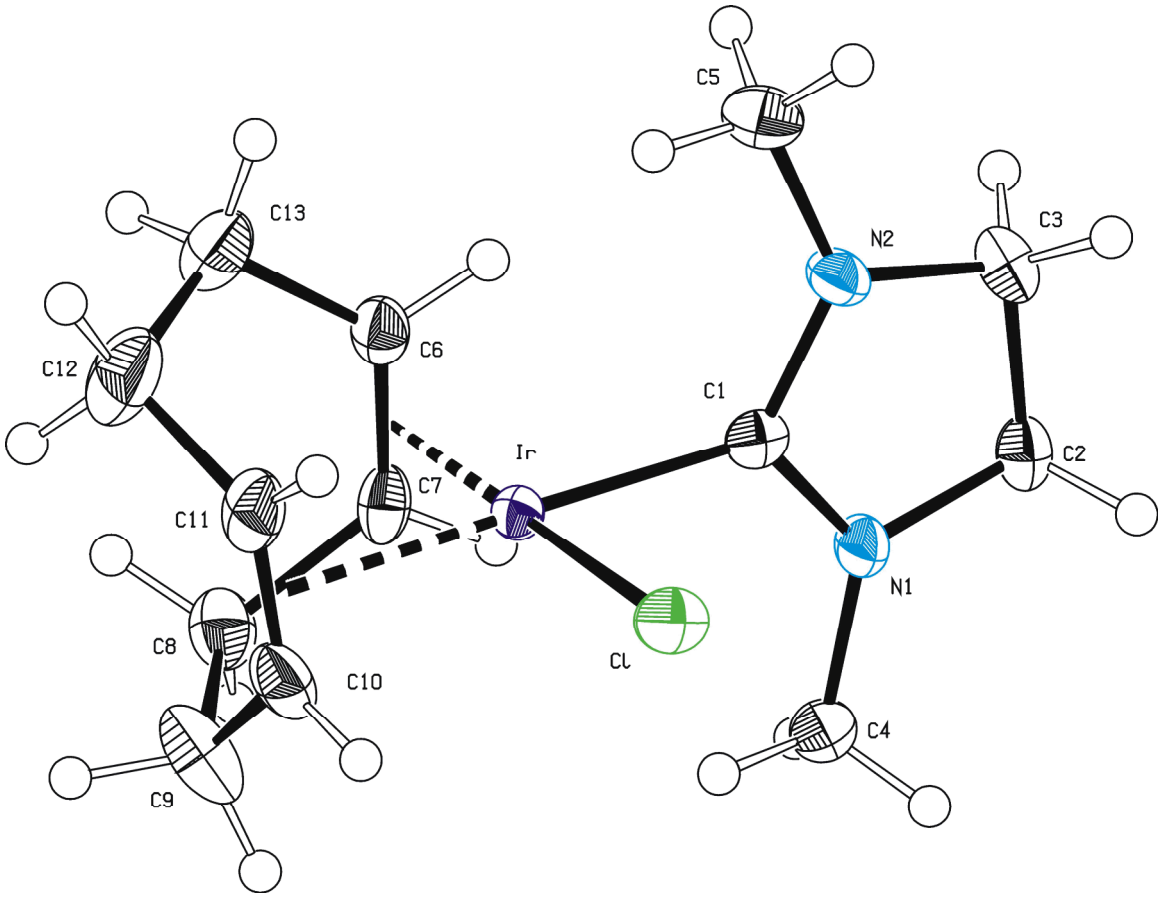
Crystal Structure Determinations

Compound 1-Cl October 15th 2007



Molecular Formula:	C_{13} H_{22} Cl Ir N_2
Crystal Color / Shape	Orange fragment
Crystal Size	Approximate size of crystal fragment used for data collection: 0.20 × 0.25 × 0.56 mm
Molecular Weight:	434.00 a.m.u.
F_{000}:	832
Systematic Absences:	h00: h≠2n; 0k0: k≠2n, 00l: l≠2n
Space Group:	Orthorhombic $P\,2_12_12_1$ (I.T.-No.: 19)

Cell Constants:	Least-squares refinement of 47286 reflections with the program "CRYSALIS" [1]; theta range 3.07° < θ < 25.34°; Mo($K\bar{\alpha}$); λ = 71.073 pm
	a = 725.73(1) pm b = 1234.28(1) pm c = 1572.79(1) pm
	V = 1408.83(2)· 10^6 pm^3; Z = 4; D_{calc} = 2.046 g cm^{-3}
Diffractometer:	Xcalibur™3; κ-CCD (Area Diffraction System; OXFORD DIFFRACTIONS); sealed tube, graphite monochromator; 50 kV; 40 mA; λ = 71.073 pm; Mo($K\bar{\alpha}$)
Temperature:	(-120±1) °C; (153±1) K
Measurement Range:	3.07° < θ < 25.34°; h: -8/8, k: -14/14, l: -18/18
Measurement Time:	10 s per film
Measurement Mode:	measured: 10 sets; 1552 films / scaled: 10 sets; 1552 films φ– and ω–movement; Increment: $\Delta\varphi/\Delta\omega$ = 1.00°; dx = 50.0 mm
LP - Correction:	Yes [1]
Intensity Correction:	No/Yes; during scaling [1]
Absorption Correction:	No/Yes; during scaling; μ = 9.648 mm^{-1} [1]
Reflection Data:	34338 reflections were integrated 127 reflections systematic absent and rejected 34211 reflections to be merged 0.0302 R_{int}: (basis F_o^2) 2576 independent reflections (all) were used in refinements 2559 independent reflections with $I_o > 2\sigma(I_o)$ 99.9 % completeness of the data set 157 parameter full-matrix refinement 16.4 reflections per parameter
Solution:	Direct Methods [2]; Difference Fourier syntheses
Refinement Parameters:	In the asymmetric unit: 17 Non-hydrogen atoms with anisotropic displacement parameters
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions (d_{C-H} = 95, 98, 99 pm). Isotropic displacement parameters were calculated from the parent carbon atom (U_H = 1.2/1.5 U_C). The hydrogen atoms were included in the structure factor calculations but not refined.
Atomic Form Factors:	For neutral atoms and anomalous dispersion [3]
Extinction Correction:	F_c (korr) = kF_c[1+ 0.001 · ε · F_c^2· λ^3/sin(2Θ)]$^{-1/4}$ SHELXL-97 [4] ε refined to ε = 0.0016(1)
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2)+(a*P)^2+b*P$ with a: 0.0191; b: 2.3014; P: [Maximum(0 or F_o^2)+2*F_c^2]/3
Shift/Err:	Less than 0.002 in the last cycle of refinement:
Resid. Electron Density:	+1.15 $e_{0;}^-$/Å^3; -0.59 $e_{0;}^-$/Å^3
R1:	$\Sigma(\|\|F_o\|-\|F_c\|\|)/\Sigma\|F_o\|$
[$F_o > 4\sigma(F_o)$; N=2559]:	= 0.0149
[all reflctns; N=2576]:	= 0.0151
wR2:	$[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

[$F_o > 4\sigma(F_o)$; N=2559]:		= 0.0373
[all reflctns; N=2576]:		= 0.0374
Goodness of fit:	$[\Sigma w(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$	= 1.174
Flack's Parameter :	x= -0.016(8)	
Remarks:	Refinement expression $\Sigma w(F_o^2-F_c^2)^2$	

The correct enantiomere is proved by Flack's Parameter.

References:

[1] CrysAlis Data Collection Software and Data Processing Software for Oxford Xcalibur diffractometer, Version 1.171, Oxford Diffraction Ltd., Oxfordshire, United Kingdom, 2005.

[2] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli M. "**SIR92**", *J. Appl. Cryst.* **1994**, *27*, 435-436.

[3] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.

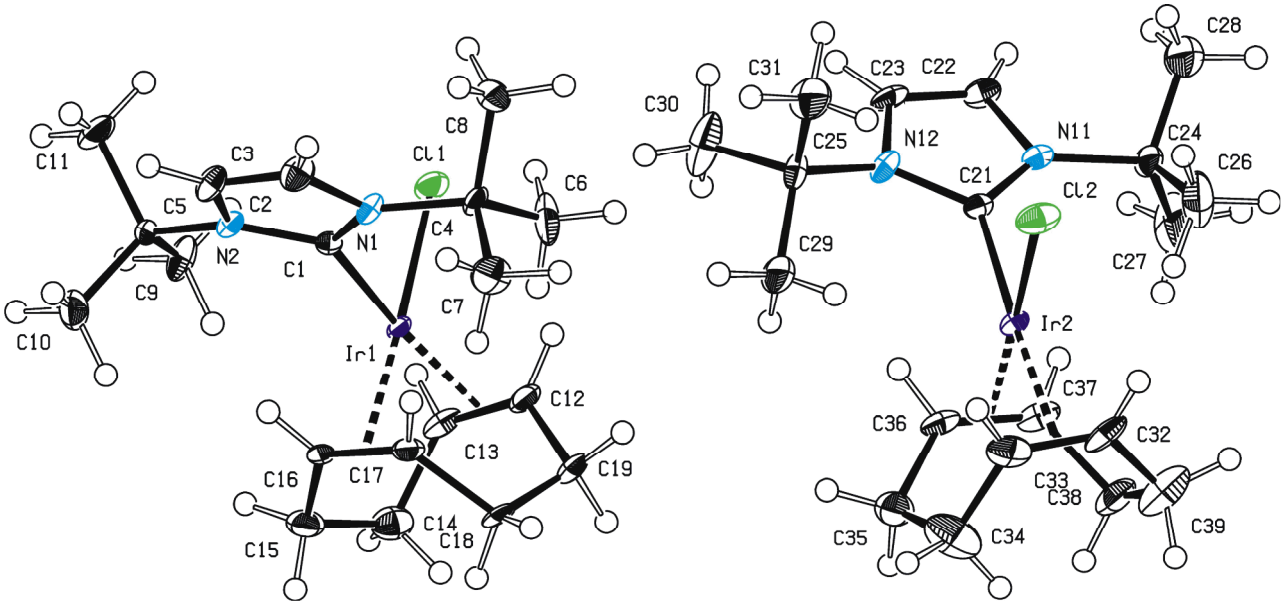
[4] Sheldrick, G. M. "**SHELXL-97**", University of Göttingen, Göttingen, Germany, (1998).

[5] Spek, A. L. "**PLATON**", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, (2007).

[6] L. J. Farrugia, "**WinGX** (Version 1.70.01 January 2005) ", *J. Appl. Cryst.* **1999**, *32*, 837-838.

[7] a) The Cambridge Structural Database: a quarter of a million crystal structures and rising; Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380-388. b) New Software for searching the Cambridge Structural Database and visualizing crystal structures; Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr.* **2002**, *B58*, 389-397.

Compound 5-Cl July 22th 2008



Molecule **A** Molecule **B**

Molecular Formula: C_{19} H_{32} Cl Ir N_2

Crystal Color / Shape	Yellow fragment
Crystal Size	Approximate size of crystal fragment used for data collection: $0.38 \times 0.51 \times 0.63$ mm
Molecular Weight:	516.14 a.m.u.
F_{000}:	2032
Systematic Absences:	h0l: l≠2n; 0k0: k≠2n
Space Group:	Monoclinic $P\,2_1/c$ (I.T.-No.: 14)
Cell Constants:	Least-squares refinement of 9670 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range $3.37° < \theta < 67.04°$; Cu($K\overline{\alpha}$); λ = 154.180 pm a = 1119.62(4) pm b = 1944.17(6) pm β = 91.4342(15)° c = 1775.86(6) pm $V = 3864.4(2) \cdot 10^6$ pm^3; $Z = 8$; $D_{calc} = 1.774$ g cm^{-3}; Mos. = 0.54
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); sealed tube; graphite monochromator; 40 kV; 30 mA; λ = 154.180 pm; Cu($K\overline{\alpha}$)
Temperature:	(-100±1) °C; (173±1) K
Measurement Range:	$3.37° < \theta < 67.04°$; h: -13/12, k: -13/22, l: -20/20
Measurement Time:	10 s per film
Measurement Mode:	measured: 17 runs; 5620 films / scaled: 17 runs; 5620 films φ– and ω–movement; Increment: $\Delta\varphi/\Delta\omega = 1.00°$; dx = 40.0 mm
LP - Correction:	Yes [2]
Intensity Correction	No/Yes; during scaling [2]
Absorption Corrections:	Mathematical absorption correction; SHX_ABS [6]; μ = 14.639 mm^{-1} Correction Factors: T_{min} = 0.0472 T_{max} = 0.4662
Reflection Data:	48868 reflections were integrated 1184 reflections systematic absent and rejected 47684 reflections to be merged 6727 independent reflections 0.1273 R_{int}: (basis F_o^2) 6727 independent reflections (all) were used in refinements 6636 independent reflections with $I_o > 2\sigma(I_o)$ 97.4 % completeness of the data set 428 parameter full-matrix refinement 15.7 reflections per parameter
Solution:	Direct Methods [3]; Difference Fourier syntheses
Refinement Parameters:	In the asymmetric unit: 46 Non-hydrogen atoms with anisotropic displacement parameters
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions (d_{C-H} = 95, 98, 99 pm). Isotropic displacement parameters were calculated from the parent carbon atom (U_H = 1.2/1.5 U_C). The hydrogen atoms were included in the structure factor calculations but not refined.
Atomic Form Factors:	For neutral atoms and anomalous dispersion [4]
Extinction Correction:	F_c (korr) = k$F_c[1+ 0.001 \cdot \varepsilon \cdot F_c^2 \cdot \lambda^3/\sin(2\Theta)]^{-1/4}$ SHELXL-97 [5] ε refined to $\varepsilon = 0.00057(3)$

Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2)+(a*P)^2+b*P$	
	with a: 0.0503; b: 21.0899; P: [Maximum(0 or F_o^2)+2$*F_c^2$]/3	
Shift/Err:	Less than 0.002 in the last cycle of refinement:	
Resid. Electron Density:	+2.42 $e_{0;}^-/Å^3$; -2.05 $e_{0;}^-/Å^3$	
R1:	$\Sigma(\|\|F_o\|-\|F_c\|\|)/\Sigma\|F_o\|$	
[$F_o > 4\sigma(F_o)$; N=6636]:		= 0.0425
[all reflctns; N=6727]:		= 0.0430
wR2:	$[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$	
[$F_o > 4\sigma(F_o)$; N=6636]:		= 0.1116
[all reflctns; N=6727]:		= 0.1120
Goodness of fit:	$[\Sigma w(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$	= 1.181

Remarks: Refinement expression $\Sigma w(F_o^2-F_c^2)^2$

References:

[1] APEX suite of crystallographic software. APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

[2] SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

[3] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli M. "**SIR92**", *J. Appl. Cryst.* **1994**, *27*, 435-436.

[4] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.

[5] Sheldrick, G. M. "**SHELXL-97**", University of Göttingen, Göttingen, Germany, (1998).

[6] Spek, A. L. "**PLATON**", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, (2007).

[7] L. J. Farrugia, "**WinGX** (Version 1.70.01 January 2005) ", *J. Appl. Cryst.* **1999**, *32*, 837-838.

[8] a) The Cambridge Structural Database: a quarter of a million crystal structures and rising; Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380-388. b) New Software for searching the Cambridge Structural Database and visualizing crystal structures; Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr.* **2002**, *B58*, 389-397.