Supplementary Information

Carbon-Sulfur Bond Cleavage of Methyl Substituted Thiophenes with Iridium(III)

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ESI/MS results for **1**.

Mass peak (m/z)	Actual(%)	Calculated(%)
813	2.7	2.1
812	12.2	7.8
811	46.5	29.6
810	48.0	28.6
809	100.0	100.0
808	48.4	26.0
807	94.8	89.3
806	18.9	7.0
805	34.3	23.7

ESI/MS results for Rxn. 9 containing compounds **5-7**.

Mass peak (m/z)	Actual(%)	Calculated(%)
900	14.2	10.4
899	37.3	34.0
898	37.9	33.4
897	100.0	100.0
896	37.1	29.5
895	86.2	86.0
894	14.0	7.8
893	25.6	22.5

ESI/MS results for Rxn. 9 containing compounds **3** and **4**..

Mass peak (m/z)	Actual(%)	Calculated(%)
798	9.1	7.5
797	39.5	29.4
796	38.2	27.5
795	100.0	100.0
794	41.8	25.1
793	93.9	89.4
792	16.8	6.7
791	32.6	23.8

ESI/MS results for **8**.

Mass peak (m/z)	Actual(%)	Calculated(%)
826	7.3	7.9
825	29.5	29.8
824	30.9	28.6
823	100.0	100.0
822	25.6	26.0
821	86.2	89.1
820	12.6	6.9
819	21.2	23.6

The peaks shown for compounds **5-7** were normalized relative to the peak at 897. The calculated % was found using the Sheffield Chemputer website and inputting the empirical formula with only one chlorine.

(http://winter.group.shef.ac.uk/chemputer/isotopes.html)

REFERENCE NUMBER: jonmg01

CRYSTAL STRUCTURE REPORT

$C_{62}\ H_{91}\ Cl_6\ Ir_5\ S_4$

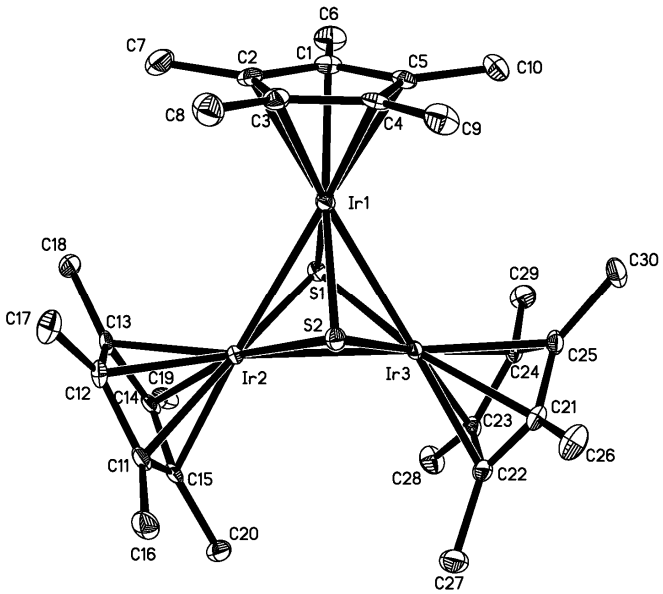
or

$\{[IrCp^*]_3(\mu_3\text{-}S)_2\}[IrCp^*Cl_3]_2 \cdot 2(2,5\text{-}Me_2\text{-thiophene})$, **2**

Report prepared for:

M. Grochowski, Prof. W. Jones

May 16, 2007



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Data collection

A crystal (0.32 x 0.12 x 0.12 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(1) K.[1] A preliminary set of cell constants and an orientation matrix were calculated from 1112 reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 10 seconds and a detector distance of 5.03 cm. A randomly oriented region of reciprocal space was surveyed: four major sections of frames were collected with 0.50º steps in ω at four different ϕ settings and a detector position of -33º in 2θ. The intensity data were corrected for absorption.[2] Final cell constants were calculated from the xyz centroids of 3925 strong reflections from the actual data collection after integration.[3] See Table S-1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR97[4] and refined using SHELXL-97.[5] The space group *P*-1 was determined based on the lack of systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0234$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.0508$ (F^2, all data).

Structure description

The structure is similar to the one suggested. All atoms lie on general positions. The structure of the cation has been reported previously with PF_6^- (refcode LEVFUN) and BF_4^- (refcode YEVMIV) counterions.[6] There are two co-crystallized 2,5-dimethylthiophene solvent molecules per iridium dication.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

[1] *APEX2*, version 2.1-0; Bruker AXS: Madison, WI, 2006.

[2] Sheldrick, G. M. *SADABS*, version 2007/2; University of Göttingen: Göttingen, Germany, 2004.

[3] *SAINT*, version 7.34A; Bruker AXS: Madison, WI, 2006.

[4] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97: A new program for solving and refining crystal structures*; Istituto di Cristallografia, CNR: Bari, Italy, 1999.

[5] *SHELXTL*, version 6.14; Bruker AXS: Madison, WI, 2000.

[6] a) Venturelli, A.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1994**, *116*, 4824; b) Nishioka, T.; Isobe, K. *Chem. Lett.* **1994**, 1661.

Some equations of interest:

$$R_{int} = \Sigma|F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R1 = \Sigma||F_o| - |F_c|| \,/\, \Sigma|F_o|$$

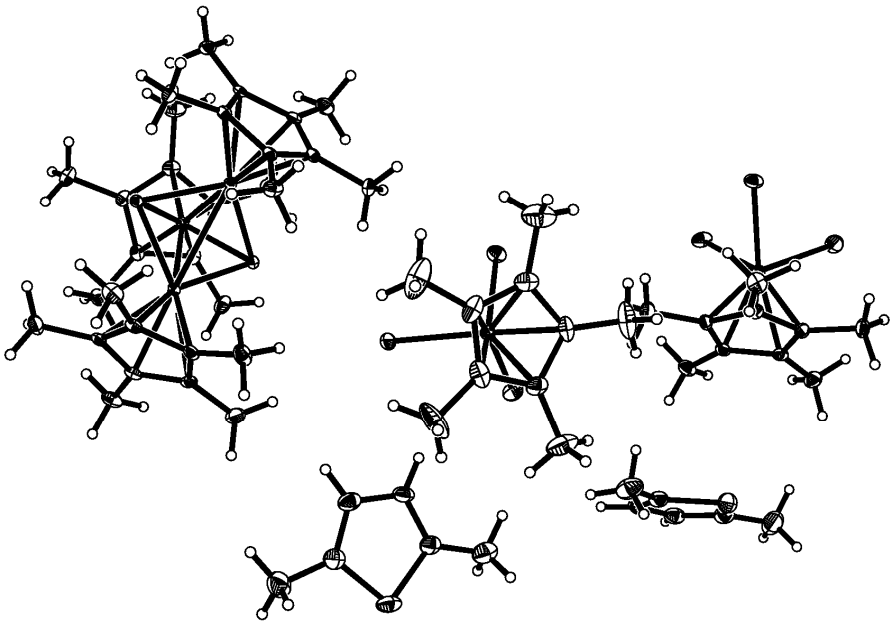
$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma[w(F_o^2)^2]]^{1/2}$$

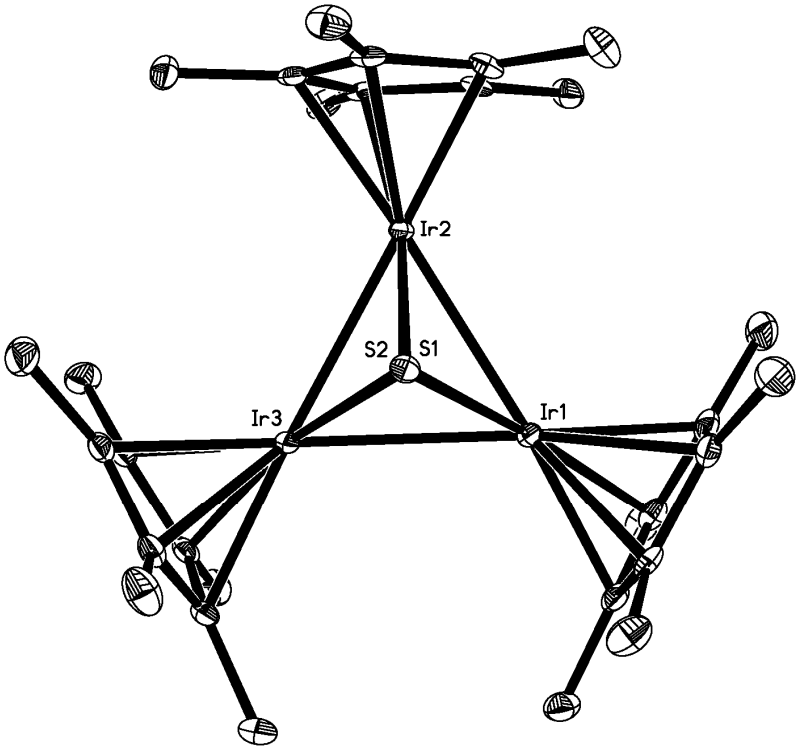
where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max(0, F_o^2) + 2/3\, F_c^2$$

$$\text{GOF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters




Ir2
S2
S1
Ir3
Ir1

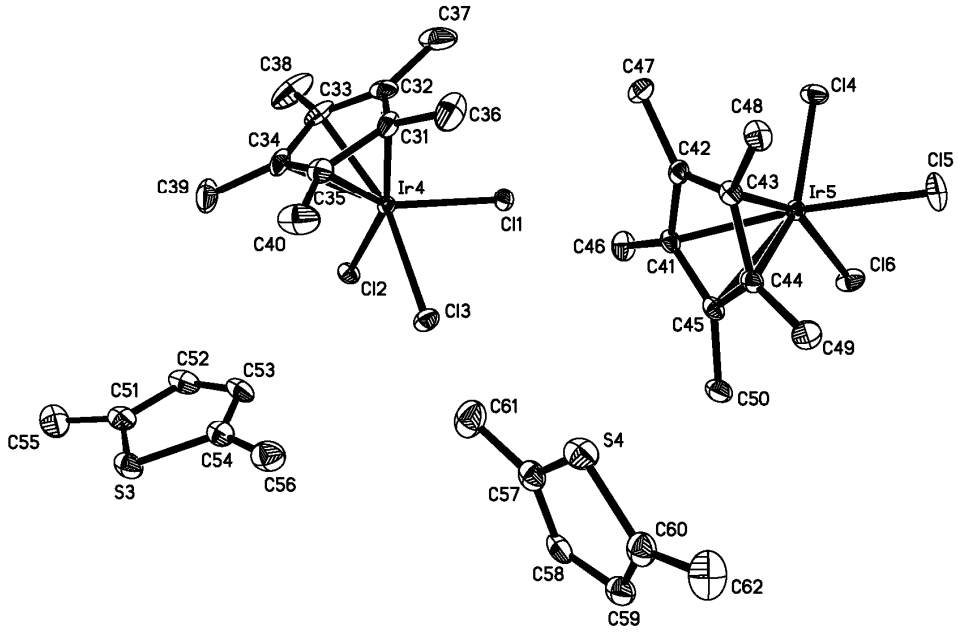

C37
C38
C33
C32
C36
C34
C31
C39
C35
Ir4
Cl1
C40
Cl2
Cl3
C47
Cl4
C48
C42
Cl5
C43
Ir5
C46
C41
Cl6
C44
C45
C49
C50
C52
C53
C51
C55
C54
S3
C56
C61
S4
C57
C60
C58
C62
C59

Table S-1. Crystal data and structure refinement for {[IrCp*]$_3$(μ_3-S)$_2$}[IrCp*Cl$_3$]$_2$, **2**.

Identification code	jonmg01	
Empirical formula	C62 H91 Cl6 Ir5 S4	
Formula weight	2138.29	
Temperature	100.0(1) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 10.9688(9) Å	α = 72.210(1)°
	b = 16.3357(13) Å	β = 78.404(1)°
	c = 20.4096(16) Å	γ = 87.161(1)°
Volume	3410.8(5) Å^3	
Z	2	
Density (calculated)	2.082 Mg/m^3	
Absorption coefficient	10.113 mm^{-1}	
F(000)	2028	
Crystal color, morphology	orange, block	
Crystal size	0.32 x 0.12 x 0.12 mm^3	
Theta range for data collection	1.90 to 32.03°	
Index ranges	$-16 \le h \le 16, -24 \le k \le 24, -30 \le l \le 30$	
Reflections collected	60766	
Independent reflections	23487 [*R*(int) = 0.0287]	
Observed reflections	20560	
Completeness to theta = 32.03°	98.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.2966 and 0.1102	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	23487 / 0 / 723	
Goodness-of-fit on F^2	1.019	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0234, *wR*2 = 0.0490	
R indices (all data)	*R*1 = 0.0296, *wR*2 = 0.0508	
Largest diff. peak and hole	2.118 and -1.343 e.Å^{-3}	

REFERENCE NUMBER: jonmg10

CRYSTAL STRUCTURE REPORT

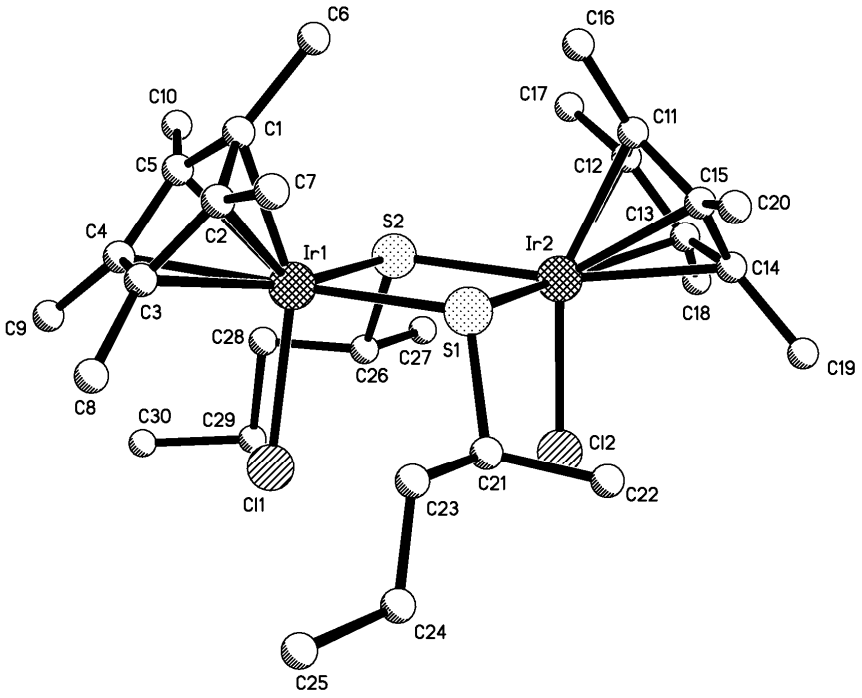
$C_{30}\ H_{52}\ Cl_2\ Ir_2\ S_2$

$[Cp^*IrCl(\mu\text{-}S\text{-}2\text{-}pentyl)]_2$, **4**

Report prepared for:

M. Grochowski, Prof. W. Jones

December 20, 2007



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Data collection

A crystal (0.16 x 0.10 x 0.01 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(1) K.[1] A preliminary set of cell constants and an orientation matrix were calculated from 181 reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 120 seconds and a detector distance of 4.98 cm. A randomly oriented region of reciprocal space was surveyed: three major sections of frames were collected with 2.00º steps in ω at three different ϕ settings and a detector position of -33º in 2θ. The intensity data were corrected for absorption.[2] Final cell constants were calculated from the xyz centroids of 2278 strong reflections from the actual data collection after integration.[3] See Table S-2 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR97[4] and refined using SHELXL-97.[5] The space group $P2_1/c$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. The Ir, Cl, and S atoms were refined with anisotropic displacement parameters; all others were refined with isotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.1462$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.3305$ (F^2, all data). *This structure report may be used for connectivity purposes only.*

Structure description

The structure is the one suggested. All atoms lie in general positions. The pentamethylcyclopentadienyl (Cp*) groups were refined as ideal rigid groups.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

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[2] Sheldrick, G. M. *SADABS*, version 2007/2; University of Göttingen: Göttingen, Germany, 2004.

[3] *SAINT*, version 7.34A; Bruker AXS: Madison, WI, 2006.

[4] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97: A new program for solving and refining crystal structures*; Istituto di Cristallografia, CNR: Bari, Italy, 1999.

[5] *SHELXTL*, version 6.14; Bruker AXS: Madison, WI, 2000.

Some equations of interest:

$$R_{int} = \Sigma|F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R1 = \Sigma||F_o| - |F_c|| \,/\, \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma[w(F_o^2)^2]]^{1/2}$$

where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max(0, F_o^2) + 2/3\, F_c^2$$

$$\text{GOF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

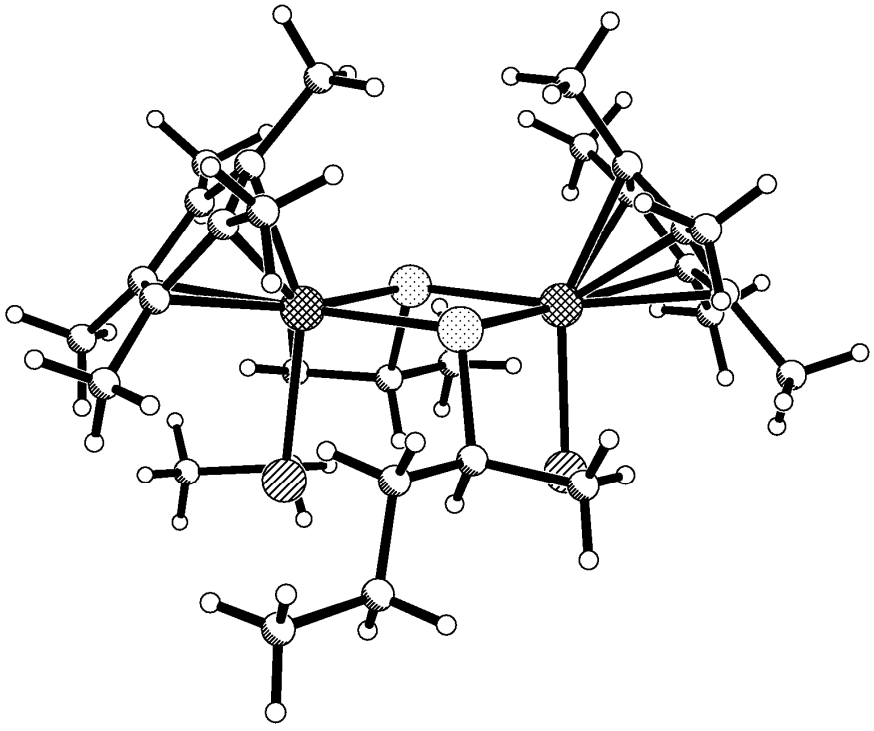


Table S-2. Crystal data and structure refinement for [Cp*IrCl(μ-S-2-pentyl)]$_2$, **4**.

Identification code	jonmg10	
Empirical formula	C30 H52 Cl2 Ir2 S2	
Formula weight	932.14	
Temperature	100.0(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.869(6) Å	α = 90°
	b = 8.794(5) Å	β = 91.713(7)°
	c = 32.001(17) Å	γ = 90°
Volume	3338(3) Å^3	
Z	4	
Density (calculated)	1.855 Mg/m^3	
Absorption coefficient	8.267 mm^{-1}	
F(000)	1808	
Crystal color, morphology	yellow, plate	
Crystal size	0.16 x 0.10 x 0.01 mm^3	
Theta range for data collection	2.11 to 25.12°	
Index ranges	$-14 \le h \le 13, -9 \le k \le 10, -38 \le l \le 38$	
Reflections collected	21303	
Independent reflections	5944 [R(int) = 0.3382]	
Observed reflections	2135	
Completeness to theta = 25.12°	99.4%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9598 and 0.3513	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5944 / 0 / 129	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.1462, wR2 = 0.2680	
R indices (all data)	R1 = 0.3215, wR2 = 0.3305	
Largest diff. peak and hole	1.948 and -2.922 e.Å^{-3}	

REFERENCE NUMBER: jonmg06

CRYSTAL STRUCTURE REPORT

$C_{25}\ H_{42}\ Cl_2\ Ir_2\ S$

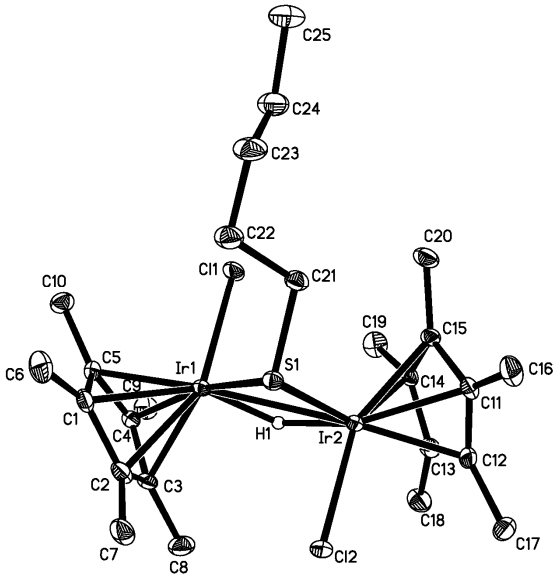
or

$[Cp^*IrCl]_2(\mu\text{-}H)(\mu\text{-}S\text{-}n\text{-}pentyl)$, **5**

Report prepared for:

M. Grochowski, Prof. W. Jones

September 09, 2007



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Data collection

A crystal (0.44 x 0.10 x 0.06 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(1) K.[1] A preliminary set of cell constants and an orientation matrix were calculated from 803 reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 10 seconds and a detector distance of 5.00 cm. A randomly oriented region of reciprocal space was surveyed: four major sections of frames were collected with 0.50º steps in ω at four different ϕ settings and a detector position of -33º in 2θ. The intensity data were corrected for absorption.[2] Final cell constants were calculated from the xyz centroids of 3930 strong reflections from the actual data collection after integration.[3] See Table S-3 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR97[4] and refined using SHELXL-97.[5] The space group $P2_1/c$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms, including H1, were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Hydrogen atom H1 was refined relative to an iridium atom. The final full matrix least squares refinement converged to $R1$ = 0.0243 (F^2, $I > 2\sigma(I)$) and $wR2$ = 0.0474 (F^2, all data).

Structure description

The structure is the one suggested. All atoms lie on general positions. The pentyl chain abuts the inversion symmetry equivalent of itself, thus allowing for an efficient packing motif.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

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[2] Sheldrick, G. M. *SADABS*, version 2007/2; University of Göttingen: Göttingen, Germany, 2004.

[3] *SAINT*, version 7.34A; Bruker AXS: Madison, WI, 2006.

[4] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97: A new program for solving and refining crystal structures*; Istituto di Cristallografia, CNR: Bari, Italy, 1999.

[5] *SHELXTL*, version 6.14; Bruker AXS: Madison, WI, 2000.

Some equations of interest:

$$R_{int} = \Sigma|F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R1 = \Sigma||F_o| - |F_c|| \,/\, \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma[w(F_o^2)^2]]^{1/2}$$

where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max(0, F_o^2) + 2/3\, F_c^2$$

$$\text{GOF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

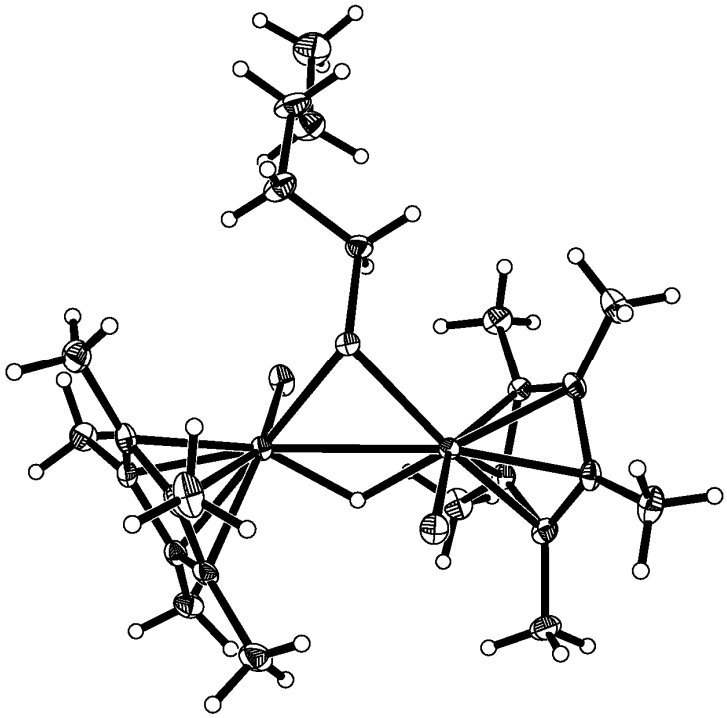


Table S-3. Crystal data and structure refinement for $[Cp^*IrCl]_2(\mu\text{-}H)(\mu\text{-}S\text{-}n\text{-}pentyl)$, **5**.

Identification code	jonmg06	
Empirical formula	C25 H42 Cl2 Ir2 S	
Formula weight	829.95	
Temperature	100.0(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.3884(14) Å	α = 90°
	b = 15.392(2) Å	β = 94.886(2)°
	c = 19.126(3) Å	γ = 90°
Volume	2753.7(7) $Å^3$	
Z	4	
Density (calculated)	2.002 Mg/m^3	
Absorption coefficient	9.936 mm^{-1}	
F(000)	1584	
Crystal color, morphology	red-orange, needle	
Crystal size	0.44 x 0.10 x 0.06 mm^3	
Theta range for data collection	1.70 to 32.58°	
Index ranges	$-14 \le h \le 14, -23 \le k \le 23, -28 \le l \le 28$	
Reflections collected	48913	
Independent reflections	9961 [R(int) = 0.0443]	
Observed reflections	8125	
Completeness to theta = 32.58°	99.3%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.5571 and 0.0911	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9961 / 0 / 282	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	$R1$ = 0.0243, $wR2$ = 0.0442	
R indices (all data)	$R1$ = 0.0368, $wR2$ = 0.0474	
Largest diff. peak and hole	1.237 and -0.909 e.$Å^{-3}$	

REFERENCE NUMBER: jonmg07

CRYSTAL STRUCTURE REPORT

$C_{30}\ H_{52}\ Cl_2\ Ir_2\ S_2$

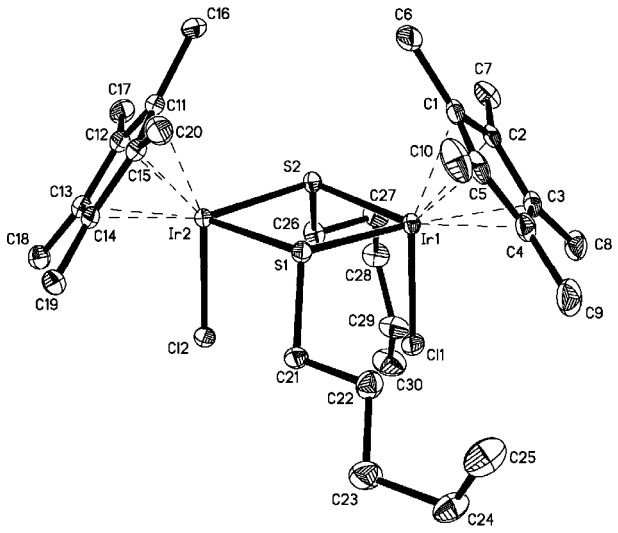
or

$[Cp^*IrCl(\mu\text{-S-n-pentyl})]_2$, **6**

Report prepared for:

M. Grochowski, Prof. W. Jones

September 13, 2007



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Data collection

A crystal (0.24 x 0.20 x 0.04 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(1) K.[1] A preliminary set of cell constants and an orientation matrix were calculated from 666 reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 15 seconds and a detector distance of 5.00 cm. A randomly oriented region of reciprocal space was surveyed: four major sections of frames were collected with 0.50º steps in ω at four different ϕ settings and a detector position of -33º in 2θ. The intensity data were corrected for absorption.[2] Final cell constants were calculated from the xyz centroids of 3981 strong reflections from the actual data collection after integration.[3] See Table S-4 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR97[4] and refined using SHELXL-97.[5] The space group *C*2/*c* was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0278$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.0572$ (F^2, all data).

Structure description

The structure is the one suggested. All atoms lie in general positions. One of the Cp* methyl groups is modeled as rotationally disordered.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

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[2] Sheldrick, G. M. *SADABS*, version 2007/2; University of Göttingen: Göttingen, Germany, 2004.

[3] *SAINT*, version 7.34A; Bruker AXS: Madison, WI, 2006.

[4] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97: A new program for solving and refining crystal structures*; Istituto di Cristallografia, CNR: Bari, Italy, 1999.

[5] *SHELXTL*, version 6.14; Bruker AXS: Madison, WI, 2000.

Some equations of interest:

$$R_{int} = \Sigma|F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R1 = \Sigma||F_o| - |F_c|| \,/\, \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma[w(F_o^2)^2]]^{1/2}$$

where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max(0, F_o^2) + 2/3\, F_c^2$$

$$\text{GOF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] / (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

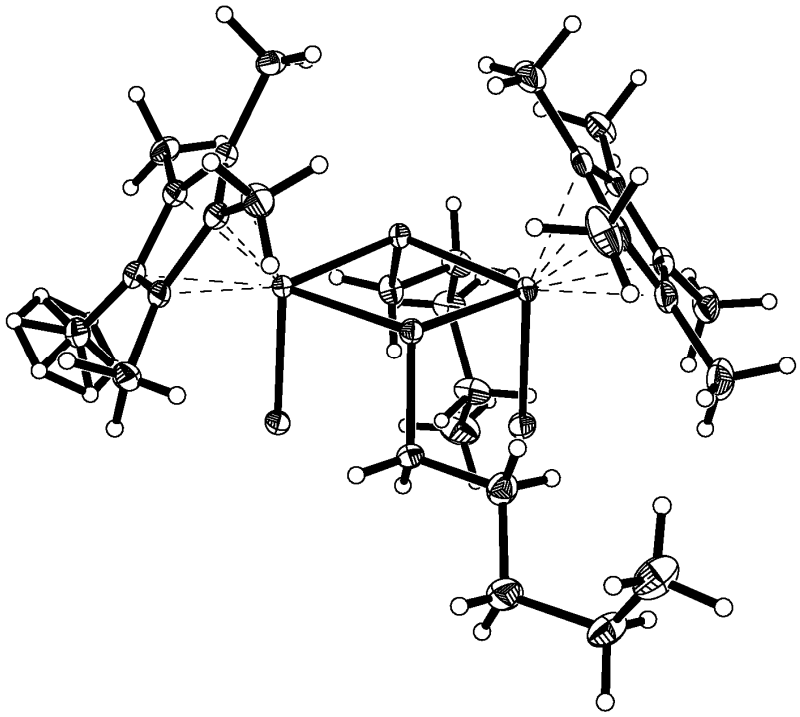


Table S-4. Crystal data and structure refinement for $[Cp^*IrCl(\mu\text{-S-n-pentyl})]_2$, **6**.

Identification code	jonmg07	
Empirical formula	C30 H52 Cl2 Ir2 S2	
Formula weight	932.14	
Temperature	100.0(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	*a* = 22.620(3) Å	α = 90°
	b = 16.173(2) Å	β = 119.903(2)°
	c = 20.926(3) Å	γ = 90°
Volume	6636.5(14) $Å^3$	
Z	8	
Density (calculated)	1.866 Mg/m^3	
Absorption coefficient	8.317 mm^{-1}	
F(000)	3616	
Crystal color, morphology	yellow-orange, plate	
Crystal size	0.24 x 0.20 x 0.04 mm^3	
Theta range for data collection	1.63 to 32.58°	
Index ranges	$-34 \le h \le 34, -24 \le k \le 24, -31 \le l \le 31$	
Reflections collected	59112	
Independent reflections	11983 [*R*(int) = 0.0560]	
Observed reflections	9367	
Completeness to theta = 32.58°	99.2%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7120 and 0.1401	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11983 / 0 / 337	
Goodness-of-fit on F^2	1.017	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0278, *wR*2 = 0.0521	
R indices (all data)	*R*1 = 0.0457, *wR*2 = 0.0572	
Largest diff. peak and hole	1.459 and -1.698 e.$Å^{-3}$	

REFERENCE NUMBER: jonmg18

CRYSTAL STRUCTURE REPORT

$C_{26}\ H_{42}\ Cl_2\ Ir_2\ O\ S$

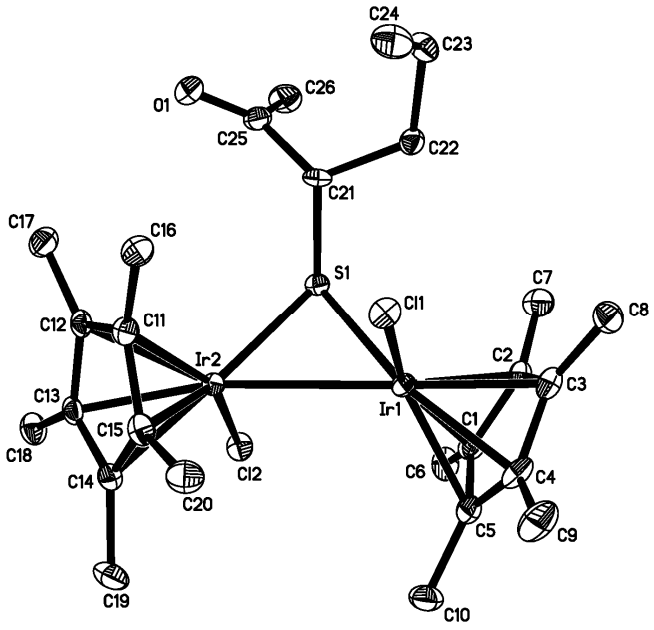
or

$[IrClCp^*]_2(\mu\text{-}H)[\mu\text{-}SCH(COCH_3)(C_3H_7)]$, **8**

Report prepared for:

M. Grochowski, Prof. W. Jones

September 11, 2008



William W. Brennessel

X-ray Crystallographic Facility

Department of Chemistry, University of Rochester

120 Trustee Road

Rochester, NY 14627

Data collection

A crystal (0.26 x 0.20 x 0.05 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(1) K.[1] A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 25 seconds and a detector distance of 4.00 cm. A randomly oriented region of reciprocal space was surveyed: four major sections of frames were collected with 0.50º steps in ω at four different ϕ settings and a detector position of -38º in 2θ. The intensity data were corrected for absorption.[2] Final cell constants were calculated from the xyz centroids of 4068 strong reflections from the actual data collection after integration.[3] See Table S-5 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR97[4] and refined using SHELXL-97.[5] The space group $Pca2_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The bridging hydride atom could not be located in the difference Fourier map. It was omitted from the atom list, but included in the molecular formula. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0370$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.0762$ (F^2, all data).

Structure description

The structure is similar to the one suggested. There are two independent molecules in the asymmetric unit with all atoms in general positions.

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

[1] *APEX2*, version 2.2-0; Bruker AXS: Madison, WI, 2007.

[2] Sheldrick, G. M. *SADABS*, version 2007/4; University of Göttingen: Göttingen, Germany, 2007.

[3] *SAINT*, version 7.46A; Bruker AXS: Madison, WI, 2007.

[4] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97: A new program for solving and refining crystal structures*; Istituto di Cristallografia, CNR: Bari, Italy, 1999.

[5] Sheldrick, G. M. *Acta. Cryst.* **2008**, *A64*, 112-122.

Some equations of interest:

$$R_{int} = \Sigma|F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R1 = \Sigma||F_o| - |F_c|| \,/\, \Sigma|F_o|$$

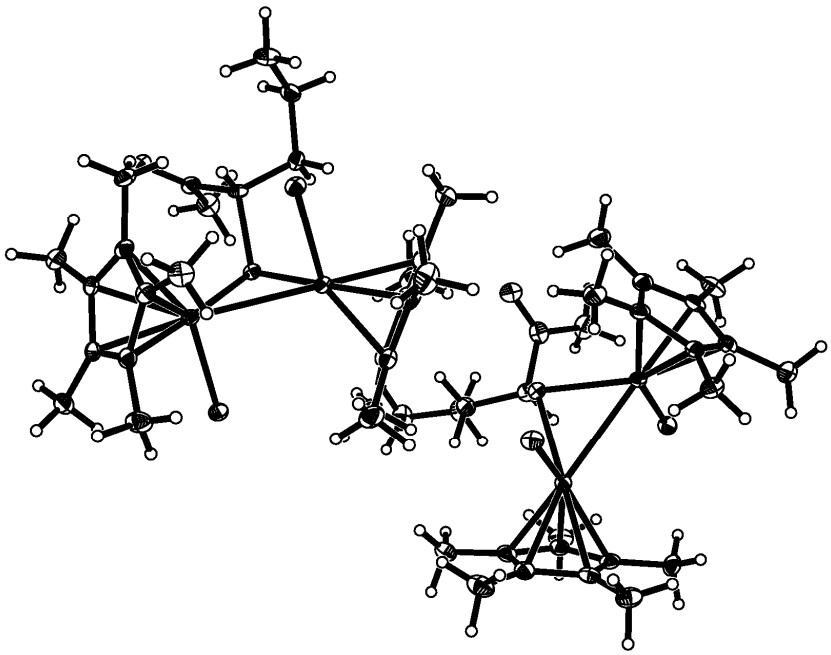
$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma[w(F_o^2)^2]]^{1/2}$$

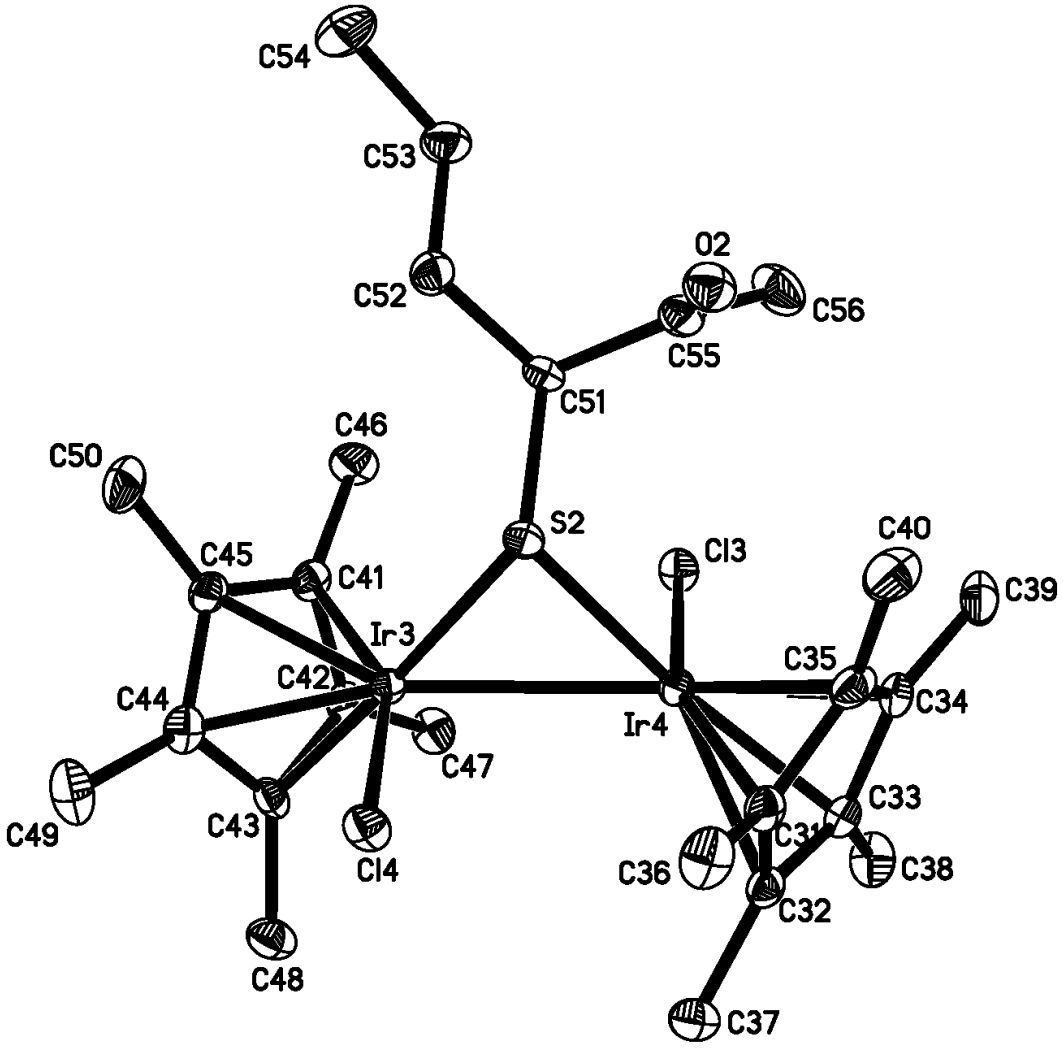
where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max(0, F_o^2) + 2/3\, F_c^2$$

$$\text{GOF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters




C54
C53
O2
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C56
C55
C51
C46
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S2
C40
C45
C41
Cl3
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Ir3
C35
C42
C44
C34
Ir4
C47
C33
C49
C43
C31
Cl4
C36
C38
C32
C48
C37

Table S-5. Crystal data and structure refinement for $[IrClCp^*]_2(\mu\text{-}H)[\mu\text{-}SCH(COCH_3)(C_3H_7)]$, **8**.

Identification code	jonmg18	
Empirical formula	C26 H42 Cl2 Ir2 O S	
Formula weight	857.96	
Temperature	100.0(1) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pca2_1$	
Unit cell dimensions	a = 17.881(4) Å	α = 90°
	b = 13.857(3) Å	β = 90°
	c = 22.402(5) Å	γ = 90°
Volume	5551(2) $Å^3$	
Z	8	
Density (calculated)	2.053 Mg/m^3	
Absorption coefficient	9.865 mm^{-1}	
F(000)	3280	
Crystal color, morphology	red-orange, plate	
Crystal size	0.26 x 0.20 x 0.05 mm^3	
Theta range for data collection	1.82 to 37.78°	
Index ranges	$-30 \le h \le 30, -23 \le k \le 23, -38 \le l \le 38$	
Reflections collected	129413	
Independent reflections	29379 [R(int) = 0.0721]	
Observed reflections	24140	
Completeness to theta = 37.78°	99.5%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.6183 and 0.1036	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	29379 / 1 / 601	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	$R1$ = 0.0370, $wR2$ = 0.0675	
R indices (all data)	$R1$ = 0.0589, $wR2$ = 0.0762	
Absolute structure parameter	-0.012(4)	
Largest diff. peak and hole	2.731 and -3.357 e.$Å^{-3}$	