Stabilization of coordinatively unsaturated Ir₄ clusters with bulky ligands: A comparative study of chemical and mechanical effects

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Supporting Information

Experimental section

Synthesis of the cluster compounds

All syntheses are performed under inert conditions (Schlenk line, argon atmosphere). The syntheses of precursor cluster $[Bu_4N][Ir_4(CO)_{11}Br]$, ligand **5**, and complexes **1**, **1'** and **3'** are described elsewhere¹. Analytical thin-layer chromatography is performed on precoated silica gel plates (0.25 mm, 60F-254, Selecto), and silica gel (Selecto 60) is used for column chromatography.

Synthesis of 2: To a solution of $[Bu_4N][Ir_4(CO)_{11}Br]$ (79 mg, 0.057 mmol) in 20 mL toluene (Aldrich, anhydrous, 99.98 %), **5** (108 mg, 0.111 mmol) is added. The solution is stirred at 80 °C for 15 h. The solvent is evaporated and the residue is dried under vacuum. The residue is separated via coloumn chromatography (300 x 40 mm, silicaflash, dichloromethane : hexane = 1 : 5). The first fraction to elute consists of **2**. (yield: 18 mg, 15 %). ³¹P{¹H}-NMR: δ 17.24 (s, 1P, equatorial), -11.13 (s, 1P, axial), ESI MS (+) m/z 3128.9 [M+Cs]. IR (cm⁻¹) in CH₂Cl₂: 2065, 2039, 2004, 1820, 1792.

Synthesis of 3: To a solution of $[Bu_4N][Ir_4(CO)_{11}Br]$ (50 mg, 0.036 mmol) in 30 mL toluene (Aldrich, anhydrous), L (100 mg, 0.103 mmol) is added. The solution is stirred at 70 °C for 72 h. The solvent is evaporated, and the residue is dried under vacuum. The residue is separated via coloumn chromatography (300 x 40 mm, silicaflash, dichloromethane : hexane = 1 : 4). The first fraction to elute consists of 3. (yield: 129 mg, 91 %). Single crystals were grown from a chloroform solution layered with methanol. ³¹P{¹H}-NMR: δ 18.24 (s, 2P, equatorial), -9.59 (s, 1P, axial), ESI MS (+) m/z 3940.9 [M]. IR (cm⁻¹) in CH₂Cl₂: 2038, 2000, 1988, 1787, 1771.

Attempt to synthesize 4: In a high pressure glass tube, $Ir_4(CO)_{12}$ (50 mg 0.045 mmol) is suspended in 10 mL toluene, and L (175 mg, 0.180 mmol) was added. The vessel is then sealed and the solution is stirred at 120 °C for 20 h. The solution is evaporated, and the solid residue is dried under vacuum. The residue is separated via coloumn chromatography (300 x 40 mm, silicaflash, dichloromethane : hexane = 1 : 5). The first fraction is **3**, and the second fraction is characterized as follows: (yield: 20 mg). ³¹P{¹H}-NMR: δ 19.13 (d, 1P, equatorial, ³J_{PP} = 42.1 Hz), 18.00 (m, 1P, equatorial), -5.28 (d, 1P, apical, ³J_{PP} = 42.1 Hz), -10.89 (s, 1P, axial) , ESI MS (+) m/z 4886.3 [M]. IR (cm⁻¹) in CH₂Cl₂: 2037, 1997, 1986, 1788, 1774.

³¹P-NMR spectrum of the attempted synthesis of 4 (see manuscript): The spectrum is complex, exhibiting a multiplet at 18.5 ppm, a doublet at -5.2 ppm, and a singlet at -10.9ppm (intensity ratio of 2.0:0.9:1.3). These data are consistent with two equatoriallybound ligands, one axially-bound ligand, and one that is bound in an apical position. Such an apical-bound phosphine ligand has been previously observed for all tetrasubstituted Ir₄ clusters that have been characterized via single-crystal X-ray diffraction²⁻⁵. This compound is different from other clusters in the series 1 - 3 because it contains ³¹P NMR resonances different from singlets. A two-dimensional homonuclear ³¹P-COSY experiment shows remote phosphorus-phosphorus coupling through three bonds involving the equatorial and apical bound phosphine ligands with a coupling constant ³J_{P-P} = 42.1 Hz. Thermal decomposition, aggregation, and CO readsorption: 2 mL of a solution of 1 - 3, as well as 1' and 3' in toluene-d8 (2.7 µmol/mL) are filtered through 0.02 micron filters and heated in high pressure glas tubes for 1 h at each temperature in the series 75, 95, 115, 135, and 155 °C. It is subsequently cooled down with water ice. Between each heating step, FTIR and NMR spectra are recorded. DLS measurements are performed for all samples before treatment, after 115 °C, and for 3, after 135 °C. The CO readsorption of clusters is performed in a glass tube that contains 2 mL of toluene solution consisting of thermally treated 1, 1', 3, and 3' (2.7 µmol / mL). The gas-phase head space in the glass tube is flushed with pure CO gas and held at a constant pressure of 1.2 atm. This CO pressure is maintained for a period of 72 h for equilibration.

Analytical section

³¹P{¹H}-NMR spectra are recorded in CDCl₃ (293 K), using either a Bruker AV-300 (300 MHz) instrument, an AVB-400 (400 MHz), or an DRX-500 (500 Mhz) instrument at the UC Berkeley College of Chemistry NMR Facility. ³¹P NMR data are referenced relative to trimethyl phosphate. For the chemical decomposition study, ¹H-NMR spectra are recorded in either chloroform-d or toluene-d8 (293 K). The data are referenced to Tetramethylsilane ($\delta = 0$ ppm). ESI-MS spectra were obtained using a Waters Q-TOF mass spectrometer equipped with a Z-spray source. The source temperature was kept at 80 °C, capillary voltage at 3.6 kV and the cone voltage at 43 V. 50 µM sample solutions in a mixture of dichloromethane and acetonitrile (1:9) were directly infused at 5 μ L/min Infra red spectroscopy is performed on an either a Bruker Tensor 27 or a Thermo scientific Nicolet 6700 FTIR spectrometer using a liquid cell (CaF₂ windows, d = 0.5 mm). DLS measurements are conducted using a Viscotek 802 DLS equipped with a 50 mW fiber coupled diode laser (λ° = 830 nm). The scattering data are collected at a set angle of 90 $^{\circ}$ on a single photon counting detector module. Approximately 12 μ L are used for each sample in a 1.5 mm Hellma cuvette. Data are collected over a period of 160-180 s at a constant temperature of 20 °C. OmniSIZE 3.0 software is used to analyze the scattering data for intensity and number distribution.

Vibrational calculations

DFT calculations are performed using the Gaussian 09 suite of ab initio programs at the b3lyp functional⁶ with the basis set $6-31G(d, p)^7$ for H, C, P, and O atoms and the Stuttgart fully relativistic effect core potential (ECP) basis set for Ir atoms. Integration is performed using an ultrafine grid. For frequency calculations, structure optimization is performed using a harmonic approximation. No solvent model is used. The vibrational frequencies are normalized using a previously described method.⁸

X-ray structure determination for 3



A vellow block 0.15 x 0.12 x 0.06 mm in size is mounted on a Cryoloop with Paratone oil. Data are collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance is 100 mm, and exposure time is 30 seconds per frame using a scan width of 0.5° . Data collection is 99.7% complete to 25.00° in θ . A total of 167022 reflections are collected covering the indices, $-14 \le h \le 14$, $-93 \le k \le 93$, - $25 \le l \le 25$. 37037 reflections are found to be symmetry independent, with an R_{int} of 0.1232. Indexing and unit cell refinement indicate a primitive, monoclinic lattice. The space group is found to be P2(1)/c (No. 14). The data are integrated using the Bruker SAINT⁹ software program and scaled using the SADABS¹⁰ software program. Solution by direct methods $(SIR-2008)^{11}$ produces a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms are refined anisotropically by full-matrix least-squares (SHELXL-97)¹². All hydrogen atoms are placed using a riding model. Their positions are constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. CCDC 844365 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Empirical formula	C210 H258 Cl9 Ir4 O21 P3	
Formula weight	4298.92	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.4374(3) Å	$\alpha = 90^{\circ}$.
	b = 77.8314(17) Å	$\beta = 99.6140(10)^{\circ}.$
	c = 21.2377(5) Å	$\gamma = 90^{\circ}.$
Volume	20269.8(8) Å ³	
Z	4	
Density (calculated)	1.409 Mg/m ³	
Absorption coefficient	2.822 mm ⁻¹	
F(000)	8768	
Crystal size	0.15 x 0.12 x 0.06 mm ³	
Crystal color/habit	yellow block	
Theta range for data collection	1.10 to 25.38°.	
Index ranges	-14<=h<=14, -93<=k<=93, -25<=l<=25	
Reflections collected	167022	
Independent reflections	37037 [R(int) = 0.1232]	
Completeness to theta = 25.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8489 and 0.6769	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	37037 / 0 / 2212	
Goodness-of-fit on F ²	1.011	
Final R indices [I>2sigma(I)]	R1 = 0.0625, wR2 = 0.0977	
R indices (all data)	R1 = 0.1090, wR2 = 0.1119	
Largest diff. peak and hole	1.423 and -1.758 e.Å ⁻³	

CIF files with crystallographic details have been submitted to the Cambridge structural database.

X-ray structure determination for 1



A yellow prism 0.12 x 0.10 x 0.08 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of 0.5° . Data collection was 99.8% complete to 25.00° in θ . A total of 183671 reflections were collected covering the indices, -17 <=h <=17, -18 <=k <=18, - $21 \le l \le 21$. 13544 reflections were found to be symmetry independent, with an R_{int} of 0.0319. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be P-1 (No. 2). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SIR-2008) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. CCDC 844364 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Empirical formula	C77 H85 Ir4 O15 P	
Formula weight	2050.22	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.9110(7) Å	α= 74.746(2)°.
	b = 15.6376(7) Å	β= 69.633(2)°.
	c = 17.6075(8) Å	$\gamma = 80.528(2)^{\circ}.$
Volume	3701.2(3) Å ³	
Z	2	
Density (calculated)	1.840 Mg/m ³	
Absorption coefficient	7.254 mm ⁻¹	
F(000)	1980	
Crystal size	0.12 x 0.10 x 0.08 mm ³	
Crystal color/habit	yellow prism	
Theta range for data collection	1.60 to 25.39°.	
Index ranges	-17<=h<=17, -18<=k<=18, -21<=l<=21	
Reflections collected	183671	
Independent reflections	13544 [R(int) = 0.0319]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5946 and 0.4765	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13544 / 0 / 888	
Goodness-of-fit on F ²	1.080	
Final R indices [I>2sigma(I)]	R1 = 0.0165, wR2 = 0.0396	
R indices (all data)	R1 = 0.0187, wR2 = 0.0411	
Largest diff. peak and hole	1.831 and -1.698 e.Å ⁻³	



Structure of **3** derived from single-crystal X-ray diffraction.



Intermolecular interaction between the axial phosphine ligand (A) and a neighbor calixarene ligand (B). The close proximity of the phenyl group in (A) to the calixarene

substituents in (B) results in asymmetry and the chiral cluster structure observed via single-crystal X-ray diffraction.



ESI mass spectrum showing the Cs adduct of $[2Cs]^+$



ESI mass spectrum showing the cation of $[3]^{+}$



ESI mass spectrum of the fraction isolated during the attempt to synthesize 4. The data matches perfectly with the radical cation $[4]^{+}$



¹H NMR spectrum of **2** in CDCl₃ at room temperature.



³¹P-NMR spectrum of **2** in CDCl₃ at room temperature.



¹H-NMR spectrum of **3** in CDCl₃ at room temperature.



³¹P-NMR spectrum of **3** in CDCl₃ at room temperature.



¹H-NMR spectrum (in CDCl₃ at room temperature) of the fraction isolated during the attempt to synthesize 4.



³¹P-NMR spectrum (in CDCl₃ at room temperature) of the fraction isolated during the attempt to synthesize **4**.



 $^{31}P{^{1}H}$ -NMR COSY spectrum of the fraction isolated during the attempt to synthesize 4.



¹H-NMR spectra in toluene-d8 of $\mathbf{1}$ after thermal treatment



¹H-NMR spectra of $\mathbf{2}$ in toluene-d8 after thermal treatment



¹H-NMR spectra of **3** in toluene-d8 after thermal treatment

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