Electronic Supplementary Information for Dalton Transactions

Supporting information

On the nature of the transition metal-main group metal bond: Synthesis and theoretical calculations on iridium gallyl complexes

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I. Experimental Data

I.1. General Considerations

All experiments were performed under an atmosphere of dry argon using standard Schlenk and glove box techniques. Toluene and hexane were purified and dried either by passing through an activated alumina purification system (MBraun SPS-800) or distilled over Na/benzophenone. Complex **1** was prepared according to published procedures.[1] Trimethylgallium was obtained commercially (Strem) and used without further purification. Benzene-d_6 was dried over potassium, stored onto molecular sieves and degassed prior to use. NMR samples were prepared under an argon atmosphere in tubes fitted with teflon Young's taps. Nuclear magnetic resonance spectra were recorded either on a Varian Gemini 200 MHz or a Varian Unity Inova 400 MHz. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. Coupling constants are expressed in hertz. The following abbreviations are used: Me, methyl; Cy, cyclohexyl; br, broad; *v*t, virtual triplet; s, singlet; d, doublet; t, triplet; m, multiplet. Infrared spectra were recorded in KBr using a Bruker Vector 22 instrument. Elemental analyses were performed with a Vario EL III Elementar Analyzer.

I.2. Single crystal X-ray analysis

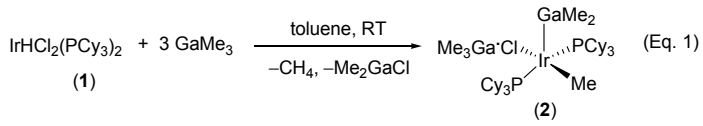
A crystal of **2** was mounted directly from solution under argon using inert oil to avoid contact with atmospheric oxygen and moisture. X–ray intensity data were collected using the program SMART[2] on a Bruker-Axs Apex CCD diffractometer with monochromatic MoKα radiation (λ = 0.71073 Å). Cell refinement and data reduction were carried out with the use of the program SAINT, the program SADABS was employed to make incident beam, decay and absorption corrections in the SAINT-Plus v. 6.0 suite.[3] The

structures were solved by direct methods with the program SHELXS and refined by full-matrix least-squares techniques with SHELXL in the SHELXTL v. 6.1 suite.[4] The final models involved anisotropic displacement parameters for all non-hydrogen atoms.

References:

1. Brinkmann, S.; Morris, R. H.; Ramachandran, R.; Park, S. *Inorg. Synth.,* **1998**, *32*, 303.
2. G. M. Sheldrick, SMART Bruker AXS, Inc., Madison, WI, USA, 2000.
3. G. M. Sheldrick, SAINT-PLUS 6.0, Bruker AXS, Inc., Madison, WI, USA, 2000.
4. G. M. Sheldrick, SHELXTL 6.10, Bruker AXS, Madison, WI, USA, 2000.

I.3. Synthesis of $MeIr(Cl{\cdot}GaMe_3)(GaMe_2)(PCy_3)_2]$, 2

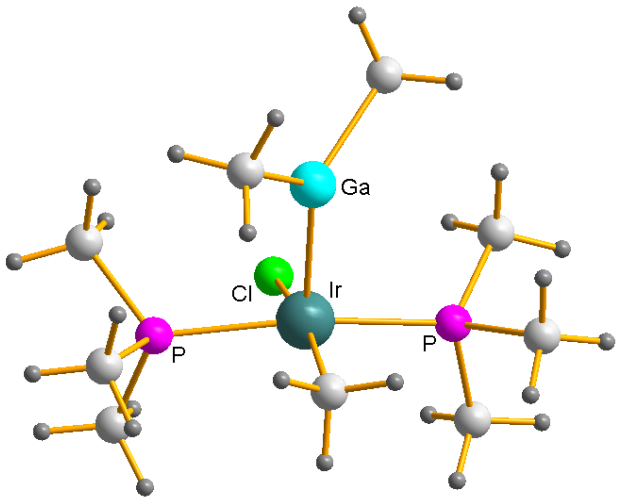


Equation 1. Synthesis of **2**

1 (500 mg, 0.61 mmol) was introduced into a specially designed cell consisting of a 20 ml glass bulb fitted to a 10 mm pathlength quartz cuvette and Young's stopcock. Toluene (5 mL) was added in the glove box under argon. To this mixture, a solution of 3 equivalent of $GaMe_3$ (210 mg, 1.83 mmol) in toluene (1 mL) was added while stirring. The purple-red color of the initial suspension slowly turned red. The evolved gas was identified by means of FTIR spectroscopy through the quartz cuvette. The FTIR spectrum showed after *ca*. three hours the bands corresponding to methane gas. After twelve hours of reaction the reaction mixture was a homogeneous solution. The volume was reduced and the solution stored at −35ºC. The crystals were filtered, washed with cold hexane (2 x 2 mL), dried under vacuum, and isolated in 93% yield as a bright red crystalline powder (577 mg). The purity of the product was

verified by elemental analysis. Bright-red X-Ray diffraction quality crystals were obtained from concentrated toluene solutions. Crystals of **2** redissolved in benzene-d_6 or toluene-d_8 start decomposition within a few hours, however, *in situ* generated **2** (in the presence of Me_2GaCl and CH_4) is stable over a period of months. ^{1}H NMR (400 MHz, 293 K, C_6D_6): δ = 0.18 (br s, $w_{1/2}$ Hz, 9H, Ga*Me*$_3$), 0.67 (br s, $w_{1/2}$ Hz, 6H, Ga*Me*$_2$), 1.18-2.00 (60 H, Cy), 1.23 (overlapped, *CH*$_3$-Ir), 2.78 (*v*t, 6H, P-C*H*); ^{13}C{^{1}H} NMR (100.58 MHz, 293 K, C_6D_6): δ = –25.52 (s, Ir-*C*), 0.96 (s, Ga*Me*$_3$), 5.40 (br, Ga*Me*$_2$); ^{31}P{^{1}H} NMR (80.96 MHz, 293 K, C_6D_6): δ = 29.0 ppm (s). Elemental analysis: Calculated for $C_{42}H_{84}ClGa_2P_2Ir$: C, 49.59; H, 8.33; Found: C,49.93; H, 8.52.

II. Cartesian coordinates of the theoretical model $MeIrCl(GaMe_2)(PMe_3)_2$.



Theoretical model used for ZORA-BP86/TZ2P calculations. Selected bond lenghts (Ă) and angles (º): Ga–Ir 2.4692; Ga–C 2.0925, 2.0950; Ir–C 2.1172; Ir–P 2.3248, 2.3206; Ir–Cl 2.4632; C–Ga–C 116.81; C–Ga–Ir 122.41, 120.75; C–Ir–P 91.67, 92.52; C–Ir–Ga 87.50; P–Ir–Ga 94.09, 96.76.

P	2.267275	-0.735255	-0.030485
Ir	-0.023871	-0.403532	-0.191383

P	-2.344062	-0.527603	-0.269873
Ga	0.124345	2.032470	0.183676
C	-1.163137	2.988152	1.528199
C	1.563827	3.228151	-0.758293
H	-0.682255	3.907491	1.886088
H	-2.099606	3.257339	1.020692
H	-1.386647	2.328725	2.373576
H	1.237149	4.275752	-0.737112
H	2.519952	3.152557	-0.222229
H	1.713781	2.909303	-1.796267
Cl	-0.174074	-1.492343	2.013017
C	0.117721	0.000879	-2.264795
H	-0.736562	0.540364	-2.699609
H	1.017711	0.556833	-2.564141
H	0.164891	-0.981979	-2.773440
C	3.425122	-0.125561	-1.333978
H	3.138682	-0.535306	-2.311385
H	3.385279	0.970037	-1.391595
H	4.452198	-0.438411	-1.099445
C	3.100073	-0.173458	1.514758
H	4.128034	-0.559935	1.566280
H	3.127399	0.924561	1.545146
H	2.514522	-0.539540	2.368616
C	2.636946	-2.544428	-0.021481
H	2.290475	-2.997807	-0.960275
H	3.716427	-2.722476	0.089695
H	2.091681	-3.001394	0.814832
C	-3.290289	-0.095182	1.248503
H	-2.830902	-0.618680	2.097216
H	-3.229502	0.985813	1.427221
H	-4.343718	-0.390460	1.141753
C	-2.841739	-2.287135	-0.536117
H	-3.936882	-2.387098	-0.547206

H	-2.435672	-2.648813	-1.490589
H	-2.422357	-2.891401	0.279425
C	-3.320751	0.336165	-1.580740
H	-4.385101	0.076894	-1.491204
H	-3.208558	1.424170	-1.477531
H	-2.962243	0.042705	-2.575827