Supplementary Material (ESI) for Dalton Transactions

Well-defined indium(III) *N*-heterocyclic carbene complexes with triflate ligands: Structural models for the $In(OTf)_3$ catalyst

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Supporting Information

Experimental data for the new complexes **1** to **4**
DFT calculations on **1**

(IMes)InMe$_2$Cl, (1): A Schlenk was charged with $InMe_3$ (387mg, 2.42mmol) and iMes-Cl (750mg, 2.20mmol). Toluene (20ml) was added by cannula at ambient temperature and the reaction was stirred for 3hrs. NMR spectroscopy (^{1}H) demonstrated that the reaction was essentially quantitative (> 95%). The solvent volume was reduced to half volume and stored at 277K overnight to yield a batch of clear and colourless crystals (885mg, 83%); *NMR* (CD_2Cl_2): ^{1}H (400MHz): 7.19 (2H, s, olefin), 7.05 (4H, s, aromatic), 2.37 (6H, s, CH_3), 2.12 (12H, s, CH_3), -1.03 (6H, s, In-CH_3). ^{13}C{^{1}H}(75.5MHz): 177.5, 140.5, 136.0, 134.9, 129.8, 124.3, 21.4, 18.0, -8.1. Elemental analysis: calcd (%) for $C_{23}H_{30}ClInN_2$: C 56.99, H 6.24, N 5.78; found C, 57.20; H, 6.21; N, 5.66.

(IMes)InMe$_2$OTf, (2): A Young's tube was charged with **1** (50mg, 0.11mmol) and CH_2Cl_2 (5ml) added via cannula. TMSOTf (20 μl, 0.11mmol) was added via syringe at ambient temperature. The reaction mixture was stirred for 5 minutes. The solvent was removed in vacuo to yield a white solid. The compound was recrystallised from CH_2Cl_2 and hexane and stored at 253K overnight to yield a batch of clear and colourless crystals (41mg, 58%). *NMR* (CD_2Cl_2) δ^1H (400MHz): 7.29 (2H, s, olefin), 7.09 (4H, s, aromatic), 2.39 (6H, s, CH_3), 2.09 (12H, s, CH_3), -0.80 (6H, s, In-CH_3); δ^{13}C{^{1}H} (75.5MHz): 176.2, 141.0, 135.7, 134.4, 130.0, 124.9, 120.1 (319Hz, q, CF_3), 21.4, 17.6, -7.1; δ^{19}F (376.5MHz): -78.7. Elemental analysis: calcd (%) for $C_{24}H_{30}F_3InN_2O_3S$ with one molecule CH_2Cl_2: C 43.94, H 4.72, N 4.10; found C, 45.60 H, 4.95 N, 4.33

(IMes)InMe(OTf)$_2$ (3): A Young's tube was charged with **1** (50mg, 0.10mmol) and CH_2Cl_2 (5ml) was added via cannula. TMS-OTf (19μl, 0.10mmol) was added via syringe at ambient temperature and the reaction mixture was stirred for 5 minutes. HOTf (9μl, 0.10mmol) was then added via syringe. Gas evolution was observed and the reaction mixture was stirred for a further 5mins. Solvent was removed in vacuo to yield a white solid. The compound was recrystallised from CH_2Cl_2 and hexane and stored at 253K overnight to yield a batch of clear and colourless crystals (45mg, 60%). *NMR* (CD_2Cl_2): δ^1H (400MHz): 7.39 (2H, s, olefin), 7.10 (4H, s, aromatic), 2.39 (6H, s, CH_3), 2.13 (12H, s, CH_3), -0.41 (3H, s, In-CH_3); δ^{13}C{^{1}H} (75.5MHz): δ = 168.7, 142.1, 135.6, 132.8, 130.4, 126.3, 119.3 (318Hz, q, CF_3), 21.4, 17.7, -5.0; δ^{19}F (376.5MHz) δ = –77.8; microanalytical data, calculated: C, 39.36; H, 3.72; N, 3.82; experimental: C, 39.20; H, 4.04; N, 3.79

Cartesian Coordinates for **1** optimised at the B3LYP/LAN2DZ level.

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C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.413153
C	1.196656	0.000000	2.168245
C	2.417430	-0.004009	1.470575
C	2.465547	-0.013518	0.060051
C	1.251207	-0.006467	-0.652713
N	-1.270723	0.048029	2.119148
C	-1.921467	1.257313	2.416821
C	-3.074804	0.930965	3.078697
N	-3.104287	-0.470788	3.171311
C	-1.991684	-1.037310	2.579040
C	-4.192469	-1.187393	3.817432
C	-5.342485	-1.512811	3.063337
C	-6.395057	-2.174676	3.730714
C	-6.320902	-2.507640	5.096883
C	-5.156958	-2.154701	5.812805
C	-4.079299	-1.497314	5.193413
C	-5.454253	-1.190694	1.585876
C	-2.829551	-1.159319	5.984300
C	-7.457347	-3.239375	5.786521
In	-1.543789	-3.276171	2.257805
C	0.555704	-3.574760	1.891563
C	1.179281	-0.018945	3.685138
C	3.798117	-0.043247	-0.665153
C	-1.284653	-0.012499	-0.805150
C	-2.603366	-4.475203	3.696485
Cl	-2.767168	-3.378477	0.061097
H	-3.860405	1.547869	3.482214
H	-1.511374	2.212539	2.134106
H	1.155009	-3.456762	2.806828
H	0.942595	-2.887304	1.129973
H	0.698341	-4.601970	1.526417
H	-2.557827	-5.523721	3.368871
H	-3.659135	-4.190246	3.775895
H	-2.147971	-4.414979	4.696435
H	3.346805	-0.010150	2.036945
H	1.270853	-0.013384	-1.740244
H	-5.083009	-2.405209	6.869384
H	-7.285456	-2.439148	3.164673
H	3.671902	0.100455	-1.743762
H	4.472820	0.739775	-0.295008
H	4.304541	-1.006795	-0.515277
H	-8.338323	-3.313969	5.139775
H	-7.157703	-4.260741	6.059171
H	-7.757738	-2.730643	6.711915
H	2.189627	0.116233	4.084670
H	0.541758	0.771485	4.101335
H	0.797052	-0.976748	4.062659
H	-1.073159	0.152905	-1.866789
H	-1.800457	-0.978049	-0.711919
H	-1.985374	0.765170	-0.474733
H	-2.987887	-1.339502	7.052579
H	-1.981621	-1.779592	5.664118
H	-2.530623	-0.111070	5.857870
H	-6.476703	-1.361409	1.232969
H	-5.191762	-0.146932	1.370631
H	-4.782480	-1.825070	0.991423