Supplementary Material (ESI) for Dalton Transactions

Supporting Material for:

Cationic Organozinc Complexes of a New *bis*(phosphinimine) Pincer Ligand: Synthesis and Structural Studies

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[4,6-(Mes-NPPh$_2$)$_2$dibenzofuran·ZnMe]$^+$[BPh$_4$]$^-$, 2b

Crystals of **2b** were grown by slow cooling of a solution of the compound in a mixture of benzene and bromobenzene from 70 °C to ambient temperature. The reflection data were consistent with the space group P(-1), and the structure was determined at a resolution of 0.84 Å. The asymmetric unit contained a single molecule of the compound. Most atoms are well ordered, with the exception of the methyl group on the zinc centre, which is disordered over two sites at a ratio of 70:30, and the nearest neighboring phenyl ring of the tetraphenylborate anion, which exhibits a concomitant two site disorder. The unit cell contains total solvent accessible voids of 255 Å^3 (7.6% of the unit cell), and accounting for this using the SQUEEZE subroutine of the PLATON software suite gave improved residuals. A total of 37 electrons were removed, and are assigned to 0.88 molecules of benzene (0.44 per molecules of benzene per asymmetric unit). The SQUEEZE processed data were used for all subsequent refinement cycles. The largest residual electron density peak (0.557 eÅ^{-3}) is associated with the disordered methyl group. Full-matrix least squares refinement on F^2 gave R_1 = 0.0656 for 2σ data and wR_2 = 0.1777 for all data (GoF = 1.021).

[4,6-(Mes-NPPh$_2$)$_2$dibenzofuran-ZnOAc]$^+$[BPh$_4$]$^-$, 3.

Crystals of **3** were grown by slow cooling a solution of the compound in a benzene/bromobenzene mixture from 100 °C to ambient temperature. The reflection data were consistent with the space group P2(1)/c, and was determined at a resolution of 0.84 Å. The asymmetric unit contained a single molecule of the compound. All non-solvent atoms in the unit cell are well ordered and have been refined anisotropically. Solvent accessible voids in the unit cell were accounted for using the SQUEEZE subroutine of the PLATON software suite, giving improved residuals. A total of 160 electrons were removed from a volume of 986 Å^3 (13.1% of the unit cell). These electrons have been assigned to 3.8 molecules of benzene (0.95 molecules of benzene per asymmetric unit). SQUEEZE processed data were used for all subsequent refinement cycles. The largest residual electron density peak (0.880 eÅ^{-3}) is associated with a molecule of benzene. Full-matrix least squares refinement on F^2 gave R_1 = 0.0620 for 2σ data and wR_2 = 0.1544 for all data (GoF = 1.019).

[4,6-(Ph-NPPh$_2$)$_2$dibenzofuran-ZnPh]$^+$[BPh$_4$]$^-$, 4.

Crystals of **4** were grown at ambient temperature from a bromobenzene solution containing the compound. The reflection data were consistent with the space group P2(1)/c, and the structure was determined at a resolution of 0.84 Å. The asymmetric unit contains a single molecule of the compound and a single well ordered molecule of bromobenzene solvent. All atoms are well ordered and have been refined anisotropically. The unit cell contains

solvent accessible voids which were accounted for using the SQUEEZE subroutine of the PLATON software suite. A total of 142 electrons were removed from a volume of 646 $Å^3$ (8.5% of the unit cell). These electrons are assigned to 1.9 molecules of bromobenzene (0.47 molecules of bromobenzene per asymmetric unit). The SQUEEZE processed data were used for all subsequent refinement cycles. The largest residual electron density peak (1.017 $eÅ^{-3}$) is associated with the phenyl substituent of zinc. Full-matrix least squares refinement on F^2 gave $R_1 = 0.0492$ for 2σ data and $wR_2 = 0.1410$ for all data (GoF = 1.051).

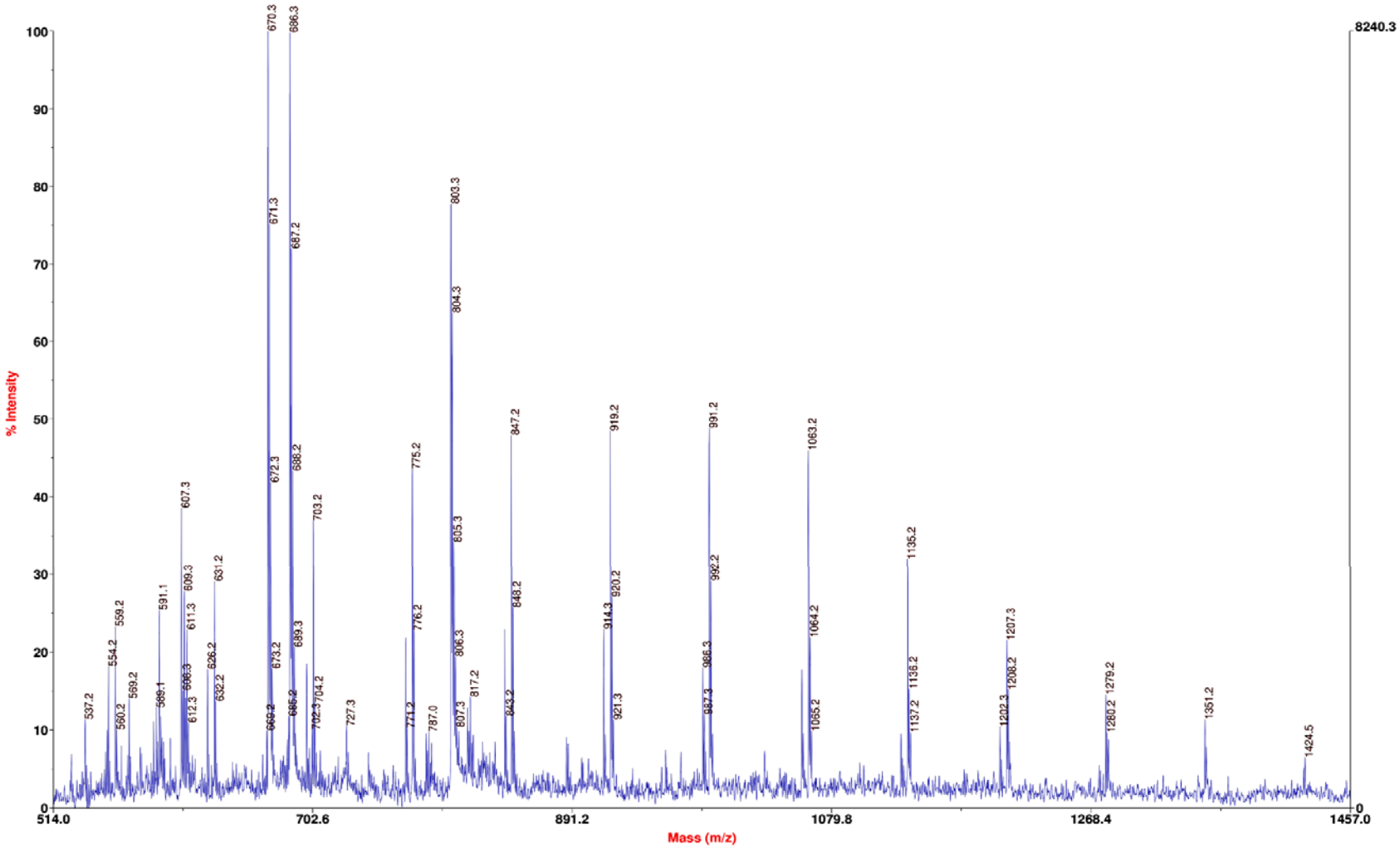


Figure 1. MALDI-TOF mass spectrum of polymer sample in the range m/z 514–1457.

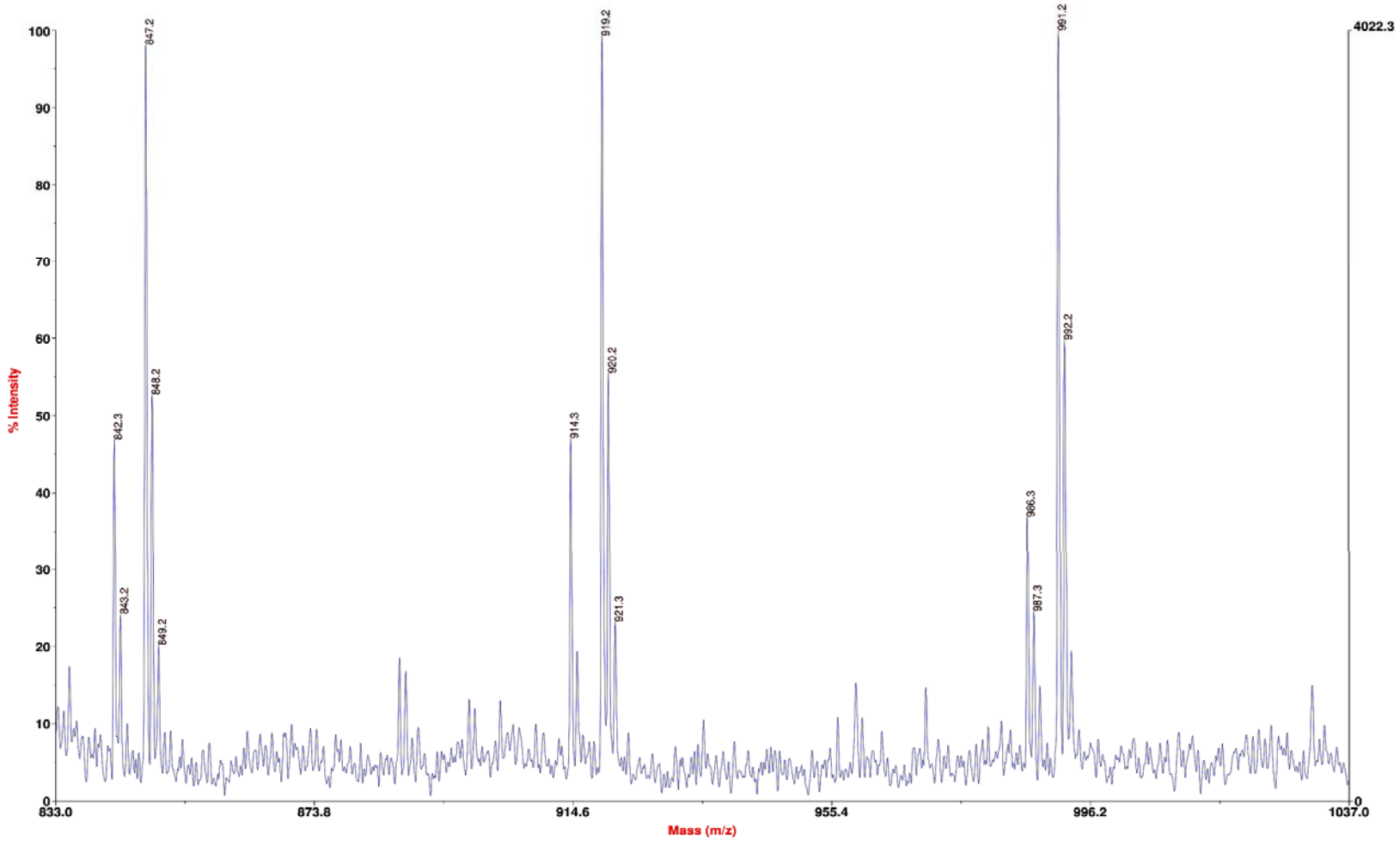
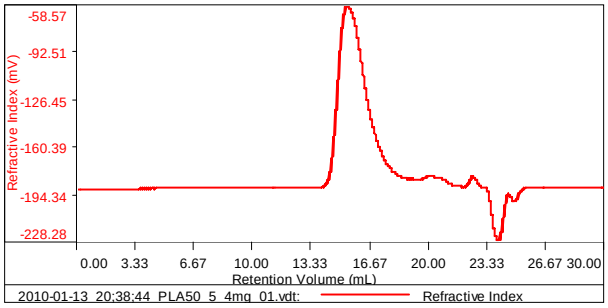


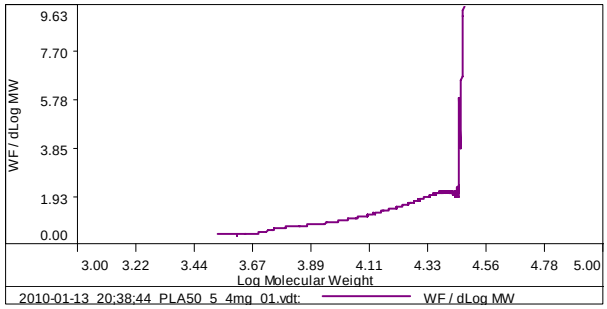
Figure 2. MALDI-TOF mass spectrum of polymer sample in the range m/z 833–1037.

PLA50 Injection volume 100ul

Sample	2010-01-13_20;38;44_PLA50_5_4mg_(
Mn	18,474
Mw	22,635
Mz	24,772
Mp	30,063
Mw/Mn	1.225
% Above	0.0000
% Below	0.0000
IV	0.3172
Rh	4.65
Rg	0.00
Wt Fr (Peak)	1.0000
MH - a	0.314
MH - k	-1.783
Bn	0.0000
Lambda	0.0000
Ave. dn/dc	0.0000
Ave. dA/dc	0.0000
Wt Fr (A)	0.0000
RI Area	250.85
UV Area	0.00
RALS Area	42.55
LALS Area	21.72
DP Area	203.27
Ret Vol	15.307
Ret Time	15.307
Above Mw	0
Below Mw	0
Peak Conc	1.0000
Pct Fr	0.0000
MW At Pct	0
Ret Vol DP	15.118
Rh-z	4.92

ID	PLA50 5_4mg
Conc	1.0000
Recovery	43.9324
dn/dc	0.2345
Method	Jan 11Sossina 5-0004.vcm





PLA50 Injection volume 90ul

Sample	2010-01-13_21;09;43_PLA50_5_4mg_I
Mn	17,693
Mw	22,541
Mz	24,775
Mp	30,095
Mw/Mn	1.274
% Above	0.0000
% Below	0.0000
IV	0.3200
Rh	4.65
Rg	0.00
Wt Fr (Peak)	1.0000
MH - a	0.107
MH - k	-0.890
Bn	0.0000
Lambda	0.0000
Ave. dn/dc	0.0000
Ave. dA/dc	0.0000
Wt Fr (A)	0.0000
RI Area	225.86
UV Area	0.00
RALS Area	38.09
LALS Area	19.41
DP Area	184.19
Ret Vol	15.287
Ret Time	15.287
Above Mw	0
Below Mw	0
Peak Conc	1.0000
Pct Fr	0.0000
MW At Pct	0
Ret Vol DP	15.115
Rh-z	4.92

ID	PLA50 5_4mg
Conc	1.0000
Recovery	43.9502
dn/dc	0.2345
Method	Jan 11Sossina 5-0004.vcm