Supporting Information for:

Arene substituted cyclopentadienyl complexes of Zr and Hf: preparation and evaluation as catalysts for ethylene trimerisation

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Attempted preparation of complex 1 via direct methods. Initial attempts to synthesise the catalysts of interest focussed on half-sandwich trichloride complexes. Reaction of $C_5H_4(SiMe_3)CMe_2Ph$ with a CH_2Cl_2 suspension of $ZrCl_4$ led to a dark brown powder after workup. Analysis by ^1H NMR spectroscopy showed two distinct sets of splitting for both the cyclopentadienyl protons and the bridging methyl protons, due to the formation of both the desired monocyclopentadienyl complex (**1**) and the zirconocene dichloride. This was confirmed by reference to the literature ^1H and ^{13}C NMR peak assignments for $[(\eta^5\text{-}C_5H_4CMe_2Ph)_2ZrCl_2]$.[1] Presumably, this mixture of compounds is a result of the insolubility of $ZrCl_4$, whereas complex **1** is highly soluble once formed and as such can react freely as more ligand is added. Efforts to tune the synthesis towards the monocyclopentadienyl complex, via modification of the temperature, varying the rate of ligand addition (dropwise over 12 hours), and solvent free reaction of the ligand with five equivalents of the metal chloride, all resulted in formation of a monocyclopentadienyl/metallocene mixture. The ratio of monocyclopentadienyl:metallocene, as judged by ^1H NMR integration of the methyl protons, altered depending upon the reaction conditions. While no formal kinetic study was undertaken, this confirms that formation of the mixture was under kinetic control, rather than through a process of thermodynamic equilibrium. Attempts to separate the mixtures by sublimation lead only to decomposition of the complexes, while attempts at recrystallisation in a wide variety of solvent mixtures were also unsuccessful due to the similar solubilities of the two compounds.

Attempts at preparation of **1** from more soluble $ZrCl_4$ adducts were likewise unsuccessful. As has been reported by Sassmannshausen and coworkers,[2] treatment of $ZrCl_4(DMS)_2$ with $C_5H_4(SiMe_3)CMe_2Ph$ led to no reaction. It has been reported that reaction of $Li[C_5H_4CMe_2Ph]$ with $ZrCl_4(THF)_2$ leads to **1**,[3] however in our hands this reaction yielded the zirconocene dichloride exclusively in all cases. Our analysis of the NMR data provided in this report suggests that this was also most likely the case in the original work.

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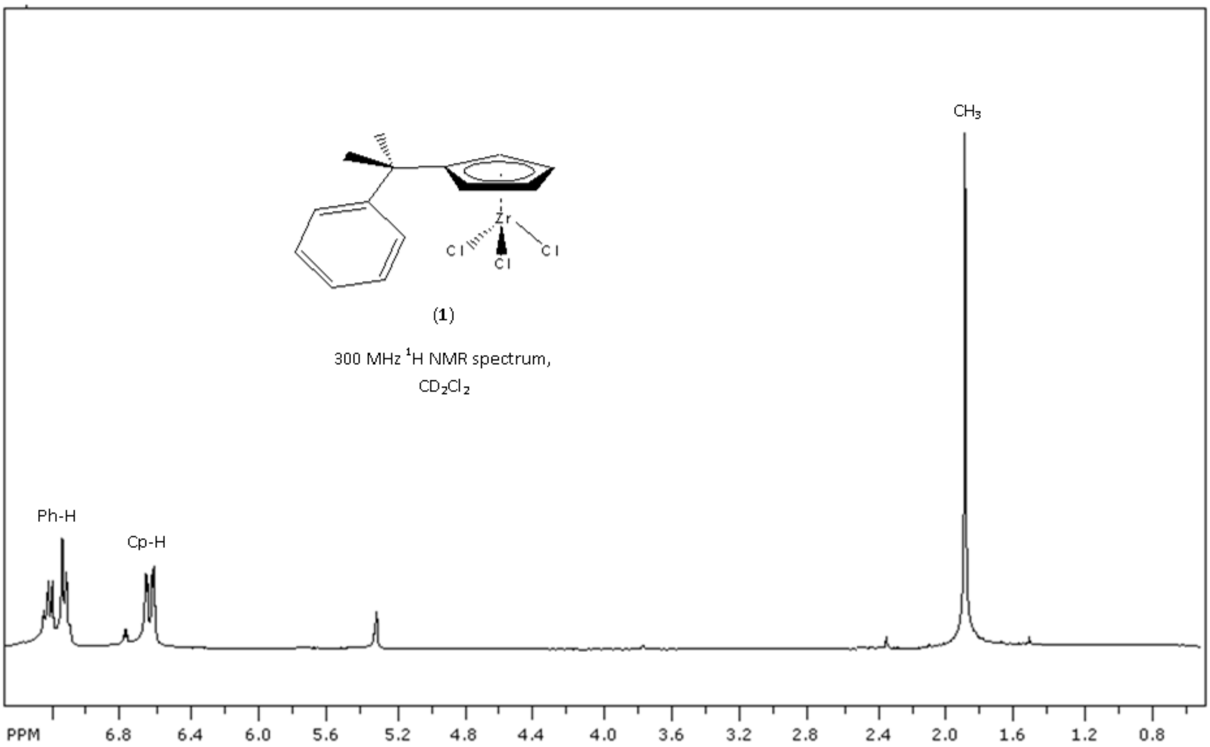
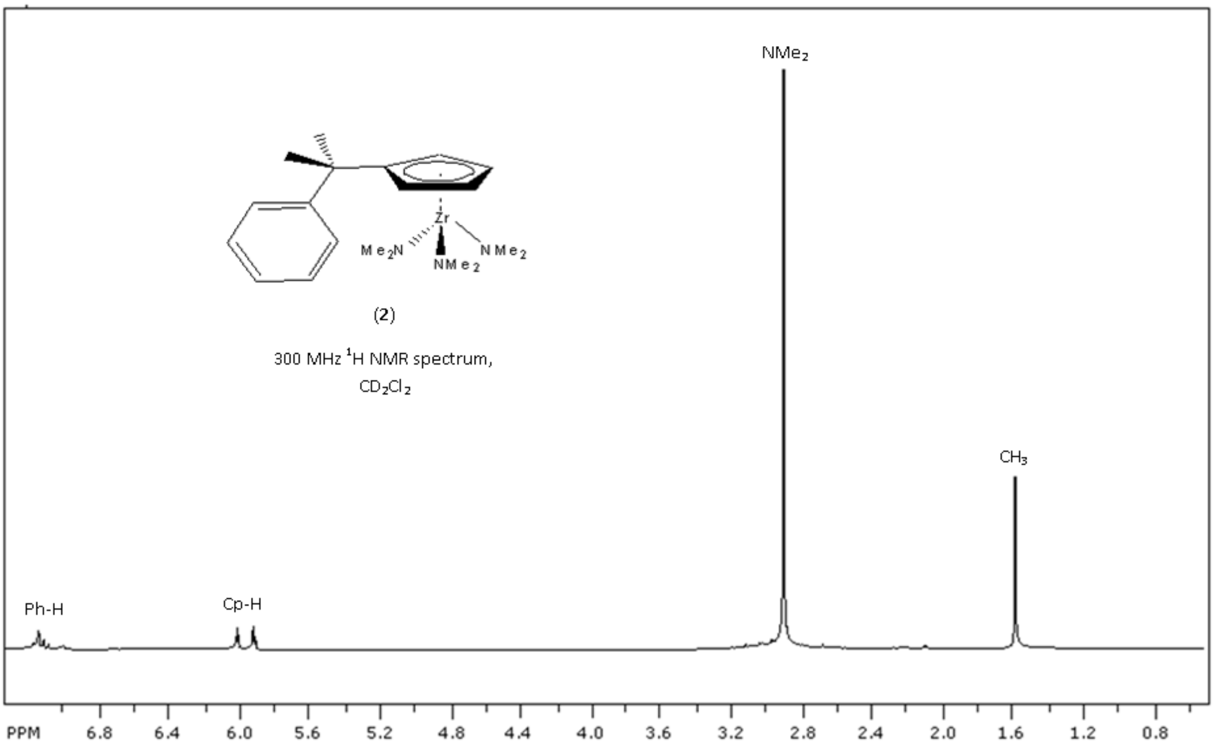
[1] E. H. Licht, H. G. Alt, and M. M. Karim, *J. Organomet. Chem*, 2000, 599, 275.

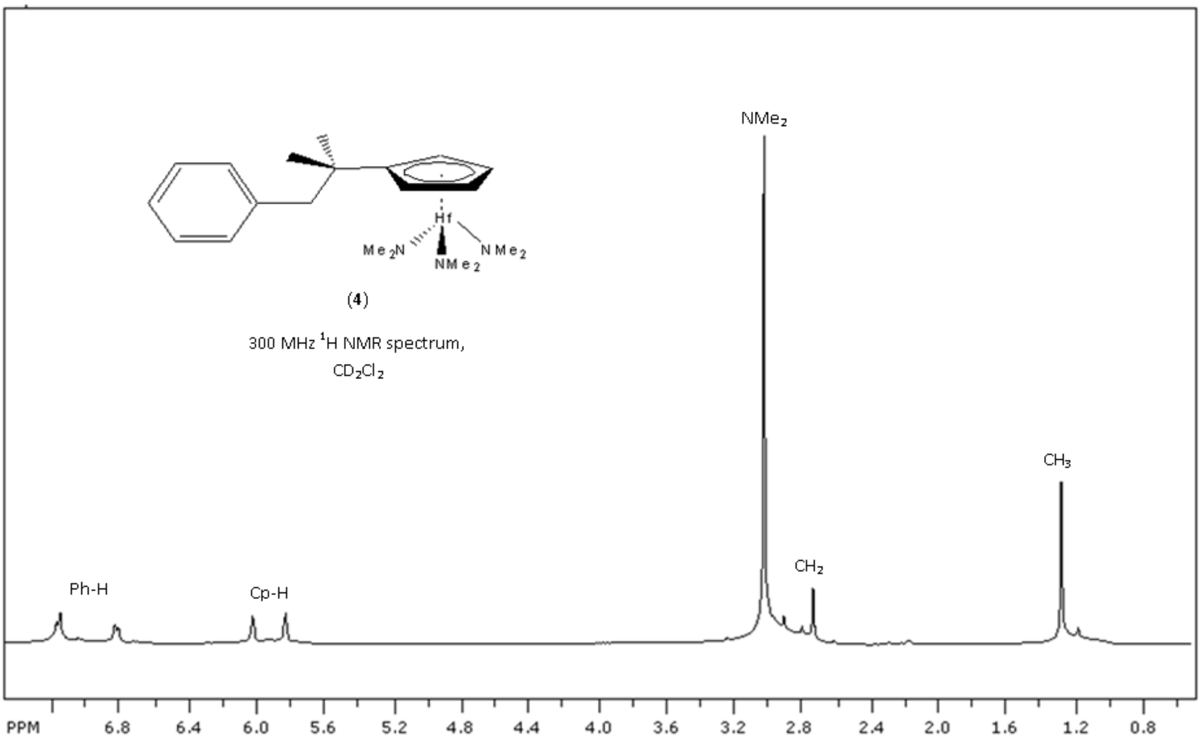
[2] J. Saβmannshausen, A. K. Powell, C. E. Anson, S. Wocadlo, and M. Bochmann, *J. Organomet. Chem*, 1999, 592, 84.

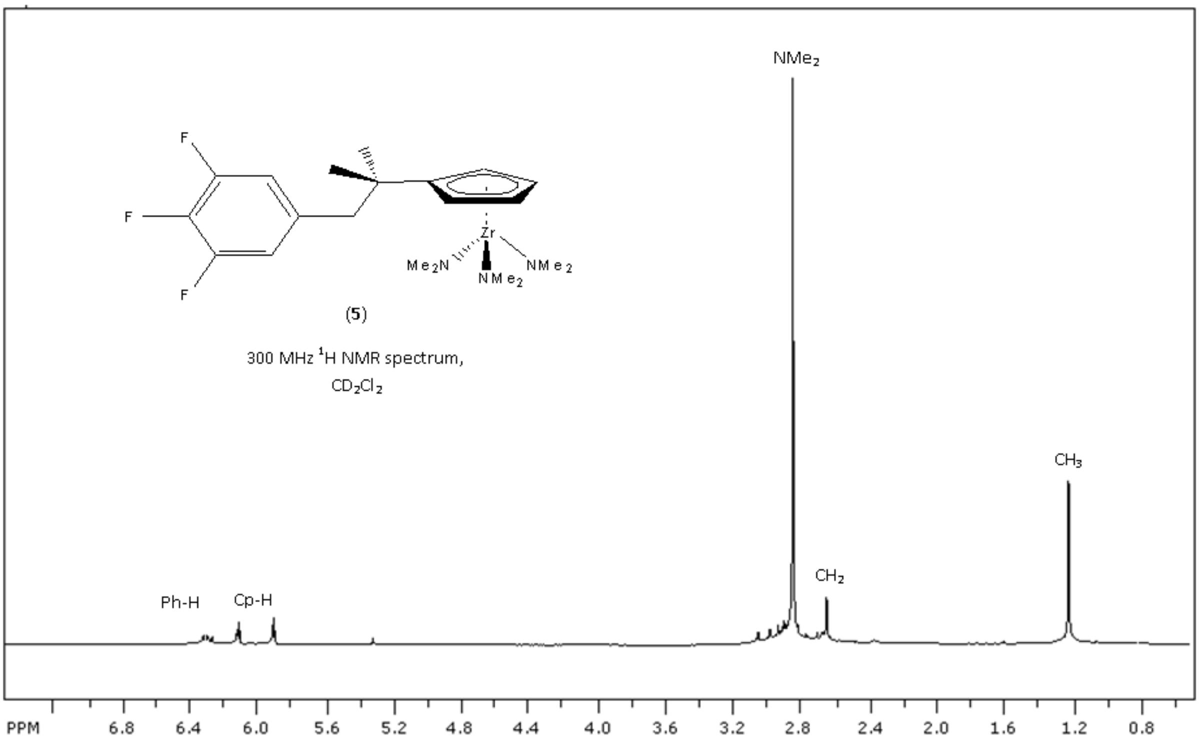
[3] P. Longo, A. G. Amendalo, E. Fortunato, A. Boccia, and A. Zambelli, *Macrol. Rapid Commun.*, 2001, 22, 339.

^{1}H NMR Spectra of Complexes 1, 2, 4 and 5






NMe$_2$
Hf
Me$_2$N
NMe$_2$
NMe$_2$
(4)
300 MHz ^{1}H NMR spectrum,
CD$_2$Cl$_2$
CH$_3$
CH$_2$
Ph-H
Cp-H
PPM
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8


NMe$_2$
F
F
F
Zr
Me$_2$N
NMe$_2$
NMe$_2$
(5)
300 MHz ^{1}H NMR spectrum,
CD$_2$Cl$_2$
CH$_3$
CH$_2$
Ph-H
Cp-H
PPM
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8