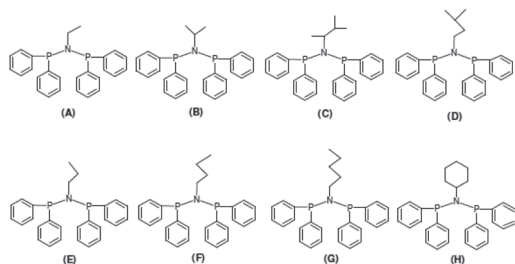


**MS27-01 Ethylene tetramerisation: link between catalyst precursor structure and catalysis** Nicoline Cloete,<sup>a</sup>
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Transition metal-catalyzed ethylene oligomerization typically produces a broad range of  $\alpha$ -olefins and the development of the technology for this selective production is an ongoing process [1]. The selective tetramerisation of ethylene to 1-octene is possible with the use of diphosphinoamine ligands together with chromium(III) and an aluminoxane activator as catalyst system [2]. The aim of this study was therefore to synthesize and characterise a range of diphosphinoamine (PNP) ligands with varying catalytic activity and selectivity (see Figure). The stereo-electronic properties of these ligands were evaluated by varying the alkyl group in a systematic way. The single crystal X-ray crystallographic study of the above-mentioned PNP ligands revealed a decreasing trend of the P-N-P bond angle to decrease as the steric bulk of the alkyl moiety increases. An important part of this investigation was concerned with the synthesis and evaluation of the solid state characteristics of the PNP ligands bonded to Cr(III). This was extended by complexing other metal cations (e.g. Pt(II) and Pd(II)) with the various PNP ligands in order to provide further information on the coordination mode of these ligands. A steric parameter was defined (Effective Tolman-based N-substituent steric effect ( $\theta_{N-sub}$ )) in which the steric bulk of the nitrogen-coordinated alkyl substituent was quantified. A comparison between  $\chi_{N-sub}$  for various diphosphinoamine ligands (free and metal-coordinated) and the catalytic selectivity (for 1-C6 and 1-C8) revealed a relatively good correlation with the catalytic selectivity increasing as  $\theta_{N-sub}$  for the varying ligands increased.



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**Keywords: ethylene oligomerisation; chromium(III)**

**MS27-02 The *trans*-Influence of the Boryl Ligand in Square-Planar Platinum(II) Complexes.** Peter Brenner,

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Transition-metal boryl complexes act as intermediates in important metal-catalysed functionalisations such as the hydro- and diboration of unsaturated organic compounds [1,2] and the selective activation of C–H-bonds of alkanes and arenes [3,4]. An important feature of the boryl ligand is its strong *trans*-influence, because it determines both the distance and the strengths of the bond between the metal and the ligand in *trans*-position [5]. In continuation of our work on boryl-platinum(II) complexes, we sought to determine to what extent the *trans*-influence of the boryl in such compounds could be fine-tuned by changing the substituents at boron. Square-planar boryl-platinum complexes can be synthesized through the oxidative addition of B–Hal bonds (Hal = F, Cl, Br, I) to [Pt(PR<sub>3</sub>)<sub>2</sub>] in high yields [5-8]. The molecular structures of all crystallographically characterized representatives display slightly distorted square-planar geometries and a *trans*-disposition of the phosphine ligands. The boryl moieties are oriented almost perpendicular to the PtP<sub>2</sub> plane and induce a strong *trans*-influence on the platinum-bound halide, as indicated by long Pt–Hal distances. The measurement of these distances in a series of such complexes allows an empirical assessment of the *trans*-influence of different boryl ligands. As a result of the *trans*-influence, the platinum-bound halide can easily be abstracted, resulting in T-shaped cationic complexes which were found to be reluctant to bind C–H bonds in the site *trans* to the boryl group [9], or substituted, resulting in, for example, unprecedented (alkyl)(boryl)complexes [10].

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**Keywords: platinum coordination compounds; boron compounds;**