

MS33-O4 Expanding the horizons of sky blue nitrosocarboranesGeorgina M. Rosair¹, Samuel L. Powley¹, Louise Schaefer¹, Wing Y. Man¹, David Ellis¹, Alan J. Welch¹

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Nitrosocarboranes are a beautiful sky blue colour in contrast to most other carborane derivatives which are colourless. However it is the ability of NO to act as both a one electron and three electron donor that inspires our use of this substituent. Since the number of polyhedral skeletal electron pairs has a key role in the structure of carboranes, NO with its one and three electron donor possibilities has potential to effect changes in carborane structure and chemistry. In this work [1] both mono and bis(carborane) nitroso species have been studied (see example below left). In all cases the nitroso group bonds to the carborane as a one electron substituent (C–N–O angle ca. 113 degrees). An unexpected challenge arose in that two of the species (e.g. Fig. 1 left) are liquid at room temperature so structure determinations were performed on crystals grown *in situ* on the diffractometer from liquid samples. Glass Lindemann 0.3mm capillaries are the only additional equipment required for a standard data collection (in addition to patience and manual dexterity).

Both mono- and dinitroso derivatives of *meta* carborane and 1,1'-bis(*m*-carborane) were synthesised and structurally characterised. However the mononitroso derivative of bis(*o*-carborane) could not be prepared by the same method, instead the colourless hydroxylamine derivative was formed. Reasons behind this were explored and identified. The dinitroso *ortho*-carborane and bis(*o*-carborane) species were also elusive with alternative products proposed. Another strategy was employed for these *ortho* compounds; since the NO group can undergo Diels-Alder cycloaddition reactions with a cyclic 1,3-diene, we prepared derivatives of the unobtainable dinitroso *ortho*-carborane and bis(*o*-carborane) (Fig. 1, right)

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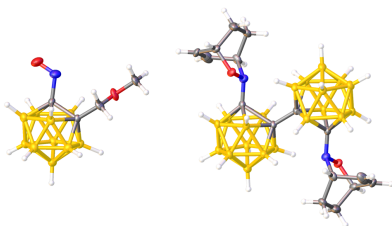


Figure 1. [1-NO-2-CH₂OCH₂-1,2-*closo*-C₂B₁₀H₁₀] (left) and isolated derivative of dinitroso bis(*o*-carborane) (right).

Keywords: Nitroso, carborane, in-situ crystallography

MS33-O5 Silolyl-FeCp complexes: is there a way to sila-ferrocene?Petra Bombicz¹, Csaba Fekete², Réka Mokrai², László Nyulászi², Ilona Kovács²

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One of the milestones in organometallic chemistry is the synthesis of ferrocene by Kealy and Pauson in 1951 [1,2] and the determination of its structure by Wilkinson and Woodward in 1952 [3]. These achievements opened up the way to the use of metallocenes in applied and material science from polymerization catalysis to UV fluorescent materials [2]. Nowadays several metallocenes are known in which not just the central iron atom is replaced by other transition metals but also the ligands are changed to heterocyclopentadienyl analogues containing other main group elements such as P, As or Sb [4,5]. Notwithstanding, the number of known metallocenes possessing silicon or germanium containing heterocycles is small.

The reaction of 1-chlorosilols and K[Fe(CO)₂Cp] in THF yielded two new η¹-silolyl-FeCp(CO)₂ complexes in good yield. We report the molecular and crystal structures of the complexes, and their attempted transformation (by heating or UV irradiation) to the metallocenes. The reason for the increased stability of these carbonyl complexes can be attributed to the increased σ-electron donating behaviour of the silicon to the central Fe, while the aromaticity of the silolyl ligand seems to have less influence [6].

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