Synthesis and Characterisation of 1,2-Diphosphino-\( \sigma \)-Carborane Metal Complexes

Sari Paavola

University of Helsinki
Faculty of Science
Department of Chemistry
Laboratory of Inorganic Chemistry

Academic Dissertation

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ABSTRACT

The aim of this work was to synthesise palladium(II) and platinum(II) complexes of 1,2-diphosphino-o-carboranes for use as polymerisation catalysts. The literature part of the thesis provides a general introduction to boranes and carboranes and reviews the existing methods for the synthesis of palladium(II) and platinum(II) complexes of 1,2-diphosphines.

Six novel 1,2-diphosphino-o-carborane complexes were synthesised and characterised: \([\text{PdCl}_2(1,2-(\text{P}^\text{iPr}_2)\text{C}_2\text{B}_{10}\text{H}_{10})]\), \([\text{PtCl}_2(1,2-(\text{P}^\text{iPr}_2)\text{C}_2\text{B}_{10}\text{H}_{10})]\), \([\text{PdClMe}(1,2-(\text{P}^\text{iPr}_2)\text{C}_2\text{B}_{10}\text{H}_{10})]\), \([\text{PdClMe}(1,2-(\text{PPh}_2)\text{C}_2\text{B}_{10}\text{H}_{10})]\) and a mixture of \([\text{PdBrMe}(1,2-(\text{PPh}_2)\text{C}_2\text{B}_{10}\text{H}_{10})]\) and \([\text{PdBrCl}(1,2-(\text{PPh}_2)\text{C}_2\text{B}_{10}\text{H}_{10})]\). As well, the structures of three previously known compounds, \(1,2-(\text{PPh}_2)\text{C}_2\text{B}_{10}\text{H}_{10}\), \([\text{PdCl}_2(1,2-(\text{PPh}_2)\text{C}_2\text{B}_{10}\text{H}_{10})]\) and \([\text{PdBr}_2(1,2-(\text{PPh}_2)\text{C}_2\text{B}_{10}\text{H}_{10})]\), and two partially disordered structures, \([\text{PdBr}_{1.133}\text{Cl}_{0.867}(1,2-(\text{PPh}_2)\text{C}_2\text{B}_{10}\text{H}_{10})]\) and \([\text{PdClMe}(1,2-(\text{PPh}_2)\text{C}_2\text{B}_{10}\text{H}_{10})]\), were solved. \(\text{PdCl}_2\) and \(\text{PdClMe}\) complexes were synthesised by the reaction of ligand with \([\text{PdCl}_2(\text{cod})]\) or \([\text{PdClMe}(\text{cod})]\). The \(\text{PtCl}_2\) complex was obtained from the corresponding reaction of the ligand with \([\text{PtCl}_2(\text{cod})]\). \(\text{PdClMe}\) complexes were also obtained from the \(\text{PdCl}_2\) complexes by replacing one \(\text{Cl}\) moiety with a \(\text{Me}\) moiety from \(\text{SnMe}_4\). The reaction of \(\text{PdClMe}\) complex with a freshly prepared mixture of magnesium and an excess of \(\text{MeBr}\) yielded a mixture of \(\text{PdBrMe}\) and \(\text{PdBrCl}\) complexes.

New complexes were characterised by NMR and IR spectroscopy, elemental analysis and single-crystal X-ray crystallography. X-ray crystallography showed that the common moiety of the complexes is similar. The carborane cage is co-ordinated bidentately through two \(\text{P}\) atoms to the metal ion, and two ancillary ligands at \textit{cis} positions complete the slightly distorted square-planar co-ordination sphere.

Polymer formation was observed when the \(\text{PdCl}_2\) and \(\text{PdClMe}\) complexes were tested for the Kharasch addition of carbon tetrachloride to methyl methacrylate and styrene and for radical polymerisation of methyl methacrylate.

Quantum chemical calculations, including topological analyses for charge density, on differently \(\text{C}_c\)-substituted 1,2-dicarba-\textit{closo}-dodecaboranes showed that the substituents have a great impact on the \(\text{C}_c-\text{C}_c\) distance and concomitantly on the bonding properties.
Supervisors
Dr. Raikko Kivekäs
Laboratory of Inorganic Chemistry
Department of Chemistry
University of Helsinki
Finland

Prof. Francesc Teixidor i Bombardó
ICMAB / CSIC
Barcelona
Spain

Reviewers
Prof. Reijo Sillanpää
Laboratory of Inorganic Chemistry
Department of Chemistry
University of Jyväskylä
Finland

Prof. Alan Welch
Department of Chemistry
Heriot-Watt University
Edinburgh
U.K.

Opponent
Prof. Bohumil Štibr
Institute of Inorganic Chemistry
Academy of Sciences of the Czech Republic
Rež
Czech Republic
PREFACE

The experimental work for this thesis was carried out in the Laboratory of Inorganic Chemistry of the University of Helsinki and, in part, in the Laboratory of Inorganic Materials and Catalysis of the Institut de Ciència de Materials de Barcelona (ICMAB). I am grateful to Prof. Markku Leskelä and Prof. Francesc Teixidor for placing the excellent research facilities of the laboratories at my disposal.

The completion of this work has depended upon the assistance of a great many people. I am indebted to my supervisors Dr. Raikko Kivekäs and Prof. Francesc Teixidor for their encouragement, unfailing support and advice, and to Dr. Clara Viñas for the help she provided in and outside the laboratory, during my stay in Barcelona.

Dr. Markku Sundberg and Dr. Rolf Uggla carried out the quantum chemical calculations and Markku was extraordinarily patient in explaining to me the theoretical background. I am also most grateful to Dr. Martti Klinga and Dr. Ilpo Mutikainen for their help with the X-ray diffractometers, to Prof. Albert Demonceau of the University of Liege for the polymerisation tests, to Ms. Anna Fernandez of ICMAB for running the NMR spectra, to the Universitat Autònoma de Barcelona for the elemental analyses and to senior systems specialist Ari Vaskin for help with computer problems. The personnel of the Department of Chemistry were generous in their assistance.

Prof. Reijo Sillanpää and Prof. Alan Welch reviewed the manuscript of the thesis and provided valuable comments, and Dr. Kathleen Ahonen revised the English language. Prof. Bohumil Štibr graciously accepted to act as my opponent. Financial support of the work was provided by the Academy of Finland, the Ella and Georg Ehrnrooth Foundation and the Magnus Ehrnrooth Foundation.

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I owe a great debt of gratitude to my dear friend and colleague Kaisa for her support and help, believing in me (Yes! I’m almost there…) and for pleasant and relaxing hours outside work.

Indeed, I wish to thank all my friends for being there for me and helping me in a multitude of ways, sometimes even without knowing it. My dearest friends Tarja, Tiina, Johanna & Ismo, and Jaana & Juha provided friendship as well as innumerable many hilarious moments. The good times spent with Carter, Donnerwetter and Mr Adams allowed work to be forgotten for a time.

Finally, my warmest thanks to my parents (Kiitos isä ja äiti!) and Petri for all the support and love they have given me.

Helsinki, May 2002

Sari

The Road goes ever on and on
Down from the door where it began.
Now far ahead the Road has gone,
And I must follow, if I can,
Pursuing it with eager feet,
Until it joins some larger way
Where many paths and errands meet.
And whither then? I cannot say.

-The Lord of the Rings / The Fellowship of the Ring / J. R. R. Tolkien-
LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications, which are referred to in the text by the Roman numerals I–VI:

I S. Paavola, R. Kivekäs, F. Teixidor, C. Viñas: Revising the [PdCl₂(1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀)] synthesis and comparison of its behavior with [PdCl₂(1,2-(PPr₂)₂-1,2-C₂B₁₀H₁₀)]. Crystal structure of [PdCl₂(1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀)]. *J. Organomet. Chem.* 2000, 606, 183-187.

II S. Paavola, F. Teixidor, C. Viñas, R. Kivekäs: Study of the o-carboranyl fragment as an uncommon substituent. Crystal structures of [PdClMe(1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀)]·CH₂Cl₂ and [PdClMe(1,2-(PPr₂)₂-1,2-C₂B₁₀H₁₀)]. *J. Organomet. Chem.* 2002, 645, 39-46; *ibid. idem* 2002, 654, 237-238 (erratum).

III S. Paavola, F. Teixidor, C. Viñas, R. Kivekäs: Pd(II) bromide complexes of 1,2-bis(diphenylphosphino)-1,2-dicarba-closo-dodecaborane. Crystal structures of [PdBr₂(1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀)]·CH₂Cl₂, [PdBr₁.₁₃₃Cl₀.₈₆₇(1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀)]·CH₂Cl₂ and [PdBrCl₀.₅₄₁Me₀.₄₅₉(1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀)]·CHCl₃. *J. Organomet. Chem.* 2002, accepted.


V M. R. Sundberg, S. Paavola, C. Viñas, F. Teixidor, R. Uggla, R. Kivekäs: Plasticity of the five-membered chelate ring in [PdCl₂(1,2-(PR₂)₂-1,2-C₂B₁₀H₁₀)] complexes (R = H or iPr). Submitted.


Data published and discussed here for the first time are referred to as VII.

The author has done the synthetic work described in the papers. Crystal structure analyses were carried out by the author and Dr. Kivekäs. Dr. Sundberg and Dr. Uggla did the quantum chemical calculations for papers V and VI. Polymerisation tests by Prof. Demonceau are continuing.
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<th>Abbreviation</th>
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<tr>
<td>AIM</td>
<td>Atoms-in-Molecules</td>
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<tr>
<td>bite angle</td>
<td>P–M–P angle</td>
</tr>
<tr>
<td>Cc</td>
<td>cage carbon, C1 or C2</td>
</tr>
<tr>
<td>cod</td>
<td>1,5-cyclooctadiene</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>dihedral angle $\omega$</td>
<td>angle between the planes through atom groups P2,M,P1 and P1,C1,C2,P2</td>
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<tr>
<td>iPr</td>
<td>isopropyl</td>
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1. INTRODUCTION

The overall goal of this work was to synthesise closo-carborane catalysts. Six novel complexes were synthesised and characterised and three of them, together with one previously known complex, were tested in the polymerisation of ethylene, in the Kharasch addition and in the radical polymerisation of methyl methacrylate. The work was done in close cooperation with research groups in Catalonia and Belgium. As an introduction to the experimental work, the literature review that follows presents an overview of boranes and carboranes and reports on existing methods for the synthesis of palladium(II) and platinum(II) complexes of 1,2-diphosphines.

1.1 Boranes and Carboranes

1.1.1 Boranes

Alfred Stock started his work on boranes in 1909.\textsuperscript{1} His first paper on the boron hydrides appeared in 1912 and in all he published 16 papers on the boranes and their derivatives. Stock synthesised and characterised seven boranes: \(\text{B}_2\text{H}_6\), \(\text{B}_4\text{H}_{10}\), \(\text{B}_5\text{H}_9\), \(\text{B}_5\text{H}_{11}\), \(\text{B}_6\text{H}_{10}\) and \(\text{B}_{10}\text{H}_{14}\), and one of uncertain composition, possibly \(\text{B}_6\text{H}_{12}\). He recognised that they fall into two classes: “boranes” \(\text{B}_n\text{H}_{n+4}\) and “hydroboranes” \(\text{B}_n\text{H}_{n+6}\),\textsuperscript{2} now known as nido and arachno boranes, respectively.

Carbon is the only element beside boron that has a capacity to catenate and to form selfbonded complex molecular networks.\textsuperscript{3} The boranes, the binary compounds of boron and hydrogen, posed serious problems of structure and bonding from the very beginning, but hydrocarbon chemistry provided very little help. Boron is in Group 13 and thus has only three valence electrons. The simplest boron hydride, diborane \(\text{B}_2\text{H}_6\), has the stoichiometry of ethane, \(\text{C}_2\text{H}_6\), but two electrons fewer.

In 1954 Lipscomb and co-workers\textsuperscript{4} introduced the idea of three-centre two-electron (3c-2e) bonding; when electrons are in short supply, a pair of electrons can bond three atoms in a triangular array. Thus, the boranes are described as electron deficient. In 1976 Lipscomb
received the Nobel prize in chemistry for his studies on the structure of boranes which in the process threw light on problems of chemical bonding.\(^5\)

The crystal structure of CaB\(_6\) reported in 1934 is the beginning of our knowledge of boron polyhedra.\(^6\) Compounds containing boron deltahedra are characterised by unusual stability compared with the reactive and often unstable neutral boron hydrides. The icosahedral B\(_{12}\) cage may be the most stable cluster in all chemistry.\(^7\)

### 1.1.2 Carboranes

Carboranes, known since the 1960’s, are boron cluster compounds with one or more polyhedral boron vertices replaced by carbon.\(^8\) The first carboranes to be discovered were C\(_2\)B\(_3\)H\(_5\), C\(_2\)B\(_4\)H\(_6\) and C\(_2\)B\(_3\)H\(_7\).\(^3\) The synthesis and properties of the three isomers of dicarba-
\textit{closo}-dodecaborane, C\(_2\)B\(_{10}\)H\(_{12}\), were reported in 1963 in both the United States and the USSR.\(^9\) Their chemistry is one of the most complete in the field of boranes and heteroboranes.\(^10\) The first monocarborane of the eight-vertex \textit{closo} series was synthesised in former Czechoslovakia in the 1980’s.\(^11\)

In dicarba-
\textit{closo}-dodecaboranes, hexaco-ordinated carbon and boron atoms adopt the regular icosahedral geometry. Dicarba-
\textit{closo}-dodecaborane has three isomers: 1,2-, 1,7- and 1,12-
dicarba-
\textit{closo}-dodecaborane, \textit{i.e.} \textit{o-}, \textit{m-}, and \textit{p-}carborane. The isomers together with the numbering of the cage are shown in Figure 1. In the figure the lines of the skeletons are not electron-pair bonds but merely clarify the cluster geometry.\(^12\) The exopolyhedral C−H and B−H are electron-pair bonds, however. Under inert atmosphere \textit{o-}carborane rearranges to \textit{m-}carborane between 465 and 500 °C, and furthermore to \textit{p-}carborane at 615 °C.\(^13\) That is, the less stable position isomer rearranges to the more stable cage configuration, because the two carbon atoms in the cage prefer to lie at the greatest possible distance from each other.\(^14\) One mechanistic scheme for the rearrangement is based on a diamond−square−diamond (dsd) process.\(^6a\) In this process the co-operative stretching and squeezing of opposite corners of bent diamond-shaped groups of atoms lead back, \textit{via} a bent square, to a diamond (Figure 2).
**Figure 1.** The isomers of dicarba-closo-dodecaborane showing the numbering of the cage. Hydrogens and boron vertices are excluded for clarity.

**Figure 2.** dsd-Process for the rearrangement of icosahedral carboranes.

The two carbon vertices in dicarba-closo-dodecaboranes bear relatively acidic H atoms, which are readily replaced by metals or organic groups. Substituents can also be introduced with good control to at least a certain number of boron vertices. Carborane compounds with M–C and M–B σ-bonds are known for most transition and non-transition metals and for some lanthanides. The first organometallic derivatives of carboranes were obtained from the reaction of lithiocarborane with compounds with a metal–halogen bond. Carboranes with open polyhedral structures are the basis of metallocarborane chemistry as they can form stable sandwich-type complexes with transition metals.

*o*-Carboranes containing alkyl, aryl, ether, ester, haloalkyl and olefinic substituents are most often prepared directly from decaborane and a suitably substituted alkyne in the presence of Lewis acid:

\[
\text{B}_{10}\text{H}_{14} + \text{RC}≡\text{CR'} \rightarrow \text{C}_2\text{B}_{10}\text{H}_{10}\text{RR'} + 2\text{H}_2
\]
Even though the very important advantage of dicarba-closo-dodecaboranes is their unique thermal and chemical stability to most organic and organometallic compounds, they do have one very important degradation reaction. Carboranes are unstable in alkaline media, where they are susceptible to nucleophilic attack by Lewis bases and undergo partial degradation. The treatment of o- or m-carborane and their carbon-substituted derivatives with alcoholic base leads to the selective removal of a single boron atom (Figure 3). Degradation can be performed with methanolic potassium hydroxide, piperidine, “wet” fluoride ion solutions ([Bu₄N]F·xH₂O), pyrrolyl, dimethylpyrrollyl and HNP(NMe₂)₃.23

**Figure 3.** Deboronation of the closo cluster. The bridging hydrogen in the 7,8-dicarba-nido-undecaborate(-1) is shown in one of the equivalent bridge positions. Unmarked vertices are BH.

### 1.1.3 Williams/Wade/Rudolph structural pattern

R. E. Williams observed in 1971 that n-vertex clusters of carboranes (CₓBₓ₋₁Hₓ) and boranes (BₓHₓ) fall into three geometrically distinct stoichiometric series: closo (c = 2), nido (c = 4) and arachno (c = 6).24,8 **closo**-Boranes are closed polyhedrons having only triangular faces. **nido**-Boranes are formed through removal of the most highly connected vertex from the closo deltahedron, and **arachno**-boranes are obtained by removing the highest connected atom from the open face of the nido cluster. Wade’s rules state that clusters with n skeletal atoms adopt closo structures if held together by (n+1) pairs, nido structures if held together by (n+2) pairs, and arachno structures if held together by (n+3) pairs of skeletal bonding electrons.25 Figure 4 presents the classical Williams/Wade/Rudolph structural pattern. Horizontal movement from closo to nido and thence from nido to arachno is possible if two pairs of electrons are added to the cluster.26 There are also hypho structures, which are held together with (n+4) pairs, and klado structures with (n+5) pairs of skeletal bonding electrons.27 Clusters of clusters are possible, too; for example, two nido-decaboranyl units, B₁₀H₁₃, can be jointed via a B–B bond.28
Figure 4. The classical Williams/Wade/Rudolph structural pattern.
1.1.4 Applications

Fossil fuels and biomass, with preformed C–C and C–H bonds, offer virtually limitless resources of raw material for organic chemistry. The chemistry of boron clusters, on the other hand, is entirely man-made and must begin with the creation of B–B and B–H bonds, in sequence, from the limited quantities of boric oxide. Boron cluster species are thus very expensive and find practical application only in some exclusive areas where no alternative exists. B$_3$H$_9$ and B$_{10}$H$_{14}$, utilised in advanced jet and rocket propulsion systems before the early 1960’s, are two examples of boron cluster species that have been produced on a multiton per year scale. Current applications are based either on the unique properties of the molecules or on the specific properties of boron itself. The ability of carboranes to form nido anionic species leads to even more derivatives.

Carboranes have been incorporated into the backbone of polymers and also in many cases as pendant groups or side chains. Thermal stability of the polymer increases when the polymer contains a carborane unit in the backbone. Figure 5 shows an example of p-carborane incorporated into the backbone of a polymer.

![Figure 5. p-Carborane incorporated into the backbone of poly(p-phenylene).](image)

Bis(dicarbollide)cobaltate(III), patented in 1974, was the first application of carborane derivative for solvent extraction of radionuclides. A variety of nuclides, both radioactive and stable, can be successfully separated and isolated with reagents of the type bis(dicarbollide)cobaltate(III). Examples of the nuclides are Li$^+$, Na$^+$, K$^+$, Rb$^+$, Ba$^{2+}$, Pd$^{2+}$ and $^{95}$Zr. Sandwich complexes [3,3’-Co(1-Me-2-{(CH$_2$)$_m$O(CH$_2$)$_n$R}-1,2-C$_2$B$_9$H$_9$)$_2$]$^-$(n = 3, 6; m = 1–3, R = OMe, CHMe$_2$, Me), [3,3’-Co(1-Ph-1,2-C$_2$B$_9$H$_{10}$)$_2$]$^-$(n = 3) and [3,3’-Co(1,7-Ph$_2$-1,7-C$_2$B$_9$H$_{10}$)$_2$]$^-$(n = 3) have performed well in liquid–liquid extraction and transport of $^{137}$Cs, $^{90}$Sr and $^{152}$Eu through supported liquid membranes. Recently, bis(dicarbollide)cobaltate(III) derivatives have been used as doping ions in polymer materials.
The first metallocarborane catalyst, \textit{closo-[3-H-3,3-(PPh\textsubscript{3})\textsubscript{2}-3,1,2-RhC\textsubscript{2}B\textsubscript{9}H\textsubscript{11}]} (Figure 6), is active in homogeneous hydrogenation, isomerisation, hydrosilylation, hydrogenolysis and hydrogen–deuterium exchange.\textsuperscript{35} In this complex the metal occupies the vacant vertex of the \textit{nido} cage and forms part of the cluster generating a \textit{closo} species. The icosahedral Rh(III) species is not catalytically active, however, but the activity is due to the presence of a small equilibrium concentration of the Rh(I) tautomer, \textit{exo-nido-[(PPh\textsubscript{3})\textsubscript{2}-Rh-µ-4,9-(H)\textsubscript{2}-7,8-C\textsubscript{2}H\textsubscript{9}B\textsubscript{10}]}\textsuperscript{29} Other metallocarboranes have been found to be active catalysts for hydrogenation,\textsuperscript{36} ethylene polymerisation, oligomerisation,\textsuperscript{37} formation of syndiotactic poly(methyl methacrylate),\textsuperscript{38} double silylation reaction\textsuperscript{39} and the Kharasch addition of carbon tetrachloride across olefins.\textsuperscript{40} \textit{o-Carborane} itself has shown some catalytic activity in the homogeneous liquid phase oligomerisation of isophthalonitrile \textsuperscript{41} and in a Friedel–Crafts-like alkylation reaction of the 9-position of \textit{o-carborane}.\textsuperscript{42}

\textbf{Figure 6.} The first metallocarborane catalyst, \textit{closo-[3-H-3,3-(PPh\textsubscript{3})\textsubscript{2}-3,1,2-RhC\textsubscript{2}B\textsubscript{9}H\textsubscript{11}]}. Unmarked vertices are BH.

\textit{exo-nido-Rhoda-} and ruthenacarboranes containing monothio and monophosphino substituents have been shown to catalyse the hydrogenation and isomerisation of 1-hexene and the hydrogenation of methacyclene.\textsuperscript{43}

In boron neutron capture therapy (BNCT), the dose of \textsuperscript{10}B in a carrier molecule travels through the blood system to the tumour.\textsuperscript{44} When the tumour is irradiated with slow neutron radiation, boron splits to form lithium and helium, destroying the host cell in the process.

Derivatives of \textit{o-carboranes} have also been employed as doping agents in semiconductor materials.\textsuperscript{45} \textit{o-Carborane} has even been used as a protecting group for aldehydes and ketones in organic synthesis.\textsuperscript{46}
1.2 Palladium complexes of 1,2-diphosphines

Bidentate phosphine ligands have played an important role in the development of catalytic applications of metal complexes. In many catalytic reactions, diphosphine ligands offer more control over regio- and stereoselectivity than the corresponding monodentate ligands.

The steric properties of diphosphines are determined by the four substituents at the two phosphorus atoms and the length of the bridge. In general, the most stable complexes are obtained when a five-membered ring can form, i.e. when the bridge between the two phosphorus atoms consists of two carbon atoms. 1,2-Bis(diphenylphosphino)ethane, the synthesis of which was reported in 1959, is probably the most extensively used bidentate phosphine ligand in organometallic chemistry.

The bite angle, $P-M-P$, is an important parameter of the complexes of bidentate ligands in a number of reactions and it has been observed to be related to the catalytic efficiency. The bite angle is a compromise between the bite angles preferred by the ligand and the metal centre. The angle preferred by the ligand is mainly a consequence of the ligand backbone and of the steric repulsion between substituents on the phosphorus atoms and on the backbone. The bite angle preferred by the metal is mainly determined by electronic requirements. For cis-co-ordinated bidentate ligands the metal preferred bite angle is approximately $90^\circ$ in square planar complexes and it changes during the catalytic reaction.

Most examples of the effects of the bite angle in catalysed reactions are for diphosphine ligands. In general, the rate and selectivity of the reaction increase with the bite angle until, at very large bite angles, they begin to decrease. The optimum bite angle varies with the reaction. In radical copolymerisation of carbon monoxide and ethene, the reaction rate first increases and then decreases as the bite angle of the $\text{Ph}_2\text{P}-(\text{CH}_2)_n\text{PPh}_2$ ligand ($n = 1-4$) increases from $72^\circ$ to $98^\circ$. The optimum bite angle in this reaction is $91^\circ$ (for ligand with $n = 3$).

Complexes containing bidentate tertiary phosphine ligands have been reported for most transition metals. Square-planar diphosphine complexes of Pd(II) and, to a lesser extent, Pt(II) have a central role in homogeneous catalysis processes. Pd(II) complexes catalyse allylic alkylation, cross-coupling reactions, Diels-Alder reactions and co-
polymerisations. In this literature discussion, focus is on bidentate tertiary phosphines, which form five-membered chelate ring complexes with Pd(II) and Pt(II) (Figure 7). Bidentate tertiary phosphines are displayed in Figures 8 and 11.

Figure 7. Five-membered chelate ring. M = Pd, Pt; R = Ph, iPr, etc.; X = or ≠ X’ = Br, Cl, Me.

1.2.1 Dichloro complexes

Complexes of cyclic polyolefins co-ordinated to palladium or platinum are used as intermediates in a variety of reactions. 56 [PdCl₂(cod)] has been prepared by the reaction of sodium tetrachloropalladate and cod, by displacement of carbon monoxide from [PdCl₂CO]₂ or benzonitrile from [PdCl₂(PhCN)₂], and by the reaction of PdCl₂ in HCl with cod:

\[
2\text{HCl} + \text{PdCl}_2 \rightarrow \text{H}_2[\text{PdCl}_4] \\
\text{H}_2[\text{PdCl}_4] + \text{cod} \rightarrow [\text{PdCl}_2(\text{cod})] + 2\text{HCl}
\]

There are many examples of the use of [PdCl₂(cod)] in the synthesis of ditertiary phosphine complexes. The procedure for the synthesis of a new complex is simple: [PdCl₂(cod)] together with a ligand is stirred at room temperature in a solvent, usually dichloromethane. The corresponding replacements of benzonitrile from [PdCl₂(PhCN)₂] and acetonitrile from [PdCl₂(MeCN)₂] by the diphosphine ligand are other important procedures for synthesising PdCl₂ complexes.

Pd(II) complexes of 1,2-diphosphines have also been synthesised simply by refluxing the ligand with an equimolar amount of PdCl₂. Further, PdCl₂ complexes have been prepared with sodium or potassium salts of palladium, Na₂[PdCl₄] and K₂[PdCl₄]. The syntheses have been performed either by stirring the mixture of the ligand and salt or by synthesising the salt in situ from stoichiometric amounts of NaCl and PdCl₂.
Table 1 presents the details of reagents and ligands used in the synthesis of PdCl₂ complexes of 1,2-diphosphines. Ligands are displayed in Figure 8.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Ligand</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PdCl₂(cod)]</td>
<td>1-3, 19-23</td>
<td>49a, 47b, 57, 58, 59, 60</td>
</tr>
<tr>
<td>[PdCl₂(PhCN)₂]</td>
<td>4-8, 24-28</td>
<td>47b, 61, 62, 63, 64</td>
</tr>
<tr>
<td>[PdCl₂(MeCN)₂]</td>
<td>7, 9, 30</td>
<td>65, 66, 67</td>
</tr>
<tr>
<td>PdCl₂</td>
<td>6, 10-14</td>
<td>61c, 68, 69</td>
</tr>
<tr>
<td>K₂[PdCl₄]</td>
<td>6</td>
<td>61c</td>
</tr>
<tr>
<td>Na₂[PdCl₄]</td>
<td>15, 16, 29, 31, 32</td>
<td>70, 71, 72, 73</td>
</tr>
</tbody>
</table>

1.2.2 Chloromethyl complexes

An easy approach to PdClMe complexes of 1,2-diphosphines is to synthesise [PdClMe(cod)] from [PdCl₂(cod)] with use of SnMe₄ as methylating agent. Several complexes can be prepared by the ligand substitution reaction of [PdClMe(cod)] with an equimolar amount of diphosphine ligand; among these are complexes of 1,2-(diphosphino)ethanes 6, 17, 76 and 18. Another method is to exchange chloride ligand in palladium complex with Me group by applying a Grignard reagent or MeLi.

1.2.3 Bromo complexes

The method most commonly applied for the synthesis of PdBr₂ complexes of 1,2-diphosphines is the reaction of PdCl₂ complex with an excess of sodium or potassium bromide. This method has been used to synthesise PdBr₂ complexes of cod, 1,2-(diphosphino)ethanes 10-15, cis-1,2-bis(diphenylphosphino)ethylene (31) and 9,10-bis(diphenylphosphino)phenanthrene (32). Dibromo complex of 1,2-bis(diphenylphosphino)-benzene (29) has been prepared by the reaction of the ligand with Na₂[PdBr₄] and by exchanging the halogen ligands of PdCl₂ complex with an excess of [NBu₄]Br.
Figure 8. 1,2-Diphosphine ligands complexed with palladium(II) (1–32) and platinum(II) (2–7, 9–14, 16–20, 24–26 and 28–30).
No examples of the synthesis of PdBrMe or PdBrCl complexes of 1,2-diphosphines are available in the literature. PdBrMe complexes of 1,3-P,N-bidentate o-diphenylphosphino-N,N-dimethylbenzylamine and 1,2-N,N’-bidentate N,N,N’,N’-tetramethylethanediamine have been synthesised by substitution of methyl group from PdMe₂ complex for a bromine ion from MeBr.⁸⁰,⁸¹ PdBrMe complex of the former ligand has also been obtained from PdBr₂ complex by replacement of one bromine ion through reaction with MeLi.⁸⁰ Acetyl bromide has been used as brominating agent, as well.⁸²

1.2.4 1,2-Diphosphino-o-carborane complexes

Numerous symmetric and asymmetric ditertiary phosphines containing o-carborane backbone have been synthesised and studied.⁸³ 1,2-Diphosphino-o-carborane ligands complexed with Pd(II) are shown in Figure 9.

![Figure 9. 1,2-Diphosphino-o-carborane ligands. Unmarked vertices are BH.](image)

The preparation of a PdCl₂ complex of 1,2-bis(diphenylphosphino)-1,2-dicarba-closododecaborane (33) was reported as early as 1965, but the product was only poorly characterised.⁸⁴ The complex was synthesised by reaction of the ligand with [PdCl₂(PhCN)₂].⁸⁴,⁸⁵ The crystal structure of this complex was solved during the present work.¹ A similar [PdCl₂(34)] complex was prepared by the corresponding reaction of 34 with [PdCl₂(cod)].⁵¹

Asymmetric 1,2-diphosphino-o-carborane 1-PPh₂-2-PMe₂-C₁₀H₁₀ (35) has also been coordinated to palladium.⁸³ The PdCl₂ complex was synthesised by reaction of the ligand with a stoichiometric amount of [PdCl₂(MeCN)₂]. The dibromo derivative was obtained by heating the dichloro complex with solid KBr.
The reaction of aryl, alkyl or alkoxy substituted closo-carboranylphosphines with \([\text{PdCl}_2\text{L}_2]\), \((\text{L} = \text{PPh}_3, \text{PhCN}, \text{PMePh}_2)\) in ethanol yields complexes in which partial degradation of the carborane cage has taken place (Figure 10).\(^{86}\)

\[
\begin{align*}
\text{PR}_2 & \quad \text{PR}_2 \\
\text{C} & \quad \text{C} \\
\text{EtOH} & \quad + \ [\text{PdCl}_2\text{L}_2] \\
\end{align*}
\]

**Figure 10.** Partial degradation of carborane cage in metal co-ordination in ethanol. \(R = \) aryl, alkyl, alkoxy substituent; \(L = \text{PPh}_3, \text{PhCN}, \text{PMePh}_2\). Unmarked vertices are BH.
1.3 Platinum complexes of 1,2-diphosphines

1.3.1 Dichloro complexes

Methods for the synthesis of PtCl$_2$ complexes of 1,2-diphosphines are generally the same as for the PdCl$_2$ complexes described above. Table 2 presents the reagents and ligands used in the synthesis of PtCl$_2$ complexes of 1,2-diphosphines. The ligands complexed with platinum are shown in Figures 8 and 11. [PtCl$_2$(cod)] is prepared by the reaction of potassium tetrachloroplatinate(II) or chloroplatinic acid with an excess of cod.$^{56,87}$

Table 2. Reagents and ligands used for the synthesis of PtCl$_2$ complexes of 1,2-diphosphines.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Ligand</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PtCl$_2$(cod)]</td>
<td>3, 18, 19, 36, 37, 40-43</td>
<td>88, 89, 90, 91, 92</td>
</tr>
<tr>
<td>[PtCl$_2$(PhCN)$_2$]</td>
<td>2-6, 12-14, 24-26, 38, 44, 45</td>
<td>69, 47b, 61c, 62, 93, 94, 95</td>
</tr>
<tr>
<td>[PtCl$_2$(MeCN)$_2$]</td>
<td>9, 30</td>
<td>66, 67</td>
</tr>
<tr>
<td>PtCl$_2$</td>
<td>7</td>
<td>96</td>
</tr>
<tr>
<td>K$_2$[PtCl$_4$]</td>
<td>6, 10, 11, 16, 28</td>
<td>61c, 64, 68, 71</td>
</tr>
<tr>
<td>Na$_2$[PtCl$_4$]</td>
<td>29</td>
<td>72a</td>
</tr>
<tr>
<td>[PtCl$_2$(Me$_2$SO)$_2$]</td>
<td>20</td>
<td>57</td>
</tr>
<tr>
<td>[PtCl$_2$(tBuCN)$_2$]</td>
<td>39</td>
<td>97</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
PR_2 \quad 36 & : R = C_6H_{11} \\
PR_2 \quad 37 & : R = \text{2-pyridyl} \\
PR_2 \quad 38 & : R = \text{CF}_3 \\
PR_2 \quad 39 & : R = \text{2-Me-Ph}
\end{align*}
\]

\[
\begin{align*}
PR_2 \quad 40 & \quad \text{Me} \quad \text{Me} \quad \text{PPh}_2 \\
PR_2 \quad 41 & \quad \text{Ph} \quad \text{PPh}_2 \quad \text{PPh}_2
\end{align*}
\]

Figure 11. 1,2-Diphosphine ligands complexed with PtCl$_2$. 

\[
\begin{align*}
42 & \quad \text{PPh}_2 \quad \text{PPh}_2 \\
43 & \quad \text{R}^1 \quad \text{R}^2 \quad \text{R}^3 = \text{CF}_3, \text{R}^2 = \text{R}^3 = \text{F} \\
44 & \quad \text{R}^1 = \text{Ph}, \text{R}^2 = \text{COOMe}, \text{R}^3 = \text{H}
\end{align*}
\]
1.3.2 1,2-Diphosphino-\(\alpha\)-carborane complexes

Even though many PtCl\(_2\) complexes of 1,2-diphosphino-\(\alpha\)-carboranes have been prepared, no crystal structures have been deposited in the Cambridge Structure Database.\(^9\) The PtCl\(_2\) complexes of \(33\) and \(46\)–\(50\)\(^9\) (Figure 12) have been prepared by displacement reactions using \([\text{PtCl}_2(\text{PhCN})_2]\) or \([\text{PtCl}_2(\text{MeCN})_2]\) as reagent:

\[
[\text{PtCl}_2(\text{RCN})_2] + 1,2-(\text{PR}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10} \rightarrow [\text{PtCl}_2(1,2-(\text{PR}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})] + 2 \text{RCN}
\]

**Figure 12.** 1,2-Diphosphino-\(\alpha\)-carboranes complexed with PtCl\(_2\). Unmarked vertices are BH.

1.4 Aim of the study

Organic diphosphines and derivatives of carboranes have been successfully applied as catalysts in various types of reactions. The aim of the work summarised below was to synthesise new Pd(II) and Pt(II) complexes of 1,2-diphosphino-\(\alpha\)-carboranes that might possess good catalytic properties.
2. RESULTS AND DISCUSSION

Six novel o-carborane complexes, displayed in Figure 13, were synthesised and characterised in this study: PdCl₂ complex 53, PtCl₂ complex 54, PdClMe complexes 55 and 56, and a mixture of PdBrCl and PdBrMe complexes 59A and 59B. In addition, crystal structures were determined for three previously known compounds 33, 52 and 57, and for two complexes with partially disordered crystal structure, [PdBr₁.₁₃Cl₀.₈₆₇(1,₂-₅PPh₂)₂₁,₂-C₂B₁₀H₁₀] (58) and [PdCl₅₇(1,₂-₅PPh₂)₂₁,₂-C₂B₁₀H₁₀)] (55').

![Figure 13. Ligands and complexes of this work. Unmarked vertices are BH.](image)

2.1 Syntheses

2.1.1 1,2-Diphosphino-o-carborane ligands

1,2-Bis(diphenylphosphino)-1,2-dicarba-closo-dodecaborane (33) and 1,2-bis(diisopropylphosphino)-1,2-dicarba-closo-dodecaborane (51) were used as ligands in this work. The synthesis of 33 was published in the early 1960’s, but the crystal structure was first solved here. VI Both the synthesis and crystal structure of 51 have been published earlier. Ligand 33 is synthesised by the reaction of dilithio-o-carborane with
chlorodiphenylphosphine. The corresponding reaction of dilithio-o-carborane with chlorodiisopropylphosphine gives 51.

2.1.2 Synthesis of Pd(II) complexes of 1,2-diphosphino-o-carboranes

2.1.2.1 Dichloro complexes

PdCl₂ complex of 33 was previously known, as mentioned above.⁸⁴,⁸⁵ In this work, [PdCl₂(1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀)] (52) was synthesised by mixing the ligand with [PdCl₂(PhCN)₂], as was done previously, and by mixing it with [PdCl₂(cod)].¹ The latter method gave better yield (96%) than the former (64%).

The synthesis of [PdCl₂(1,2-(PPr₂)₂-1,2-C₂B₁₀H₁₀)] (53) was carried out with the ligand 51 and [PdCl₂(cod)] in CH₂Cl₂.¹ The unfavourable effect of a mild nucleophile was seen in the attempted recrystallisation of the product in acetonitrile: when the closo complex 53 was heated to reflux just 5 to 10 minutes in acetonitrile, a mixture of 53 and deboronated [Pd₂(µ-Cl)₂{7,8-(PPr₂)₂-7,8-C₂B₉H₁₀}₂] species (Figure 14) was obtained. The deboronated species has earlier been synthesised from 51 and [PdCl₂(PhCN)₂] in ethanol.⁸⁶

![Figure 14. [Pd₂(µ-Cl)₂{7,8-(PPr₂)₂-7,8-C₂B₉H₁₀}₂]; R = iPr. Unmarked vertices are BH.](image)
2.1.2.2 Chloromethyl complexes

The PdClMe complexes [PdClMe(1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀)] (55) and [PdClMe(1,2-(P'Pr₂)₂-1,2-C₂B₁₀H₁₀)] (56) were synthesised by two different methods (Figure 15). In Method A, cod in [PdClMe(cod)] was replaced by 33 or 51, and in Method B one Cl ion in 52 and 53 was replaced by a Me group from SnMe₄. The reaction conditions were similar to the conditions in the synthesis of [PdClMe(cod)].

Figure 15. Synthesis of [PdClMe(1,2-(PR₂)₂-1,2-C₂B₁₀H₁₀)] complexes. R is Ph for 33, 52, 55 and 'Pr for 51, 53, 56. Unmarked vertices are BH.

Complex 55 was obtained in 80% yield by both methods. Method A yielded 56 in almost the same manner and yield, but Method B gave only a 37% yield with a reaction time of 10 days and considerable excess of SnMe₄.
2.1.2.3 Bromo complexes

The synthesis of [PdBr\(_2\)(1,2-(PPh\(_2\))\(_2\)-1,2-C\(_2\)B\(_{10}\)H\(_{10}\))] (57) was first attempted following the procedure reported in the literature.\(^{83,85}\) Complex 52 was allowed to react with four equivalents of KBr for two hours, instead of the earlier reported one hour, but \(^{31}\)P\(_{\{^1\text{H}\}}\) NMR characterisation of the isolated solid (58) indicated that the reaction still was not complete.\(^{\text{III}}\)

The \(^{31}\)P\(_{\{^1\text{H}\}}\) NMR spectrum of 57 should display only one resonance, but several peaks were present in the spectrum. Ethanol was not used in the separation step, in contrast to the reported method, to prevent possible degradation of the cage.

The partially brominated complex, easily confirmed by \(^{31}\)P\(_{\{^1\text{H}\}}\) NMR spectroscopy, was still obtained after a reaction time of 24 hours and with use of 10 equivalents of KBr. When the reaction was continued for eight more days, and an even larger excess of KBr was used, the fully dibrominated complex 57 was finally obtained.\(^{\text{III}}\)

The complex 58 has a partially disordered structure: halide positions of the complex unit are disordered. To obtain a pure monobrominated palladium complex, 55 was mixed with an excess of MeBr. No reaction took place, however. When a freshly prepared mixture of magnesium with an excess of MeBr reacted with 55, a mixture of two asymmetric complexes (59A and 59B) was obtained.\(^{\text{III}}\)

2.1.3 Synthesis of the PtCl\(_2\) complex of 1,2-bis(diisopropylphosphino)-1,2-dicarba-closo-dodecaborane

The platinum complex [PtCl\(_2\)(1,2-(P\(^{\text{IPr}}\))\(_2\)-1,2-C\(_2\)B\(_{10}\)H\(_{10}\))] (54) was synthesised by the same procedure as the corresponding palladium complex: by replacing cod in [PtCl\(_2\)(cod)] with ligand 51.\(^{\text{IV}}\) The reaction did not, however, proceed as well as the synthesis of the PdCl\(_2\) complex. Cod was only partially replaced by the carborane ligand and a mixture of [PtCl\(_2\)(cod)] and 54 was obtained. Attempts to separate the complexes on a silica column failed. Neither longer reaction time nor excess of the ligand gave the pure complex.
2.2 Characterisation

The novel complexes were characterised by single crystal X-ray analysis, NMR and IR spectroscopy and elemental analysis. Crystallographic data are listed in Tables 3 and 4 and selected geometrical parameters are presented in Tables 5 and 6.

The common moiety in the synthesised complexes is similar. The carborane cage is co-ordinated bidentately through two P atoms to the metal ion, and two ancillary ligands at cis positions complete the slightly distorted square-planar co-ordination sphere. Shortening of the C_c–C_c bond upon complexation is clearly seen for complexes bearing phenyl substituents on phosphorus atoms. The C_c–C_c distance of 1.722(4) Å in the free ligand 33 shortens to 1.680(4)–1.695(5) Å in the complexes 52, 55 and 57-59. Shortening is not so pronounced for the complexes bearing isopropyl substituents. Another clear influence of the co-ordination appears in the torsion angle P1–C_c–C_c–P2. Upon complexation, the torsion angle decreases from –10.9(3)° and 12.1(2)° in free ligands 33 and 51, respectively, to close to zero [0.4(3) to –3.4(4)°] in the complexes. The dihedral angle \( \omega \) (the angle between the planes through atom groups P2,M,P1 and P1,C1,C2,P2) varies noticeably in the different complexes.

The C1–C2 distances are clearly longer in metal complexes with o-carborane backbone than in 1,2-diphophine complexes with other than o-carborane backbone [1.403(6)–1.527(5) Å]. The P–C–C–P torsion angles are clearly larger in complexes with ethane backbone. Infrared spectra of the complexes show typical absorptions of the carborane cage; thus, strong bands are seen in the 2546–2660 cm\(^{-1}\) region (B–H stretching). \(^{11}\)B NMR spectra resonances in the range 0.02 to –10.48 ppm confirm the preservation of the closo cage.

Perspective views of the complex units are presented in Figures 16, 17, 19, 21, 22, 24 and 25.
**Table 3.** Crystallographic data for 33, 52-CH₂Cl₂, 53-CHCl₃, 54-0.5CH₂Cl₂ and 55-CH₂Cl₂.

<table>
<thead>
<tr>
<th></th>
<th>33</th>
<th>52-CH₂Cl₂</th>
<th>53-CHCl₃</th>
<th>54-0.5CH₂Cl₂</th>
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</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C₂₆H₃₀B₁₀P₂</td>
<td>C₂₇H₃₂B₁₀Cl₄P₂Pd</td>
<td>C₁₅H₃₉B₁₀Cl₅P₂Pd</td>
<td>C₁₄H₃₉B₁₀Cl₂P₂Pt</td>
<td>C₂₈H₃₅B₁₀Cl₃P₂Pd</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
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<td>774.77</td>
<td>673.15</td>
<td>684.94</td>
<td>754.35</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>space group</strong></td>
<td>P₂₁/n (no. 14)</td>
<td>P–1 (no. 2)</td>
<td>P₂₁2₁2₁ (no. 19)</td>
<td>C2/c (no. 15)</td>
<td>P₂₁c (no. 14)</td>
</tr>
<tr>
<td><strong>a [Å]</strong></td>
<td>16.273(2)</td>
<td>12.312(4)</td>
<td>15.189(3)</td>
<td>42.785(12)</td>
<td>18.141(4)</td>
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<tr>
<td><strong>b [Å]</strong></td>
<td>10.332(11)</td>
<td>13.797(4)</td>
<td>17.413(3)</td>
<td>10.320(14)</td>
<td>9.873(5)</td>
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<tr>
<td><strong>c [Å]</strong></td>
<td>17.642(2)</td>
<td>10.999(5)</td>
<td>11.136(2)</td>
<td>32.238(11)</td>
<td>19.173(3)</td>
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<tr>
<td><strong>α [°]</strong></td>
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<td>110.58(2)</td>
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<tr>
<td><strong>β [°]</strong></td>
<td>111.880(10)</td>
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<td><strong>γ [°]</strong></td>
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<td>86.36(3)</td>
<td>90</td>
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<td><strong>V [Å³]</strong></td>
<td>2752.6(5)</td>
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<td>2945.3(9)</td>
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<td>3396.1(19)</td>
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<td><strong>D_calcd [g cm⁻³]</strong></td>
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<td>1.518</td>
<td>1.688</td>
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<td>0.0478</td>
<td>0.0693</td>
<td>0.0676</td>
<td>0.0546</td>
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**Table 4.** Crystallographic data for 55', 56, 57-CH₂Cl₂, 58-CH₂Cl₂ and 59-CHCl₃.

<table>
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<th>55'</th>
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<th>58-CH₂Cl₂</th>
<th>59-CHCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C₂₇H₃₃B₁₀ClP₂Pd</td>
<td>C₁₅H₄₁B₁₀ClP₂Pd</td>
<td>C₂₇H₃₂B₁₀Br₂Cl₂P₂Pd</td>
<td>C₂₇H₃₂B₁₀Br₁.₁₃Cl₂₈₆P₂Pd</td>
<td>C₂₇.₄₅H₃₂.₃₇B₁₀BrCl₃₅₄₁P₂Pd</td>
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<td>863.69</td>
<td>825.14</td>
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<td><strong>Crystal system</strong></td>
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<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
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<td>P–1 (no. 2)</td>
<td>P₂₁/n (no. 14)</td>
<td>P–1 (no. 2)</td>
<td>P–1 (no. 2)</td>
<td>P₂₁c (no. 14)</td>
</tr>
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<td><strong>a [Å]</strong></td>
<td>11.040(2)</td>
<td>8.062(2)</td>
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<td>110.06(2)</td>
<td>90</td>
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<td>90</td>
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<td>110.06(2)</td>
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<td>0.0693</td>
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**Table 5.** Selected geometrical parameters (Å, °) for structures 33, 52·CH₂Cl₂, 53·CHCl₃, 54·0.5CH₂Cl₂ (complex units 54A and 54B), 57·CH₂Cl₂ and 58·CH₂Cl₂.

<table>
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<th>Bond/Angle</th>
<th>33</th>
<th>52·CH₂Cl₂</th>
<th>53·CHCl₃</th>
<th>54A</th>
<th>54B</th>
<th>57·CH₂Cl₂</th>
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<td>M–P1</td>
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<td>2.2325(13)</td>
<td>2.243(3)</td>
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<td>2.235(4)</td>
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<tr>
<td>M–P2</td>
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<td>2.220(3)</td>
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<td>2.238(2)</td>
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<tr>
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<td>2.351(3)</td>
<td>2.348(3)</td>
<td>2.4745(4)</td>
<td>2.469(4)*</td>
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<tr>
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<td>-</td>
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<td>2.353(5)</td>
<td>2.4666(4)</td>
<td>2.467(3)*</td>
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<tr>
<td>P1–C1</td>
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<td>1.876(4)</td>
<td>1.887(14)</td>
<td>1.880(5)</td>
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<td>1.870(4)</td>
<td>1.879(12)</td>
<td>1.861(12)</td>
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<td>X1–M–X2</td>
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<td>89.69(13)</td>
<td>87.78(12)</td>
<td>87.33(12)</td>
<td>93.879(13)</td>
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<td>P1–C1–C2</td>
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<td>114.1(8)</td>
<td>114.4(8)</td>
<td>113.0(8)</td>
<td>114.35(17)</td>
<td>114.3(5)</td>
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<tr>
<td>P2–C2–C1</td>
<td>110.6(2)</td>
<td>114.6(2)</td>
<td>114.1(8)</td>
<td>113.2(7)</td>
<td>113.3(7)</td>
<td>114.19(18)</td>
<td>114.1(5)</td>
</tr>
<tr>
<td>P1–C1–C2–P2</td>
<td>-10.9(3)</td>
<td>0.4(3)</td>
<td>3.4(12)</td>
<td>-2.0(10)</td>
<td>-3.0(10)</td>
<td>-0.2(2)</td>
<td>-0.8(7)</td>
</tr>
<tr>
<td>Dihed. angle ω</td>
<td>-</td>
<td>6.72(10)</td>
<td>17.0(5)</td>
<td>11.7(6)</td>
<td>28.1(2)</td>
<td>6.36(6)</td>
<td>6.59(19)</td>
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</tbody>
</table>

X1 = X2 = Cl for 52·CH₂Cl₂, 53·CHCl₃, 54A and 54B and X1 = X2 = Br for 57·CH₂Cl₂ and 58·CH₂Cl₂.

* The Pd–Cl distances [2.342(10) and 2.343(10) Å] are restrained.
<table>
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<tr>
<th>Bond/Angle</th>
<th>55·CH₂Cl₂</th>
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<th>56</th>
<th>59·CHCl₃</th>
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<td>2.2305(9)</td>
<td>2.232(2)</td>
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<tr>
<td>Pd–P2</td>
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<td>2.2804(9)</td>
<td>2.3507(19)</td>
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</tr>
<tr>
<td>Pd–Br</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.5064(10)</td>
</tr>
<tr>
<td>Pd–Cl₁</td>
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<td>2.3368(11) (Cl₁a)</td>
<td>2.365(2)</td>
<td>2.384(6)</td>
</tr>
<tr>
<td>Pd–C₃</td>
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<td>2.118(8) (C₃a)*</td>
<td>2.157(6)</td>
<td>2.106(10)*</td>
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<tr>
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<td>1.898(2)</td>
<td>1.882(7)</td>
<td>1.878(6)</td>
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<tr>
<td>P₂–C₂</td>
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<td>1.879(3)</td>
<td>1.879(7)</td>
<td>1.866(6)</td>
</tr>
<tr>
<td>C₁–C₂</td>
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<td>1.684(3)</td>
<td>1.724(9)</td>
<td>1.698(8)</td>
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<tr>
<td>P₁–Pd–P₂</td>
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<td>90.22(3)</td>
<td>91.53(7)</td>
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<tr>
<td>C₃–Pd–Cl₁</td>
<td>85.89(15)</td>
<td>89.5(2) *</td>
<td>86.10(18)</td>
<td>-</td>
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<td>Br–Pd–Cl₁</td>
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<td>-</td>
<td>-</td>
<td>83.76(15)</td>
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<tr>
<td>P₁–C₁–C₂</td>
<td>113.8(3)</td>
<td>113.10(16)</td>
<td>114.2(4)</td>
<td>113.3(4)</td>
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<tr>
<td>P₂–C₂–C₁</td>
<td>113.8(3)</td>
<td>114.06(16)</td>
<td>114.8(4)</td>
<td>113.1(5)</td>
</tr>
<tr>
<td>P₁–C₁–C₂–P₁</td>
<td>-3.4(4)</td>
<td>3.0(2)</td>
<td>2.0(6)</td>
<td>-3.0(5)</td>
</tr>
<tr>
<td>Dihed. angle ω</td>
<td>25.25(11)</td>
<td>24.74(8)</td>
<td>22.5(3)</td>
<td>32.38(13)</td>
</tr>
</tbody>
</table>

* The Pd–C₃ distances are restrained.
2.2.1 Crystal structure of 1,2-bis(diphenylphosphino)-1,2-dicarba-closo-dodecaborane

Crystal structure analysis showed the C$_2$B$_{10}$ cage in 33 (Figure 16) to have the expected near icosahedral architecture. The torsion angles C$_c$–C$_c$–P–C(Ph) [112.3(2), 82.1(2), −135.6(2) and −169.2(2)$^\circ$] describe the different orientation of the PPh$_2$ groups. The angles P–C$_c$–X (X = C$_c$ or B) of 110.4(2)–129.6(2)$^\circ$ also show pronounced deformations of the PPh$_2$ groups away from ideal radial positions on cluster carbons. This results in C$_1$ symmetry for the molecule. The P1–C1–C2–P2 torsion angle of −10.9(3)$^\circ$ agrees with the values reported for o-carboranes bearing bulky substituents at C$_c$. The C$_1$–C$_2$ distance of 1.722(4) Å is in agreement with the earlier reported observations, being significantly shorter than in the 1,2-S$_2$-substituted compounds [1.858(5) and 1.816(6) Å] but longer than in the monophosphine compound 1-PPh$_2$-1,2-C$_2$B$_{10}$H$_{11}$ [1.666(9) Å].

The C1–C2 distance also agrees with the value of 1.719(3) Å for 51. The P–C(Ph)

Figure 16. Perspective drawing of 33. H atoms have been omitted for clarity.
distances of 1.822(3)−1.836(3) Å and the P−Cc distances of 1.874(3) and 1.890(3) Å fall within the normal range reported for comparable PPh₂ substituted closo-carboranes.¹⁰⁴b,¹⁰⁶

2.2.2 Characterisation of Pd(II) complexes of 1,2-diphosphino-o-carboranes

2.2.2.1 Dichloro complexes

Crystal structure analysis revealed that the PdCl₂ complexes 52 and 53 (Figure 17) have a very similar co-ordination sphere.¹⁴ The bond lengths in the co-ordination sphere of 52·CH₂Cl₂ and 53·CHCl₃ are equal within experimental errors, or the differences are only barely significant. The difference in the geometry of the two complexes is significant, however. The dihedral angle ω is only 6.72(10)° in bisdiphenylphosphine complex 52·CH₂Cl₂, while in the bisdiisopropylphosphine complex 53·CHCl₃ it is 17.0(5)°.

Figure 17. Perspective views of the complex units of 52 and 53. H atoms have been omitted for clarity.
The Cl–C2 and P–C₆ distances of 52-CH₂Cl₂ and 53-CHCl₃ are equal or nearly equal to the corresponding distances in the o-carborane complex [PdCl₂(34)]·2THF. The Pd–P and Pd–Cl distances are slightly longer in 52-CH₂Cl₂ and 53-CHCl₃, however, and the P1–Pd–P2 and Cl1–Pd–Cl2 angles are unequal. The difference can be explained by the electron-withdrawing capacity of the Cl atoms bonded to the P atoms in [PdCl₂(34)]·2THF.

The bond lengths in the co-ordination sphere of 52-CH₂Cl₂ and 53-CHCl₃ are in good agreement with the corresponding values in [PdCl₂(6)]·CH₂Cl₂ with ethane backbone. The Pd–P bonds in the three complexes are equal within experimental errors and the Pd–Cl distances are only slightly shorter in 52-CH₂Cl₂ and 53-CHCl₃ than in the compared compound. In a comparison of 52-CH₂Cl₂ and 53-CHCl₃ with [PdCl₃(28)], a complex with benzene backbone, the biggest differences are found in the P–C distances and in the P1–Pd–P2 and Cl1–Pd–Cl2 angles.

The ¹H NMR spectrum of 53 indicates that the two methyl groups in the isopropyl groups are non-equivalent. The methyl groups appear at the same chemical shift, but the coupling constants ²J(H,H) and ³J(P,H) are different: 6.9 and 24.1 Hz for one methyl group and 11.7 and 7.1 Hz for the other (Figure 18). The ¹³C{¹H} spectrum shows two different resonances, at 21.29 and 20.00 ppm, in agreement with the two different methyl groups in each isopropyl group.

2.2.2.2 Chloromethyl complexes

PdClMe complexes provide excellent examples of the effect that trans influence has on bond distances. When a ligand is co-ordinated to a metal ion, it influences the bonding between the metal ion and every other ligand. The bond length can be considered as the most straightforward measure of bond strength, and hence of trans influence.

The trans influence of the Me group is seen clearly in the present PdClMe complexes 55 and 56 (Figure 19). Crystal structure analysis reveals that the Pd–P2 bonds, which are trans to Me, are clearly longer (by ca. 0.1 Å) than the Pd–P1 bonds, which are trans to Cl. The Pd–P1 distances are equal or differ only slightly from the values observed for the corresponding distances in PdCl₂ complexes 52 and 53.
Figure 18. Methyl region in the $^1$H NMR spectrum of 53.

Figures 19. Molecular views of 55 and 56. H atoms have been omitted for clarity.
The dihedral angles $\omega$ are almost the same in 55-CH$_2$Cl$_2$ and 56 [25.25(11) and 22.5(3)$^\circ$, respectively]. Values of the dihedral angles $\omega$ suggest that the energy barrier needed in solution to flip to the reciprocal conformer is very low. In solution these conformers could be expected to average to a complex where two C$_c$, two P and Pd, Cl and methyl carbon atoms lie in a plane. Thus, both 55 and 56 can be assumed to present an averaged $C_s$ geometry in solution. This should generate a 2:2:2:2:1:1 or similar pattern in the $^{11}$B NMR spectra, which is in agreement with the spectra obtained at room temperature. The P1–Pd–P2 angles are close to 90$^\circ$ in both complexes.

The $^1$H NMR resonances of 55 and 56 confirm the non-equivalence of the two phosphorus atoms, and the $C_s$ symmetry for the complexes. In both spectra the resonance for the ancillary Me group is split by the two chelating phosphorus nuclei. The $^{13}$C{$^1$H} NMR spectra do not show this non-equivalence, however. The resonance of the Me group is split by only one of the P atoms, most probably the one trans to Me. In the $^{31}$P{$^1$H} NMR spectrum, each resonance is split by the other phosphorus with a $^2J(P,P) = 39.6$ Hz for 55 (Figure 20) and 30.9 Hz for 56.

![Figure 20](image_url)

*Figure 20. The $^{31}$P{$^1$H} NMR spectrum of 55.*
When 55 is crystallised from chloroform/n-hexane, the complex appears in the triclinic system and the ancillary ligands are disordered (complex 55'). The ancillary ligands in 55' (Figure 21) are disordered in such a way that the position trans to P1 is occupied 69.76(15)% by Cl and 30.24(15)% by Me (labelled as Cl1a and C3a) and the position trans to P2 is occupied 30.24(15)% by Cl and 69.76(15)% by Me (labelled as Cl1b and C3b).VII

**Figure 21.** Molecular view of 55'. H atoms have been omitted for clarity. The ancillary ligands are disordered.

The different trans influence of the Me and Cl moieties is clearly evident in 55', too. The Pd–P2 distance trans to C3b, the position with larger occupancy of Me, is longer (by ca. 0.05 Å) than the Pd–P1 distance trans to C3a. Logically, the Pd–P distances in 55' fall between those found in 55.
2.2.2.3 Bromo complexes

As expected, the $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectrum of 57 presents only one resonance, confirming, together with the single crystal X-ray analysis, that fully dibrominated product is obtained.\[^{\text{III}}\]

The Pd–Br distances in 57·CH$_2$Cl$_2$ (Figure 22) agree well with those found in [PdBr$_2$(29)] $^{2.4607(10)}$ and $^{2.4734(10)}$ Å.\[^{72b}\]

The X-ray analysis of 58·CH$_2$Cl$_2$ (Figure 22) reveals that the halide positions of the complex unit are disordered.\[^{\text{III}}\]

\begin{itemize}
\item The halide position $\text{trans}$ to P2 is occupied $51.4(7)%$ by bromide and $48.6(7)%$ by chloride, and the halide position $\text{trans}$ to P1 is occupied $61.9(7)%$ by bromide and $38.1(7)%$ by chloride. It is not possible to conclude about the degree of bromination from these values.
\end{itemize}

\textbf{Figure 22.} Perspective views of 57 and 58. H atoms have been omitted for clarity. The halide positions of 58 are disordered.

X-ray analyses of bromo complexes 57·CH$_2$Cl$_2$ and 58·CH$_2$Cl$_2$ reveal that these structures are isostructural with the structure of dichloro complex 52·CH$_2$Cl$_2$. All three complexes crystallise in triclinic space group P–1 (no. 2) with $Z = 2$. Corresponding axes and angles are equal within 0.2 Å and 2°. The volumes deviate slightly, the volume of 57·CH$_2$Cl$_2$ being the largest ($21.1\text{ Å}^3$ larger than 52·CH$_2$Cl$_2$) because bromide ion is larger than chloride ion. Thus,
it seems likely that the substitution process is gradual and the starting dichloro complex 52, partially brominated \([\text{PdClBr}(1,2-(\text{PPh}_2)_2\cdot 1,2\cdot \text{C}_2\text{B}_{10}\text{H}_{10})]\) and dibrominated complex 57 are present in the crystals in variable amounts and form a solid solution. The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum confirms the existence of three complexes in the reaction mixture after 2 h. The singlets of the PdBr\(_2\) and PdCl\(_2\) complexes and the two doublets of the PdBrCl complex are clearly seen in the spectrum (Figure 23).

![Figure 23. The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of 58.](image)

As mentioned above, the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of the product obtained from the reaction of 55 with a freshly prepared mixture of magnesium and an excess of MeBr indicates the existence of two asymmetric complexes in the solution.\(^{\text{III}}\) The two species display very similar chemical shifts, but it is known that replacing one chloride for bromide in Pd(II) complexes does not appreciably alter the chemical shifts of the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum.\(^{82,109}\) Single crystal X-ray study of 59·CHCl\(_3\) confirmed that the complex unit is partially disordered, consisting of a mixture of two complexes: \([\text{PdBrCl}(1,2-(\text{PPh}_2)_2\cdot 1,2\cdot \text{C}_2\text{B}_{10}\text{H}_{10})]\) (59A, 54.1(13)\%) and \([\text{PdBrMe}(1,2-(\text{PPh}_2)_2\cdot 1,2\cdot \text{C}_2\text{B}_{10}\text{H}_{10})]\) (59B, 45.9(13)\%) (Figure 24). In the co-ordination sphere of the metal the Br ion occupies one position while the other ancillary ligand position is disordered with Cl and Me. Even though the co-ordinating behaviour of the “Pd(1,2-(PPh\(_2\))\(_2\)-1,2-C\(_2\)B\(_{10}\)H\(_{10}\)” moiety of 59·CHCl\(_3\) is similar to that of the same moiety in
complexes 52·CH₂Cl₂, 57·CH₂Cl₂ and 58·CH₂Cl₂, the structure of 59·CHCl₃ is not isostructural with the structures of the three latter complexes.

Figure 24. Perspective view of 59. H atoms have been omitted for clarity. The position trans to P₂ is disordered with Cl and Me.

The different trans influence of the Me group and Br ion is also clearly seen in 59·CHCl₃. Thus, the Pd–P₂ bond trans to Me/Cl is clearly longer (0.1 Å) than the Pd–P₁ bond trans to Br, and, as a consequence, the P₁–Pd–P₂ angle is smaller in 59·CHCl₃ than in 57·CH₂Cl₂ and 58·CH₂Cl₂. Another marked difference between 59·CHCl₃ and the three isostructural complexes is in the conformation of the molecules. In 59·CHCl₃ the dihedral angle ω is 32.38(13)°, while in 52·CH₂Cl₂, 57·CH₂Cl₂ and 58·CH₂Cl₂ the angles are 6.36(6)–6.72(10)°.
2.2.3 Characterisation of the PtCl$_2$ complex of 1,2-bis(diisopropylphosphino)-1,2-dicarba-closododecaborane

Co-ordination of the isopropyl ligand 51 to PtCl$_2$ does not induce any major changes in the co-ordination sphere relative to the corresponding PdCl$_2$ complex 53·CHCl$_3$. The M−Cl distances are equal within experimental errors, and the M−P distances are equal or close to equal.

X-ray structure analysis reveals that the asymmetric unit of the PtCl$_2$ complex 54·CH$_2$Cl$_2$ is formed of two [PtCl$_2$(1,2-(P$i$Pr$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$)] complex units [labelled 54A and 54B] (Figure 25) and one disordered dichloromethane solvent molecule. The complex units have fairly similar co-ordination spheres, as expected. The C$_c$−C$_c$ distances in 54A and 54B agree well with the distances in other o-carborane complexes synthesised in this work. A difference in the P2−Pt−P1 angle values is found between 54A and 54B, however.

**Figure 25. Molecular views of 54A and 54B. H atoms have been omitted for clarity.**

Two other notable differences appear between 54A and 54B. Crystallographic symmetry for both complex units is C$_1$, but unit 54B is more symmetric, adopting approximate C$_s$ symmetry with the pseudo mirror plane perpendicular to the co-ordination plane and passing through the atoms Pt1b, B3b, B6b, B8b and B10b. In 54A mutual orientations of the iPr groups are markedly different. The second molecular feature of interest in 54A and 54B is the marked difference in the dihedral angle $\omega$: the angle is clearly larger in 54B than in 54A [28.1(2)
versus 11.7(6°)]. Thus, the dihedral angle ω varies considerably with the phosphorus atoms acting as hinges. Since, in the case of the solution chemistry, the dihedral angles ω are close to 0°, it may be that in solution the energy barrier between reciprocal conformers is low, as was found for 55·CH₂Cl₂ and 56. Thus, in solution these conformers can be expected to average to a complex where the Cₓ, P, Pt and Cl atoms lie in a plane, resulting in average C₂ᵥ symmetry for the molecule. The 2:2:6 pattern in the ¹¹B NMR spectra confirms this.

Comparison of 54A and 54B with PtCl₂ complexes having an ethane backbone reveals some differences. The Pt–P bond lengths are slightly shorter in 54A and 54B than in [PtCl₂(19)]¹⁰²a, but they are equal within experimental errors or nearly equal to those in [PtCl₂(36)].¹⁰²b The Pt–Cl bond lengths are close to equal in 54A, 54B, [PtCl₂(19)] and [PtCl₂(36)].

The 3¹P{¹H} NMR spectra of the platinum complexes are characterised by the presence of satellite peaks due to ¹⁹⁵Pt–³¹P coupling. As one third of the Pt nuclei are ¹⁹⁵Pt having a spin of 1/2 and two thirds are ¹⁹⁶Pt having no spin, there are three lines with an intensity ratio ca. 1:4:1 in the spectrum. The satellite peaks are clearly seen in the 3¹P{¹H} NMR spectrum of 54 in Figure 26. The coupling constant ¹Jₚt–ₚ = 3617 Hz agrees well with the values of 3594 and 3583 Hz for [PtCl₂(6)] and [PtCl₂(28)], respectively.⁶⁴,⁶⁶

Figure 26. The 3¹P{¹H} NMR spectrum of 54.
2.3 Co-ordination chemical shifts of 1,2-diphosphines

Phosphorus-31 NMR is an excellent probe for molecules containing phosphorus: the $^{31}P$ nucleus is 100% naturally abundant and has a large magnetic moment. These features make $^{31}P$ NMR a more sensitive technique than $^{13}C$ NMR.$^{61b}$

The differences between organic diphosphines and $o$-carboranyldiphosphines can easily be examined in symmetric PdCl$_2$ complexes. These complexes are suitably compared because only one isomer is possible and several examples of complexes with organic diphosphines are available in the literature. Furthermore, symmetric [PdCl$_2$(P–P)] complexes generate only one $^{31}P$ NMR resonance.

1,2-Bis(diphenylphosphino)-1,2-dicarba-closo-dodecaborane (33) and 1,2-bis(diisopropylphosphino)-1,2-dicarba-closo-dodecaborane (51) ligands can be compared with the comparable organic ligands 1,2-bis(diphenylphosphino)ethane (6), 1,2-bis(diisopropylphosphino)ethane (7), 1,2-bis(diphenylphosphino)benzene (29) and 1,2-bis(diisopropylphosphino)benzene (28), which contain ethane and benzene backbones. The rigidity of the cluster makes the chelating sites of 33 and 51 more similar to the chelating sites in 29 and 28 than to those in 6 and 7. Comparison of the X-ray diffraction analyses of [PdCl$_2$(6)] and [PdCl$_2$(28)] shows, however, that there are no major structural deviations in the neighbourhood of the metal.$^{61a,64}$

Table 7 compares two sets of data, the first for diphosphines with electron-withdrawing groups (Ph) and the second for diphosphines with electron-donating groups (iPr) on phosphorus atoms. The backbone varies in the same way in the two sets: ethane, benzene and $o$-carborane.

The $\delta$ values range widely, but comparison of the co-ordination chemical shift (ccs) values [ccs = $\delta$(Complex) – $\delta$(Ligand)]$^{110}$ shows interesting trends. Although the ccs values for the first set are fairly similar, at 70–78 ppm, the value of 6 (ethane) and 29 (benzene) are almost identical, while value for 33 ($o$-carborane) is lower. For the second set the difference in the ccs values for ethane/benzene and $o$-carborane is pronounced.

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Table 7. $^{31}\text{P}^{1}{H}$ NMR chemical shift and ccs data for ligands and PdCl$_2$ complexes of diphosphines with electron-withdrawing (Ph) (6, 29, 33) and electron-donating (Pr) groups (7, 28, 51), in ppm. ccs = δ(Complex) – δ(Ligand). The backbone in the two sets of 1,2-diphosphines is, downwards, ethane, benzene and o-carborane.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>δ(Ligand)</th>
<th>δ(Complex)</th>
<th>ccs</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>–13.2</td>
<td>64.2</td>
<td>77.4</td>
<td>64, 111</td>
</tr>
<tr>
<td>29</td>
<td>–13.6</td>
<td>64.4</td>
<td>78.0</td>
<td>112, 72b</td>
</tr>
<tr>
<td>33</td>
<td>7.73</td>
<td>78.3</td>
<td>70.6</td>
<td>113, I</td>
</tr>
<tr>
<td>7</td>
<td>9.4</td>
<td>100.7</td>
<td>91.3</td>
<td>114, 65</td>
</tr>
<tr>
<td>28</td>
<td>–5.3</td>
<td>92.3</td>
<td>97.6</td>
<td>64</td>
</tr>
<tr>
<td>51</td>
<td>32.8</td>
<td>69.1</td>
<td>36.3</td>
<td>101, I</td>
</tr>
</tbody>
</table>

As the ccs value is a measure of the bonding capacity of the diphosphines in a similar group of ligands, the larger the ccs value the stronger is the chelating bond. Thus, 33 and 51 are weaker co-ordinating ligands than 29 and 28, and 29 and 28 are comparable to 6 and 7 with ethane backbones. This result is as expected on the basis of the strong electron-withdrawing capacity of the o-carboranyl moiety.

2.4 Polymerisation tests

PdCl$_2$ complexes 52 and 53 and PdClMe complexes 55 and 56 were tested in the polymerisation of ethylene. Tests were carried out in a 100 ml Büchi glass reactor at 0–50°C in ethylene pressure of 10 bars. As co-catalyst was used 800 equivalents of methylaluminoxane (MAO) or 40 equivalents of diethylaluminum chloride on its own or with one equivalent of trityl tetrakis(pentafluorophenyl)borate. No polymer was obtained.

A further set of tests was carried out with [PdClMe(cod)] and 1,2-diphosphino-o-carboranes 33 and 51 at 20 and 55 °C for 1 to 23 hours. The co-catalyst was as described above. Oligomers were detected by gas chromatography analysis of the reaction mixture only in one case (40 equiv. diethylaluminum chloride/ 55°C/ 6 h). The products obtained were essentially internal and/or branched olefins; linear α-olefins represented only 15% of the total amount of products. No reaction was observed in the polymerisation of 1-hexene.
Complexes 52, 53, 55 and 56 were also tested for the Kharasch addition of carbon tetrachloride to methyl methacrylate and styrene.\textsuperscript{40,115} Instead of the expected addition products polymer formation was observed.\textsuperscript{vii} The molecular weights of the polymers, poly(methyl methacrylate) and polystyrene, were ca. 33000–87000 and 1200–1800, respectively, and the polydispersity index was about 1.5–1.6 for both.

The activities of $o$-carboranyldiphosphine complexes 52, 53, 55 and 56 in radical polymerisation of methyl methacrylate were compared with the activities of the simple palladium complexes 60-65 shown in Figure 27.\textsuperscript{116} Polymer yields were higher with PdClMe complexes 55, 56 and 65 than with PdCl$_2$ complexes 52, 53 and 60-64. Polymer yields were also higher with phenyl-containing than with i-propyl-containing catalysts. Interestingly, $o$-carboranyl complex 52 was more active than the related chelate complexes 63 and 64. One reason for this enhanced activity may be related to the bite angles. Comparison of the bite angles of the three complexes shows the bite angle of 52 [92.44(5)$^\circ$] to fall between the bite angles of 63 [85.82(7)$^\circ$]\textsuperscript{61a} and 64 [97.98(4)$^\circ$]\textsuperscript{117}. Evidently, then, the bite angle of 52 is more optimal for polymerisation of methyl methacrylate, while the angles of the other two complexes are too small (63) and too large (64).

![Figure 27](image)

\textit{Figure 27.} Pd(II) complexes whose activities were compared with those of complexes 52, 53, 55 and 56.
2.5 Quantum chemical calculations

The nature of the C–C bonding in 1,2-dicarba-closo-dodecaborane derivatives has received only limited attention (at least from the computational point of view), even though distances ranging from 1.634(3) to 1.858(5) Å have been observed in experimental studies.\textsuperscript{104a} These distances are clearly longer than expected for a covalent C–C single bond, 1.530(15) Å.\textsuperscript{118} To study the C–C bonding modes in o-carboranes, geometry optimisations were carried out for the series of compounds illustrated in Figure 28.\textsuperscript{VI} DFT was applied to optimise the structures of differently C-substituted 1,2-dicarba-closo-dodecaboranes at the B3LYP/6-31G* level of theory.

![Figure 28. Optimised compounds. Unmarked vertices are BH.](image)

The structure optimisations produced geometries close to the experimental values. The geometrical parameters show unmistakenly that the substituent at carbon considerably influences the C–C distance, agreeing very well with the earlier results of crystal structure analyses.\textsuperscript{104a} The X–C–C angle and X–C–C–X torsion angle vary slightly with the substituent.

To obtain insight into the nature of the interaction in the C–C bonds in the optimised compounds, topological analysis based on AIM theory\textsuperscript{119} was carried out for the charge densities.\textsuperscript{VI} Special emphasis was laid on the parameters at the bond critical points lying
between the cage carbon atoms. The meaning of the different characteristic parameters is discussed in reference 120.

Ellipticity, charge density and its Laplacian and electronic energy density of the bond critical points were calculated for each C–C bond at the B3LYP/6-31G* level of theory. As seen in Figure 29, there is a strong correlation between the electronic energy density and the C–C distance. When the C–C distance increases, the electronic energy density concomitantly becomes less negative. Also, the electronic charge density decreases accordingly.

The ellipticity values deviate noticeably from zero. Although this normally indicates double bond character, in the present compounds the bond lengths are clearly too long and the electron energy densities too small to support double bonding. Instead, in this case the ellipticity values describe a curvilinear behaviour for the C–C bonding. Correlation between ellipticity values and C–C distances means that the bonding is increasingly curved as the C–C distance increases.

Figure 29. Scatter plot of C–C distance vs. electronic energy density at the respective bond critical points for optimised compounds with X and PH₃/SH substituents.
The calculated AIM parameters at the bond critical points of the C−C bonds clearly indicate attraction between the carbon atoms despite the long C−C distances. However, there is marked charge depletion at the bond critical point upon increase of the C−C distance. The substituents have a great impact on the C−C distance and simultaneously on the bonding properties.

Structure optimisations by DFT methods for the simplified 1,2-(PH2)2-1,2-C2B10H10 ligand (66) and its PdCl2 complex were carried out to study the effect of co-ordination and to gain insight into the electronic properties. Comparison of the results of theoretical calculations on 66 and [PdCl2(66)] with the results of X-ray analyses of 33 and 51, revealed noticeable trends. Shortening of the C−C bond upon complexation was indicated by both methods. Concomitant closing of the P−C−C angles was found for the optimised structures but was not apparent in the X-ray results. Also the changes in P−C−C−P torsion angles upon complexation showed different trends. Theoretical results for the PH2 ligand showed the P−C−C−P angle to change only slightly upon complexation, with most of the angle values close to 0°. The experimental X-ray results for ligands 33 and 51 bearing bulky PPr2 and PPh2 substituents at the cluster carbons showed the angle values to deviate markedly from 0°, as described above, and the angle decreases upon complexation close to 0°. These findings can be understood in terms of the different size of substituents at the cluster carbons. Probably all the geometrical parameters in a P−C−C−P fragment are dependent on one another and vary with the substitution at the cluster carbons and with complexation.

AIM analyses were carried out for the P−C and C−C bonds in 66 and [PdCl2(66)] to study the electronic properties. Both charge density and electronic energy density at the bond critical point indicate that the P−C bond becomes stronger upon complexation. This strengthening is seen as a trend in bond shortening in the experimental structures. The bonds also become more covalent, which appears in the decrease of the Laplacian values. Only minor changes are seen in the values of the C−C bond, although shortening of the bond occurs during complexation. Clearly the interaction is very weak. Indeed, the values at the respective bond critical points are in accordance with this. Even significant changes in C−C bond distances do not result in marked changes in the bonding properties.
For comparison, optimisations were also carried out for 1,2-diphosphinoethane and its \( \text{PdCl}_2 \) complex.\(^V\) Marked changes occur in the \( \text{P}^{\ldots}\text{C}^\cdot\text{C}^\cdot\text{P} \) angle and the \( \text{P}^\ldots\text{C}^\cdot\text{C}^\cdot\text{P} \) torsion angle upon complexation. The \( \text{C}^\cdot\text{C} \) bond length remains essentially the same, but the \( \text{P}^\ldots\text{C} \) bond length displays slight shortening upon complexation. This trend is seen in both the experimental and computed moieties.

3. CONCLUSIONS

In a search for \textit{closo}-complexes that might act as catalysts in polymerisation reactions, ligands 1,2-bis(diphenylphosphino)-1,2-dicarba-\textit{closo}-dodecaborane and 1,2-bis(diisopropylphosphino)-1,2-dicarba-\textit{closo}-dodecaborane were complexed with Pd(II) and Pt(II). Six novel complexes were synthesised and characterised: \([\text{PdCl}_2(1,2-(\text{PiPr}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\), \([\text{PtCl}_2(1,2-(\text{PPr}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\), \([\text{PdClMe}(1,2-(\text{PPr}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\), \([\text{PdClMe}(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\) and a mixture of \([\text{PdBrMe}(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\) and \([\text{PdBrCl}(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\). As well, the structures of three previously known compounds, \([\text{PdCl}_2(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\) and \([\text{PdBr}_2(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\), and two partially disordered structures, \([\text{PdBr}_{1.133}\text{Cl}_{0.867}(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\) and \([\text{PdClMe}(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\), were solved. X-ray analyses confirmed as expected, that 1,2-diphosphino-\textit{o}-carboranes co-ordinate to the metal bidentately through the two \( \text{P} \) atoms, while the ancillary ligands complete the slightly distorted square-planar co-ordination around the metal. Dihedral angles \( \omega \) vary markedly, with the \( \text{P} \) atoms acting as hinges. X-ray results also showed that complexation of 1,2-diphosphino-\textit{o}-carborane ligands with Pd(II) and Pt(II) metals induces changes in the \( \text{C}_c^\cdot\text{C}_c \) bond length and in the \( \text{P}_1^\ldots\text{C}_c^\cdot\text{C}_c^\cdot\text{P}_2 \) torsion angle.

Results of structure optimisations agreed very well with the earlier results of crystal structure analyses, confirming that different substituents at \( \text{C}_c \) atoms effect wide variation in the \( \text{C}_c^\cdot\text{C}_c \) bond distance. As the \( \text{C}_c^\cdot\text{C}_c \) distance increases from 1.625 to 1.882 Å, the bonding nature changes from covalency \textit{via} protocovalency into closed-shell interactions. Structure optimisations of \( \text{PdCl}_2 \) complex with \textit{o}-carborane backbone indicated that the plasticity of the five-membered chelate ring is steered by the atoms or groups connected to phosphorus. Plasticity is seen in variance of the \( \text{C}_c^\cdot\text{C}_c \) bond lengths, \( \text{P}^\ldots\text{C}_c^\cdot\text{C}_c^\cdot\text{P} \) angles and \( \text{P}^\ldots\text{C}_c^\cdot\text{C}_c^\cdot\text{P} \).
torsion angles. Plasticity of the P–C_O–C_O–P fragment would probably be an advantage for a Pd(II) catalyst.

To date, only o-carborane derivatives that have shown catalytic activity in polymerisations are complexes with 7,8-dicarba-nido-undecaborate(-1) cage. Preliminary results of polymerisation tests with \([\text{PdCl}_2(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\), \([\text{PdCl}_2(1,2-(\text{PPr}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\), \([\text{PdClMe}(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\) and \([\text{PdClMe}(1,2-(\text{PPr}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\) complexes are promising, showing that closo carborane complexes, too, can act as catalysts. \([\text{PdCl}_2(1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10})]\) is even more active in radical polymerisation of methyl methacrylate than are the related PdCl\(_2\) chelate complexes containing 1,2-bis(diphenylphosphino)ethane and 1,1’-bis(diphenylphosphino)ferrocene ligands. Understanding of the reaction mechanism and the specificity of the polymerisation catalysed with complexes of this work promises to shed new light on carborane catalysts and could suggest new directions for the development of carborane complexes.

Much work has been done on o-carborane since its synthesis in the early 1960’s. Major industrial applications remain to be developed, but without a doubt, they will come, sooner or later, and only our imagination is the limit in seeking new applications and derivatives. It is hoped that this work has pushed the frontiers of boron science a little bit forward.
REFERENCES

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10. For an extensive review of carboranes other than C2B10H12, see ref. 8.


50. Ref. 47a, Table 10.


98. Cambridge Structural Database, October 2001 version.


