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Structural characterisation of cationic methylallyl, methylindenyl and pentamethylcyclopentadienyl nickel complexes containing the bulky phosphine 1,2-bis(diisopropylphosphino)ethane†

Manuel Jiménez Tenorio, M. Carmen Puerta,* Isabel Salcedo and Pedro Valerga

Departamento de Ciencia de Materiales e Ingeniería Metalúrgica y Química Inorgánica,
Facultad de Ciencias, Universidad de Cádiz, Apartado 40, 11510 Puerto Real, Cádiz, Spain.
E-mail: carmen.puerta@uca.es

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A novel high-yield, convenient synthetic method for the complex [Ni(COD)$_2$] has been developed based upon the use of dibutylmagnesium as reducing agent. The cationic complexes [Ni(η^3-CH$_2$C(R)CH$_2$)(dippe)][BPh$_4$] (R = Me **1a** or H **1b**; dippe = Pr$^i_2$PCH$_2$CH$_2$PPr$^i_2$) were obtained by reaction of [Ni(COD)$_2$] with BrCH$_2$C(R)=CH$_2$ in diethyl ether, followed by treatment with dippe and NaBPh$_4$ in methanol. [Ni(2-MeInd)(dippe)][BPh$_4$] **2** (2-MeInd = 2-methylindenyl) and [Ni(C$_5$Me$_5$)(dippe)][BPh$_4$] **3** were respectively prepared by reaction of either [Ni(2-MeInd)Br(PPh$_3$)] or [Ni(C$_5$Me$_5$)Br(PPh$_3$)] with dippe and NaBPh$_4$ in methanol. The crystal structures of **1a**, **2** and **3** were determined. All of the compounds show pseudo-square planar "two legged" piano stool structures. The methylallyl ligand in **1a** shows η^3 coordination as expected, whereas in **2** the occurrence of an allyl–ene distortion in the 2-methylindenyl ligand leads to an intermediate η^3/η^5 coordination mode. An intermediate allyl–ene/diene distortion is present in the C$_5$Me$_5$ ligand in **3**, although in this case a symmetrical η^5 coordination is observed. All compounds were also characterised in solution by NMR spectroscopy.

Introduction

Nickel π-allyl complexes are used as selective reagents in organic synthesis for the introduction of allyl units in carbon skeletons.[1,2] Over the past few years there has been considerable interest in the development of Ni-based polymerisation catalysts,[3] and in particular the ability of certain nickel allyl complexes to act as efficient catalysts for olefin polymerisation has been noted.[4–9] The catalytic activity of neutral nickel complexes can be increased dramatically by addition of organoaluminium halides or methylaluminoxane (AlMeO)$_n$ (MAO), as a result of an increase in the cationic character of the metal centre.[3,4,9] Thus, cationic allylnickel complexes are capable of acting as catalysts for the oligomerisation and polymerisation of alkenes without the use of additional Lewis acids. It appears that cationic coordinatively unsaturated nickel compounds, containing one or more weakly bound ligands, and with steric congestion around the metal are potential catalysts for olefin polymerisation. Allylnickel complexes bearing bulky phosphine ligands comply with these conditions. Very recently, several neutral and cationic nickel indenyl derivatives have been reported.[10–15] Given the existing relationship between allyl and indenyl complexes due to the so called "indenyl effect" (relatively facile ring slippage of the indenyl ligand involving change from η^5 to η^3 coordination), such species have also proven effective as catalysts for the oligomerisation of ethylene,[11] or even the polymerisation of phenylacetylene.[15] Nickel indenyl complexes can be considered as a link between η^5-cyclopentadienyl and η^3-allyl derivatives. However, compared to any of the latter species, their chemistry is very poorly developed, and is only now beginning to be studied in detail.[10] Continuing our work on transition metal complexes containing bulky phosphine ligands,[16] we have prepared and characterised a series of cationic allyl, 2-methylindenyl and η^5-pentamethylcyclopentadienyl nickel derivatives. The crystal structures of [Ni(η^3-CH$_2$C(Me)CH$_2$)(dippe)][BPh$_4$] **1a** (dippe = Pr$^i_2$PCH$_2$CH$_2$PPr$^i_2$), [Ni(2-MeInd)(dippe)][BPh$_4$] **2** (2-MeInd = 2-methylindenyl) and [Ni(η^5-C$_5$Me$_5$)(dippe)][BPh$_4$] **3** were determined. In this fashion we have been able to establish a systematic structural comparison of the changes produced around the metal centre when passing from η^3 to η^5 coordination.

Results and discussion

Preparation and spectral characterisation

The most general procedure for the preparation of η^3-allyl nickel complexes is the reaction of allyl halides with a source of Ni^0, the complex [Ni(COD)$_2$] being commonly used.[1] The preparation of [Ni(COD)$_2$] usually involves reduction of a nickel(II) complex in the presence of 1,5-cyclooctadiene. Manganese powder[17] or sodium[18] have been used as reducing agents. Usually, a rather long time is required for completion due to the heterogeneous nature of the reaction mixture. Furthermore, [Ni(COD)$_2$] is only isolated after a careful and often tedious work-up of the reaction mixture. We have introduced a modification which allows the preparation of [Ni(COD)$_2$] in a rapid and efficient way, and in good yields (70–80%), starting from the nickel pyridine complex [NiCl$_2$(py)$_4$].[19] The improved method is based on the use of dibutylmagnesium as homogeneous reducing agent, which considerably reduces the reaction time, and makes easier isolation of the desired compound (see Experimental section), eqn. (1). Presumably, an unstable

$$[\mathrm{NiCl_2(py)_4}] + 2\mathrm{COD} \xrightarrow[\mathrm{THF},\ -80\ ^\circ\mathrm{C}]{\mathrm{Bu_2Mg}} [\mathrm{Ni(COD)_2}] \quad (1)$$

nickel dibutyl complex is formed first. This undergoes reductive elimination of octane generating in this way Ni^0, which is trapped by COD in the form of [Ni(COD)$_2$].

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† Dedicated to Professor D. Rafael Usón, on the occasion of his 75th birthday, as recognition of his outstanding contribution to the development of Organometallic Chemistry in Spain.

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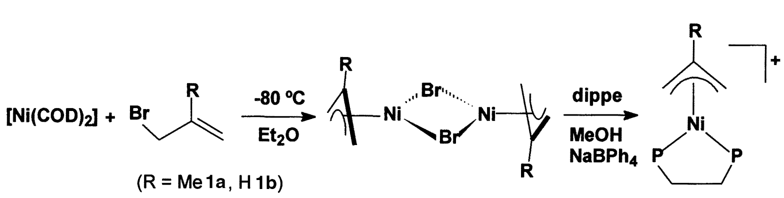
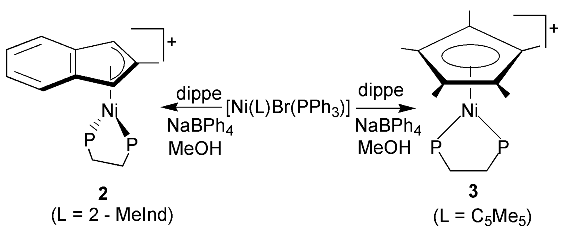


(2)

The reaction of [Ni(COD)$_2$] with 2-methylallyl bromide or allyl bromide in diethyl ether affords the corresponding η^3-allyl dimeric species [{Ni(η^3-CH$_2$C(R)CH$_2$)(μ-Br)}$_2$] (R = Me or H),[1] which are cleaved by addition of dippe in MeOH. Treatment with NaBPh$_4$ afforded the yellow cationic complexes [Ni(η^3-CH$_2$C(R)CH$_2$)(dippe)][BPh$_4$] (R = Me **1a** or H **1b**), eqn. (2).

The complexes [Ni(2-MeInd)(dippe)][BPh$_4$] **2** and [Ni(η^5-C$_5$Me$_5$)(dippe)][BPh$_4$] **3** were respectively obtained by reaction of either [Ni(2-MeInd)Br(PPh$_3$)] or [Ni(C$_5$Me$_5$)Br(PPh$_3$)] with dippe and NaBPh$_4$ in MeOH at room temperature, eqn. (3).



(3)

The use of a halide scavenger, *e.g.* Ag$^+$, was found unnecessary for the preparation of **2** and **3**, at variance with the method used for the synthesis of the cationic derivatives [Ni(1-MeInd)(PPh$_3$)(PR$_3$)]$^+$ (R = Ph or Me).[11] All compounds are diamagnetic, and display one singlet in their ^{31}P-{^{1}H} NMR spectra. Apart from some signal broadening, no further change is observed when the NMR spectra of any of the cationic compounds reported in this work are recorded at temperatures as low as −80 °C. The *syn* and *anti* protons of the methylallyl ligand in **1a** appear as two separate singlet resonances at δ 2.46 and 4.21 respectively in the ^{1}H NMR spectrum. The protons of the allyl ligand in **1b** give two resonances: one doublet (4H) and one quintet (1H), corresponding to an AX$_4$ spin system. No decoalescence of the *syn* and *anti* protons occurs when the temperature is lowered. This suggests a very low energy barrier for the *syn*/*anti*-H exchange, usually associated with changes from η^3 to η^1 coordination in the allyl ligand, which renders them equivalent.

The ^{1}H NMR spectrum of compound **2** exhibits a single resonance at δ 5.97 for the protons attached to the C$_5$ ring of the 2-methylindenyl ligand, indicative of C_s symmetry. ^{13}C-{^{1}H} NMR data are useful for assessing indenyl hapticity in complexes,[12] in particular the parameter $\Delta\delta$. This parameter represents the difference in chemical shift between the ^{13}C-{^{1}H} NMR resonances of the ring-junction carbon atoms in an indenyl complex and in "free" indenyl (*i.e.* sodium indenyl). If $\Delta\delta \ll 0$ ppm η^5 hapticity is expected, whereas $\Delta\delta \gg 0$ ppm indicates η^3 hapticity, with the indenyl ligand attached in an allyl-like fashion.[20] In case of **2**, $\Delta\delta \approx -8$ ppm at 298 K. This is consistent with an intermediate η^3/η^5 hapticity, which can be rationalised in terms of slip–fold distortions away from the η^5 coordination mode for the 2-methylindenyl ligand.[21]

The ^{1}H and ^{13}C-{^{1}H} NMR spectra of compound **3** are very simple, and correspond to a species having C_{2v} symmetry, with typical η^5 coordination for the C$_5$Me$_5$ ligand. Only four resonances are observed for the phosphine carbon atoms in the ^{13}C-{^{1}H} NMR spectrum, whereas the carbon atoms of the C$_5$ ring appear as one singlet at δ 104.6.

Solid state structures

The crystal structures of compounds **1a**, **2** and **3** were determined. Relevant bond lengths and angles are listed in Tables 1, 2 and 3. ORTEP[22] views of the complex cations are shown in Figs. 1, 2 and 3 respectively. The three compounds display pseudo square planar "two legged" piano stool structures. The P(1)–Ni(1)–P(2) angles are close to 90°, with Ni–P bond distances 2.15–2.18 Å, in the range observed for other nickel–dippe complexes.[16,23] The relative orientations of the isopropyl groups of the dippe ligands are very similar in the three complexes.

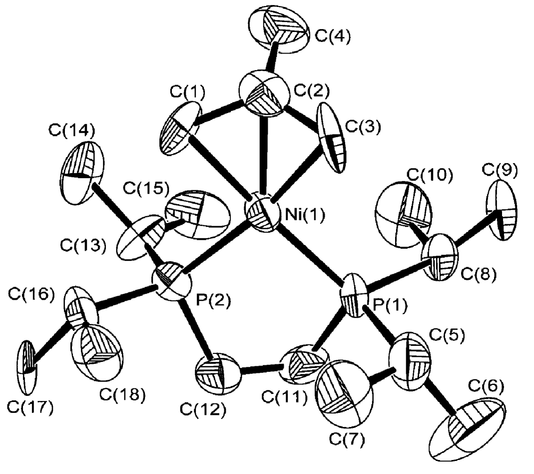


Fig. 1 ORTEP drawing (50% probability thermal ellipsoids in all cases) of [Ni(η^3-CH$_2$C(CH$_3$)CH$_2$)(dippe)]$^+$. H atoms are omitted.

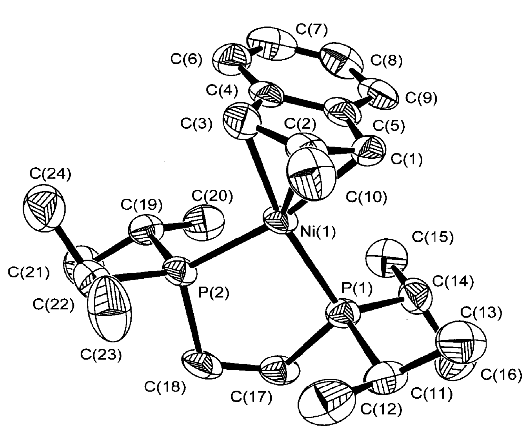


Fig. 2 ORTEP drawing of [Ni(2-MeInd)(dippe)]$^+$.

In the case of compound **1a** (Table 1) the C(1)–C(2) and C(2)–C(3) bond lengths in the methylallyl ligand correspond to a bond order intermediate between single and double. The Ni(1)–C(1), Ni(1)–C(2) and Ni(1)–C(3) separations are very similar, pointing to a symmetrical η^3 coordination, and comparing well with the dimensions found for other methylallyl nickel complexes.[7] The dihedral angle formed by the plane containing the atoms P(1)–Ni(1)–P(2) and that containing C(1)–C(2)–C(3) is 61.4(2)°.

In compound **2** (Table 2) nickel is bonded to the C$_5$ ring of the 2-methylindenyl ligand. The bond distances Ni(1)–C(1), Ni(1)–C(2) and Ni(1)–C(3) are only slightly longer than those found in the methylallyl complex **1a**. The Ni(1)–C(4) and Ni(1)–C(5) separations are *ca.* 0.25 Å longer, in the limit considered for a Ni–C bond. The C–C bond distances within the C$_5$

Table 1 Selected bond lengths (Å) and angles (°) for [Ni(η^3-CH$_2$C(CH$_3$)CH$_2$)(dippe)][BPh$_4$] **1a** with estimated standard deviations in parentheses

Ni(1)–C(1)	2.03(2)	Ni(1)–C(2)	2.01(2)
Ni(1)–C(3)	2.00(2)	Ni(1)–P(1)	2.156(5)
Ni(1)–P(2)	2.147(5)	C(1)–C(2)	1.43(2)
C(2)–C(3)	1.37(3)	C(2)–C(4)	1.51(3)
P(1)–Ni(1)–P(2)	90.6(2)	C(1)–C(2)–C(3)	116(2)

Table 2 Selected bond lengths (Å) and angles (°) for [Ni(2-MeInd)(dippe)][BPh$_4$] **2** with estimated standard deviations in parentheses

Ni(1)–C(1)	2.092(9)	Ni(1)–C(2)	2.066(9)
Ni(1)–C(3)	2.03(1)	Ni(1) ··· C(4)	2.298(9)
Ni(1) ··· C(5)	2.30(1)	Ni(1)–P(1)	2.153(3)
Ni(1)–P(2)	2.174(3)	C(1)–C(2)	1.42(1)
C(2)–C(3)	1.40(2)	C(3)–C(4)	1.38(2)
C(4)–C(5)	1.43(2)	C(1)–C(5)	1.49(1)
C(2)–C(10)	1.47(1)		
P(1)–Ni(1)–P(2)	90.36(10)	FA/°	10.0(11)
HA/°	10.3(12)	ΔM–C/Å	0.24

Table 3 Selected bond lengths (Å) and angles (°) for [Ni(η^5-C$_5$Me$_5$)(dippe)][BPh$_4$] **3** with estimated standard deviations in parentheses

Ni(1)–C(1)	2.177(9)	Ni(1)–C(2)	2.120(8)
Ni(1)–C(3)	2.160(8)	Ni(1)–C(4)	2.141(8)
Ni(1)–C(5)	2.16(1)	Ni(1)–P(1)	2.180(2)
Ni(1)–P(2)	2.186(2)	C(1)–C(2)	1.45(1)
C(2)–C(3)	1.41(1)	C(3)–C(4)	1.46(1)
C(4)–C(5)	1.46(1)	C(1)–C(5)	1.36(1)
P(1)–Ni(1)–P(2)	89.58(9)		

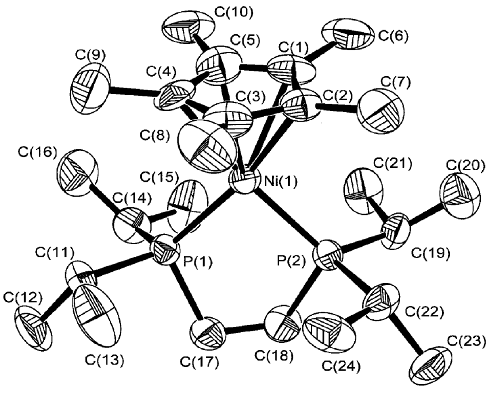
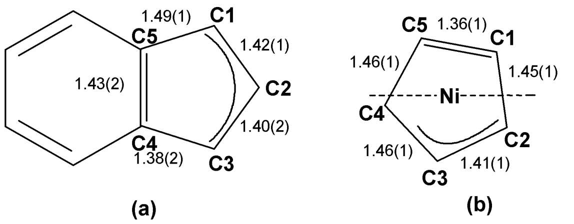


Fig. 3 ORTEP drawing of [Ni(η^5-C$_5$Me$_5$) (dippe)]$^+$.

ring are rather irregular. The C(1)–C(2), C(2)–C(3) and C(4)–C(5) separations, as well as C(3)–C(4), suggest an intermediate bond order between single and double, whereas C(1)–C(5) is longer. In fact, the value of 1.49(1) Å found for C(1)–C(5) corresponds to a single C–C bond. Thus, the nickel atom appears slipped towards the carbon atoms C(1), C(2) and C(3) of the ring. This pattern of variations in bond distances has recently been observed in other indenyl[10] and 1-methylindenyl[11–15] nickel complexes, and has been explained in terms of an allyl–ene distortion in the indenyl ligand (Scheme 1, (a)). Such distortion, often referred to as slip–fold, is present to more or less extent in all indenyl complexes structurally characterised.[10] The distortion in the 2-methylindenyl ligand can be quantified by calculating parameters such as the hinge angle (HA), folding angle (FA) and slip value (ΔM–C), as a measure of the degree of slip–fold distortion (Table 2).[24] In our case, HA = 10.3(12)°, FA = 10.0(11)°, and ΔM–C = 0.24 Å. These parameters compare well with the values found for other indenyl and 1-methylindenyl nickel complexes, and indicate that the 2-methylindenyl ligand in **2** has an intermediate η^3/η^5 hapticity in the solid state, consistent with NMR data regarding its structure in solution. The plane defined by the atoms P(1)–Ni(1)–P(2) and C(1)–C(2)–C(3) form a dihedral angle of 82.8(10)° in compound **2**, a value much closer to perpendicularity than the 61.4(2)° found for the same dihedral angle in the case of the η^3-methylallyl complex **1a**.



Scheme 1 Comparative diagram showing allyl–ene distortions in: (a) the 2-Methylindenyl ligand in **2**; (b) the pentamethylcyclopentadienyl ligand in **3** (intermediate allyl–ene/diene distortion).

The structure of the cation [Ni(η^5-C$_5$Me$_5$)(dippe)]$^+$ in compound **3** (Table 3) resembles very much that of the 16-electron iron derivative [Fe(η^5-C$_5$Me$_5$)(dippe)]$^+$.[25] The least-squares plane defined by the atoms of the C$_5$ ring of the C$_5$Me$_5$ ligand forms a dihedral angle of 88.1(4)° with the plane defined by the atoms P(1)–Ni(1)–P(2). At variance with compound **2**, the nickel atom is not "slipped" with respect to the C$_5$Me$_5$ ligand. All the Ni–C separations are in the interval 2.12–2.18 Å, being in general longer than those found in the methylallyl complex **1a**. Close examination of the dimensions of the C$_5$ ring of the C$_5$Me$_5$ ligand revealed that distortions are also present in this case. Two types of distortions for C$_5$Me$_5$ groups in complexes of the type [Ni(C$_5$Me$_5$)L$_2$] have been reported.[20,26] One of them is allyl–ene distortion, similar to that described for complex **2**, in which two adjacent C–C bonds are short, and the C–C bond opposite these two bonds can be even shorter. The other is diene distortion, in which the C$_5$Me$_5$ ring has two non-adjacent, equally short C–C bonds. None of these structures involves a slipped C$_5$Me$_5$ ring. In our case an intermediate allyl–ene/diene distortion is observed (Scheme 1, (b)), similar to that present in the complexes [Ni(C$_5$Me$_5$)X(PEt$_3$)] (X = SC$_6$H$_4$Me or OMe).[26] This is consistent with the orientation of the carbon atoms of the C$_5$Me$_5$ ring with respect to the plane containing the atoms P(1)–Ni(1)–P(2), according to the model proposed by Andersen and co-workers.[26]

Interestingly, compounds **1a**, **1b** and **2**, but not **3**, catalyse reactions such as the oligomerisation of phenylacetylene and acetylene and the polymerisation of styrene. The detailed structural characterisation presented here will be useful for understanding the efficiency of these and other related species as catalysts for polymerisation reactions of alkynes and olefins. Such studies are currently being carried out, and results will be reported in due course.

Experimental

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk techniques. THF, Et$_2$O and light petroleum (boiling point range 40–60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. 1,2-Bis(diisopropylphosphino)ethane was obtained according to the literature.[27] [Ni(2-MeInd)Br(PPh$_3$)] and [Ni(C$_5$Me$_5$)Br(PPh$_3$)] were prepared by suitable adaptations of reported procedures,[10,28] whereas [Ni(COD)$_2$] was obtained by a modified method. Experimental details are given. IR spectra were recorded in Nujol mulls on a Perkin-Elmer FTIR Spectrum 1000 spectrophotometer, NMR spectra on Varian Unity 400 MHz or Gemini 200 MHz spectrometers. Chemical shifts are given in ppm from $SiMe_4$ (^{1}H and ^{13}C-{^{1}H}) or 85% H_3PO_4 (^{31}P-{^{1}H}). The protons of the phosphine alkyl substituent groups for all compounds appeared in the corresponding ^{1}H NMR spectra as a series of overlapping multiplets in the range δ 0.5–3, and were not assigned. Microanalyses were performed by the Serveis Científico-Tècnics, Universitat de Barcelona.

Preparations

[Ni(COD)$_2$]. To a solution of [$NiCl_2(py)_4$] (3.5 g, 7.8 mmol)[19] in tetrahydrofuran (20 ml), COD (3.6 ml, 23.4 mmol) was added. The mixture was cooled in a liquid N_2–ethanol bath, and dibutylmagnesium (15.6 ml of a 1 M solution in tetrahydrofuran, 15.6 mmol) added dropwise. Once the addition was finished the yellow-orange mixture was stirred for one hour at room temperature. Then the solvent was removed *in vacuo*. The residue was treated with methanol, and the yellow solids were filtered off using a coarse frit (number 1 or 2). The precipitate was washed several times with methanol until no colour was observed in the washing liquor. Afterwards, it was further washed with one portion of ethanol and one of light petroleum, and dried *in vacuo*. This crude product appeared to be pure enough for synthetic purposes. It can be recrystallised by repeated extractions with diethyl ether in the same frit, collecting the extracts in a Schlenk flask. Concentration and cooling to −20 °C afforded yellow crystals. Yield: 1.66 g, 80%.

[Ni(η^3-CH$_2$C(R)CH$_2$)(dippe)][BPh$_4$] (R = Me 1a or H 1b). To a slurry of [Ni(COD)$_2$] (0.54 g, 2 mmol) in diethyl ether (20 ml) cooled in a liquid N_2–ethanol bath, 3-bromo-2-methylpropene (for **1a**) or allyl bromide (for **1b**) was added (2 ml of a stock 1 M solution in diethyl ether, 2 mmol). The mixture was warmed to room temperature and stirred for one hour. During this time it changed from yellow to red. At this stage dippe (0.3 ml, 1 mmol) was added. The mixture was stirred for 15 minutes and then the solvent removed *in vacuo*. The residue was extracted with methanol. The orange-brown solution was filtered through Celite in order to remove finely divided black metallic nickel, not always but very often present in the reaction mixture. An excess of solid $NaBPh_4$ (*ca.* 0.4 g) was added to the filtered solution. The yellow or orange microcrystalline precipitate generated was filtered off, washed with ethanol and light petroleum and dried *in vacuo*. The complexes were recrystallised from acetone–ethanol. Data for **1a**: yield 0.52 g, 75% based on the amount of phosphine. Calc. for $C_{42}H_{59}BNiP_2$: C, 72.6; H, 8.49. Found: C, 72.4; H, 8.42%. NMR (CD_3COCD_3): ^{1}H, δ 1.68 (s, $CH_2C(C\mathit{H}_3)CH_2$); 2.46 (s, $C\mathit{H}^{syn}H^{anti}C(CH_3)C\mathit{H}^{syn}H^{anti}$); and 4.21 (s, $CH^{syn}\mathit{H}^{anti}C(CH_3)CH^{syn}\mathit{H}^{anti}$). ^{31}P-{^{1}H}, δ 85.9 (s); ^{13}C-{^{1}H}, δ 18.49, 18.56, 19.1, 19.5 (s, $P(CH(\mathit{C}H_3)_2)$); 23.5 (s, $CH_2C(\mathit{C}H_3)CH_2$); 21.75 (m, PCH_2); 26.26 (m, $P(\mathit{C}H(CH_3)_2)$); 63.7 (dd, $^2J_{CP} = 16.2$, $^2J_{CP'} = 3.4$ Hz, $\mathit{C}H_2C(CH_3)\mathit{C}H_2$); and 120.8 (s, $CH_2\mathit{C}(CH_3)CH_2$). Data for **1b**: yield 0.44 g, 65% based on the amount of phosphine. Calc. for $C_{41}H_{57}BNiP_2$: C, 72.3; H, 8.38. Found: C, 72.1; H, 8.39%. NMR (CD_3COCD_3): ^{1}H, δ 4.61 (d, $^3J_{HH} = 7.2$, $C\mathit{H}_2CHC\mathit{H}_2$) and 5.31 (q, $^3J_{HH} = 7.2$ Hz, $CH_2C\mathit{H}CH_2$); ^{31}P-{^{1}H}, δ 85.1 (s); ^{13}C-{^{1}H}, δ 18.6, 18.9, 19.3 (s, $P(CH(\mathit{C}H_3)_2)$); 21.4 (m, PCH_2); 26.1 (m, $P(\mathit{C}H(CH_3)_2)$); 63.5 (d, $^2J_{CP} = 12.2$ Hz, $\mathit{C}H_2CH\mathit{C}H_2$) and 115.3 (s, $CH_2\mathit{C}HCH_2$).

[Ni(2-MeInd)Br(PPh$_3$)]. To a solution containing 2-methylindene (2-MeIndH, 0.36 ml, *ca.* 2.7 mmol) in diethyl ether (100 ml), LiBu^n was added (1.7 ml of a 1.6 M solution in hexanes, *ca.* 2.7 mmol). The resulting solution of Li(2-MeInd) was then added to a slurry of [$NiBr_2(PPh_3)_2$] (3.77 g, *ca.* 5.1 mmol)[29] in diethyl ether (60 ml) at room temperature. A red colour immediately developed. The mixture was stirred for 12 h and filtered through Celite. The solvent was removed *in vacuo*, and the residue thoroughly washed with light petroleum (2 × 15 ml) in order to eliminate free PPh_3. Then the solids were extracted with toluene and the solution was filtered. Upon concentration and addition of light petroleum, a red precipitate of [Ni(2-MeInd)Br(PPh$_3$)] was obtained. It was filtered off, washed with light petroleum and dried. It was used without further purification. Yield 0.57 g, 40%, based on 2-methylindene. NMR (CD_3COCD_3): ^{1}H, δ 2.65 (s br, $H^{C(10)}$); 5.70, 6.08 (s br, $H^{C(1),\,C(3)}$) and 6.8–7.8, (m, $H^{C(6)–C(9)}$ + $P(C_6H_5)_3$); ^{31}P-{^{1}H}, δ 30.2 (s); ^{13}C-{^{1}H}, consists of very broad features.

NOTE: the numbering scheme used for the identification of the NMR signals for this compound, as well as for **2**, is based on the atom labelling of the 2-methylindenyl ring which appears on the ORTEP diagram shown in Fig. 2, and also in Scheme 1(a).

[Ni(2-MeInd)(dippe)][BPh$_4$] 2. To a solution of [Ni(2-MeInd)Br(PPh$_3$)] (0.53 g, 1 mmol) in methanol (20 ml), dippe (0.3 ml, 1 mmol) was added. The mixture was stirred for 12 h at room temperature. Addition of an excess of solid $NaBPh_4$ (*ca.* 0.4 g) yielded a red-orange precipitate, which was filtered off, washed with ethanol and light petroleum and dried *in vacuo*. Single crystals suitable for structure analysis were obtained by recrystallisation from dichloromethane–light petroleum. Yield: 0.5 g, 65%. Calc. for $C_{48}H_{61}BNiP_2\cdot CH_2Cl_2$: C, 75.1; H, 8.05. Found: C, 74.8; H, 7.98%. NMR (CD_3COCD_3): ^{1}H, δ 2.44 (s, $H^{C(10)}$); 5.97 (s, $H^{C(1)}$, $H^{C(3)}$), 7.12 (m, $H^{C(6)}$, $H^{C(9)}$) and 7.34 (m, $H^{C(7)}$, $H^{C(8)}$). ^{31}P-{^{1}H}, δ 95.0 (s); ^{13}C-{^{1}H}, δ 15.4 (s, C(10)); 17.8, 19.0, 19.2 (s, $P(CH(\mathit{C}H_3)_2)$); 21.2 (m, PCH_2); 27.3 (m, $P(\mathit{C}H(CH_3)_2)$); 78.2 (t, $^2J_{CP} = 4.5$ Hz, C(1), C(3)); 117.6 (s, C(2)); 119.2 (s, C(6), C(9)); 120.76 (s, C(4), C(5)) and 126.43 (s, C(7), C(8)).

[Ni(η^5-C$_5$Me$_5$)Br(PPh$_3$)]. To a solution containing pentamethylcyclopentadiene (C_5Me_5H, 0.41 ml, *ca.* 2.7 mmol) in diethyl ether (100 ml), LiBu^n was added (1.7 ml of a 1.6 M solution in hexanes, *ca.* 2.7 mmol). The resulting solution of $Li(C_5Me_5)$ was then added to a slurry of [$NiBr_2(PPh_3)_2$] (3.77 g, *ca.* 5.1 mmol) in diethyl ether (60 ml) at room temperature. A red colour gradually developed. The mixture was stirred for 12 hours, and filtered through Celite. The solvent was removed *in vacuo*, the residue washed with light petroleum (2 × 15 ml) and then extracted with toluene. Filtration followed by concentration and addition of light petroleum afforded a precipitate of [Ni(η^5-C$_5$Me$_5$)Br(PPh$_3$)]. It was filtered off, washed with light petroleum, dried and used without further purification. Yield: 0.58 g, 40%, based on pentamethylcyclopentadiene. NMR (CD_3COCD_3): ^{1}H, δ 1.30 (s, $C_5(CH_3)_5$); 7.45, 7.59, 7.85 (m, $P(C_6H_5)_3$); ^{31}P-{^{1}H}, δ 40.8 (s); ^{13}C-{^{1}H}, δ 9.42 (s, $C_5(\mathit{C}H_3)_5$); 104.1 (s, $\mathit{C}_5(CH_3)_5$); 128.1, 130.2, 135.1 (s, $P(C_6H_5)_3$).

[Ni(η^5-C$_5$Me$_5$)(dippe)][BPh$_4$] 3. To a slurry of [Ni(η^5-C$_5$Me$_5$)Br(PPh$_3$)] (0.53 g, 1 mmol) in methanol (20 ml), dippe (0.3 ml, 1 mmol) was added. A pale green colour immediately developed. The mixture was stirred for 1/2 hour at room temperature. Addition of an excess of solid $NaBPh_4$ (*ca.* 0.4 g) yielded a green microcrystalline precipitate, which was filtered off, washed with ethanol and light petroleum and dried *in vacuo*. It was recrystallised from a acetone–light petroleum. Yield: 0.46 g, 60%. Calc. for $C_{48}H_{67}BNiP_2$: C, 74.4; H, 8.65. Found: C, 74.1; H, 8.52%. NMR (CD_3COCD_3): ^{1}H, δ 1.86 (s, $C_5(CH_3)_5$); ^{31}P-{^{1}H}, δ 90.4 (s); ^{13}C-{^{1}H}, δ 11.4 (s, $C_5(\mathit{C}H_3)_5$); 18.5, 19.8 (s, $P(CH(\mathit{C}H_3)_2)$); 21.1 (m, PCH_2); 26.0 (m, $P(\mathit{C}H(CH_3)_2)$) and 104.6 (s, $\mathit{C}_5(CH_3)_5$).

Crystal structure determinations

Crystals suitable for X-ray diffraction analysis were mounted onto a glass fibre and transferred to an AFC6S-Rigaku automatic diffractometer (Mo-Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å). Crystal data and details on data collection and refinements are given in Table 4. The structures were solved by Patterson methods and subsequent expansion of

Table 4 Summary of crystallographic files for compounds **1a**, **2** and **3**

	1a	**2**	**3**
Formula	$C_{42}H_{59}BNiP_2$	$C_{48}H_{61}BNiP_2\cdot 0.83\ CH_2Cl_2$	$C_{48}H_{67}BNiP_2$
M	695.35	854.40	775.48
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a/Å	11.338(4)	13.252(3)	14.207(4)
b/Å	32.72(1)	16.619(4)	21.302(5)
c/Å	10.643(4)	10.964(5)	14.514(4)
α/°		100.65(2)	
β/°		105.09(3)	100.72(2)
γ/°		94.31(2)	
V/Å^3	3948(2)	2272(1)	4316(2)
Z	4	2	4
μ(Mo-Kα)/cm^{-1}	5.99	6.49	5.55
T/K	293	293	293
Measured reflections	3287	7090	6513
Unique reflections	3287 ($R_{int} = 0.000$)	6792 ($R_{int} = 0.116$)	6284 ($R_{int} = 0.032$)
Observed reflections ($I > 2\sigma_I$)	2306	4490	3700
$R1/wR2$ ($I > 2\sigma_I$)	0.093/0.279	0.102/0.297	0.081/0.252
(all data)	0.125/0.309	0.146/0.392	0.138/0.295

the models using DIRDIF.[30] For compound **1a** all non-hydrogen atoms in the cation were anisotropically refined. The remaining non-hydrogen atoms were isotropically refined. The absolute structure Flack parameter was 0.00(7). The occupation factor for the dichloromethane solvate molecule in **2** was refined to a value of 0.83, and this occupation was fixed in the course of the last refinement cycles. All the non-H atoms in this molecule were isotropically refined. The remaining non-H atoms, and all non-hydrogen atoms in **3**, were anisotropically refined. All hydrogen atoms were included at idealised positions, and allowed to ride on the parent carbon atoms. All calculations for data reduction and structure solution were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN[31] software system and full-matrix least-squares refinements were carried out by minimising $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL 97.[32]

CCDC reference number 186/2317.

See http://www.rsc.org/suppdata/dt/b0/b008441g/ for crystallographic files in .cif format.

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