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Journal of Organometallic Chemistry 587 (1999) 258–266

Journal of Organometallic Chemistry

Synthesis and characterization of Ni-, Pd- and Pt-complexes of functionalized, tripodal phosphine ligands

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Received 6 May 1999

Dedicated to Professor E. Lindner on the occasion of his 65th birthday.

Abstract

The tripodal ether, ester and cyano functionalized phosphine ligands (tdppcymome) (**a**), (tdppcyme) (**b**), and (tdppcycn) (**c**), respectively, of the cyclohexane backbone type *cis,cis*-1,3,5-$(PPh_2)_3$-1,3,5-$(R)_3$-C_6H_5 (tdppcyR) (with R = $-CH_2OCH_3$, $-COOCH_3$, $-CN$) are each treated with the cyclooctadiene complexes $M(COD)Cl_2$ (**1**, **2**) (M = Pt, Pd) and $NiCl_2$ (**3**). The potentially tridentate ligands form with these transition metals four-coordinated, bidentate dichloro complexes *cis*-$M^{II}(\eta^2$-tdppcyR)Cl_2 (**1a**–**c**, **2a**–**c**, **3a**–**c**), in which two diphenylphosphino donor groups are bound to the metal center, and one phosphorus remains uncoordinated. Treatment of the ether functionalized complex **1b** with $SnCl_2$ a bimetallic platinum tin complex *cis*-Pt(tdppcyme)Cl($SnCl_3$) (**1e**) is obtained. Detailed NMR investigations were undertaken to characterize structural properties. The platinum and palladium complexes have square-planar coordination geometries, whereas the nickel compounds show a different behavior with a temperature-dependent change from square-planar to tetrahedral arrangements. For Ni(tdppcyme)Cl_2 (**3b**) a single-crystal X-ray structure determination was performed which established the η^2-coordination of the phosphine ligand and the square-planar geometry of the nickel complex in the solid state. The cyclohexane backbone of the ligand prefers the boat conformation. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Tripodal phosphine; Nickel; Palladium; Platinum; X-ray

1. Introduction

Tertiary polyphosphines are favorite ligands in organometallic devices because of their steric and basic versatility over a wide range, which results from a specific variation of the carbon backbone and the substituents at the phosphorus [1–3]. Therefore, specially designed tripodal phosphines, as part of transition metal complexes with remarkable chemical behavior and unusual coordination geometries, play an important role in stoichiometric and catalytic reactions. We have recently reported on the preparation and characterization of tripodal phosphine ligands based on a cyclohexane backbone in which three diphenylphosphine groups, which are bound stereospecifically *cis,cis* to the 1,3,5 positions, coordinate in a tridentate way facially to metal fragments like Mo(0), Rh(I/III), and Ir(I/III) in an octahedral or five-coordinate ligand sphere [4–8]. The constraints given by the backbone lead to a specific coordination behavior of these ligands, generating a metal template {M(η^3-tripod)} of an adamantane type polyhedron with three P–M–P angles close to 90°. The opportunity to add other functional groups at the *ipso* positions of the cyclohexane ring offers the advantage of controlling the electron density at the metal center [9,10].

However, in the case of the d-block metals nickel, palladium, and platinum, frequently a bidentate coordination of only two phosphorus donors in a square-planar or pseudo-tetrahedral arrangement (with the occurrence of diamagnetism and paramagnetism) around the metal center is observed, whereas in the case of a potentially tridentate ligand the third phosphorus arm should remain uncoordinated [11]. Depending on

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[1] X-ray structure analysis.

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PII: S0022-328X(99)00331-9

the ligand backbone the latter is able to participate in an intramolecular exchange process with the two coordinated phosphine arms. Alternatively, the non-coordinated phosphine arm can also be used to bind to a second metal to build up homobimetallic or trimetallic complexes [12].

Phosphine complexes of the described kind were recognized as homogenous precursors in hydrogenation and hydroformylation catalysis with excellent activities, e.g. the platinum compounds are used with tin(II) salts as co-catalysts [13–18].

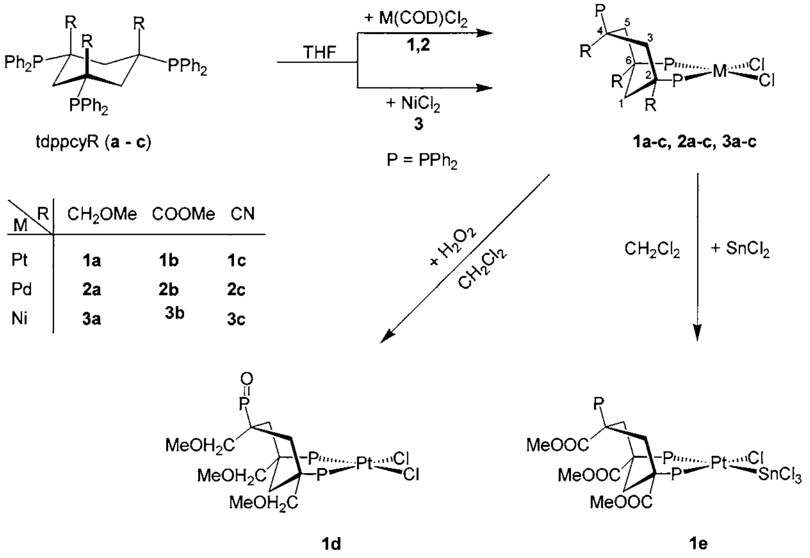
Therefore, it was of interest to investigate the coordination behavior of the tripod-ligands (tripod = *cis*, *cis*-1,3,5 - tris(diphenylphosphino) - 1,3,5 - tris(methoxymethyl)-cyclohexane (tdppcymome) (**a**), *cis*,*cis*-1,3,5-tris(diphenylphosphino) - 1,3,5 - tris(methoxycarbonyl) cyclohexane (tdppcyme) (**b**), *cis*,*cis*-1,3,5-tricyano-1,3,5-tris(diphenylphosphino)cyclohexane (tdppcycn) (**c**)) toward Ni(II), Pd(II), and Pt(II) which prefer square-planar or pseudo-tetrahedral coordination geometries leading to $M(\eta^2\text{-tripod})Cl_2$ dihalogen complexes. The structural and dynamic properties of these organometallic templates will be discussed.

2. Results and discussion

2.1. Synthesis and properties of the bidentate Pt(II), Pd(II), and Ni(II) phosphine complexes cis-M(η²-tdppcyR)Cl₂ (1a–d, 2a–c, 3a–c) and cis-Pt(η²-tdppcyme)Cl(SnCl₃) (1e)

When the platinum or palladium cyclooctadiene complexes $M^{II}(COD)Cl_2$ (**1**, **2**) or dehydrated $NiCl_2$ (**3**), respectively, are treated with equimolar amounts of the potentially tripodal ether, ester or cyano functionalized phosphine ligands tdppcymome (**a**), tdppcyme (**b**), or tdppcycn (**c**) in shortly before distilled and degassed THF at 20–70°C for 2–4 h, the corresponding bidentate, four-coordinated and bivalent dichloro triphosphine transition metal complexes *cis*-$M^{II}(\eta^2\text{tdppcyR})Cl_2$ (M = Pt, Pd, Ni; R = CH_2OMe, COOMe, CN) are formed in good yields (Scheme 1). After concentration of the solvents the products can be obtained by addition of pentane to the reaction solutions or suspensions, respectively. The worked up precipitates are isolated as colorless (**1a**–**c**), or colorless to yellow (in the order **2c**,**a**,**b**), or off-white (**3c**) to light-brown (**3a**,**b**) powders, respectively. They are moderately soluble in chlorinated hydrocarbons and insoluble in unpolar solvents. In the solid state the compounds are not very air-sensitive and can be stored under an argon atmosphere for several months, while they are very susceptible to oxygen in solution.

It is mainly the free uncoordinated phosphorus of the tdppcyR ligands that is labile concerning oxidation. Even if freshly distilled and several times degassed THF is used as solvent in the synthesis, traces of the corresponding oxidation products are hard to prevent. To elucidate NMR spectroscopic data in respect of oxides or the potential occurrence of coordination isomers, a controlled oxidation reaction was carried out with the ether functionalized platinum complex **1a**. For that purpose a molar excess of aqueous H_2O_2 was added to a solution of **1a** in dichloromethane (Scheme. 1). After precipitating with pentane the oxide $Pt(tdppcymome[O])Cl_2$ (**1d**) with one oxidized uncoordinated P=O arm could be obtained and characterized. The reaction product was isolated as a white, microcrys-



M \ R	CH_2OMe	COOMe	CN
Pt	**1a**	**1b**	**1c**
Pd	**2a**	**2b**	**2c**
Ni	**3a**	**3b**	**3c**

Scheme 1. Synthesis of bidentate tripodal phosphine complexes with d^8-metals Pt(II), Pd(II), and Ni(II) of the type *cis*-$M(\eta^2\text{-tdppcyR})Cl_2$ [+ $SnCl_2$].

talline powder which was no longer air-sensitive, dissolves in chlorinated solvents and is insoluble in unpolar hydrocarbons.

When a solution of the ether functionalized platinum dichloro complex Pt(tdppcyme)Cl_2 (**1b**) was treated with an equimolar suspension of dehydrated $SnCl_2$, in carefully degassed dichloromethane at r.t. for about 3 h, a deep-orange solution formed. After reducing the solvent and precipitating with pentane the yellowish–orange bimetallic platinum tin complex Pt(tdppcyme)Cl($SnCl_3$) (**1e**) was obtained (Scheme 1). With regards to stability and solubility, the compound is comparable to its educt **1b**.

2.2. Spectroscopic characterization

NMR spectroscopic investigations of the ether, ester and cyano functionalized metal chloro triphosphine complexes M(tdppcyR)Cl_2 **1a**–**d**, **2a**–**c**, and **3a**–**c** are in good agreement with geometric structures which are represented by structural formulas in Scheme 1. The metal centers of the d^8 complexes are surrounded in a square-planar arrangement by two *cis*-oriented chloro and phosphorus donor ligands, respectively. The potentially tridentate tripodal phosphine ligands coordinate to the central atoms only in a *dihapto* style, whereas the third diphenylphosphine unit remains uncoordinated as a free 'arm-off' group. The molecules have a non-axial C_s symmetry with a mirror plane through the atoms C^4–C^1–M (Scheme 1).

In each $^{31}P\{^1H\}$-NMR spectrum of the platinum and palladium compounds **1a**–**d** and **2a**–**c** two groups of signals appear in a peak area ratio of 2:1. The signals with the double integral which stem from the two coordinated phosphorus nuclei underwent, in the case of the platinum complexes **1a**–**d**, only small coordination downfield shifts ($\Delta\delta = +2$–3 ppm), while the values for the palladium complexes **2a**–**c** underwent more substantial changes from about $\Delta\delta = +18$ to $+26$ ppm. The singlets with single integrals derive from the free uncoordinated phosphorus in each case and are shifted to a higher field with $\Delta\delta$ values between -1 and -9. An exception is Pt(tdppcymome[O])Cl_2 (**1d**) in which the phosphorus of the free phosphine arm is oxidized and therefore appears in the spectrum shifted to lower field by $\Delta\delta = +13.3$ ppm in comparison with the non-oxidized complex **1a**. Contrary to the palladium compounds, the singlet resonances of the coordinated phosphorus groups of the platinum complexes **1a**–**d** are flanked by two ^{195}Pt satellites. The $^{195}Pt\{^1H\}$-NMR spectra of **1a**–**d** show a triplet resonance in accordance with the prevailing assumption of an η^2-coordination of the ligands.

The reduced motions of the molecules in the solid state generate two crystallographically inequivalent coordinated phosphine groups. Thus, the solid state ^{31}P CP/MAS-NMR spectra show a separation of the signals into two evidently distinguishable resonances belonging to two coordinated, chemically inequivalent phosphorus nuclei. These signals can be definitely ascribed to the metal bound phosphine groups on account of their large $^1J_{PtP}$ couplings (3418 and 3687 Hz (**1c**)) (Fig. 1). The two coordinated ^{31}P nuclei differ in chemical shifts by $\Delta\delta \sim 6$ ppm and in coupling constants $\Delta J_{PtP} = 269$ Hz, respectively.

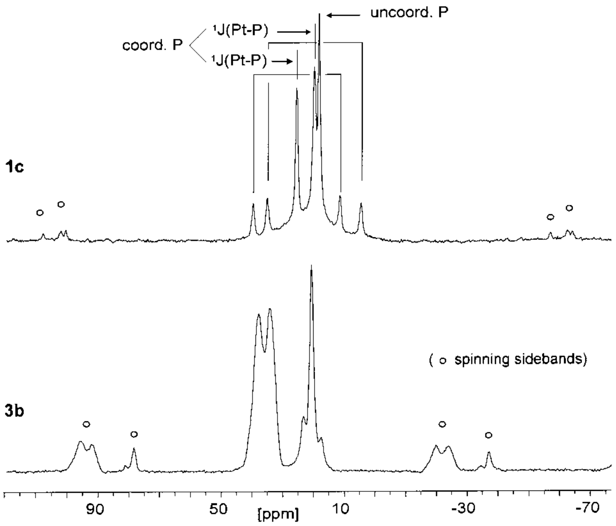


Fig. 1. Solid state ^{31}P-CP/MAS-NMR spectra of the complexes Pt(tdppcycn)Cl_2 (**1c**) and Ni(tdppcyme)Cl_2 (**3b**).

The C_s symmetry and the above-mentioned coordination conditions of the complexes are also coincident with the number and manner of proton resonances in their ^1H-NMR spectra. In particular, the platinum compounds **1a**–**d** and the palladium complex Pd(tdppcycn)Cl_2 (**2c**) show signal groups, which can also be attributed to pairs of endocyclic and exocyclic (only **1a**,**d**) diastereotopic methylene hydrogen atoms H_A and H_B, respectively, as to groups of two different exocyclic methyl units (**1a**,**b**,**d**). The final assignment, as listed in the Section 4, could be made with respect to (a) the typical chemical shifts; (b) multiplicities or multiplet patterns, respectively; and (c) the integral ratio of 2:1 of the proton pairs in the positions outside the mirror plane to the ones in the positions in the mirror plane. Whereas in complex Pt(tdppcyme)Cl_2 (**1b**) the fine structure of the proton signals could be observed, a detailed analysis of the proton spectra of the palladium complexes **2a**,**b** was not practicable.

The signals and multiplet patterns in the $^{13}C\{^1H\}$-NMR spectra can be assigned to the different carbon species and moreover, due to the symmetry conditions of the individual groups to the ring positions 3, 5 or 1, or to 2, 6 or 4, respectively. It is noteworthy that within the platinum species the resolution of the alkane region of the endocyclic methylene carbon atoms increases in the order ether (**1a**,**d**) < ester (**1b**) <

cyano (**1c**) functionalized complex. The carbon nuclei C^3 and C^5 are herein part of an AM[X]$_2$ spin system, in which they interact on the one hand with the phophorus $P_{uncoord}$ (= M) through a $^2J_{PC}$ coupling and on the other hand with the two metal coordinated phosphorus nuclei P_{coord} (= X,X′) through $^2J_{PC}$ and $^4J_{PC}$ couplings, respectively. This generates N-lines, which could be analyzed in the case of the cyano complex Pt(tdppcycn)Cl_2 (**1c**). In Pt(tdppcyme)Cl_2 (**1b**) the doublet of the AM part could be assigned, while the ether complexes **1a**,**d** give no differentiated multiplets.

With regards to the exocyclic atoms, the α-connected carbon nuclei to the cyclohexane ring positions 2 and 6 form an A[X]$_2$ spin system (X = ^{31}P). The frequency differences of the N-lines $N = |^2J_{PC} + {}^4J_{PC}|$ of the ester compounds **1b**, **2b** and the cyano complex **1c** are between 4.62 and 7.35 Hz. Instead of this the respective methylene ^{13}C atoms of the ether complexes **1a**,**d**, **2a** give singlets with approximately natural line widths. The carbon nuclei of the remaining complexes **1b**,**c**,**d**, **2b**, which are bound to $CP_{uncoord}$ and lie in the mirror plane, show doublets due to very small couplings $^2J_{PC} \geq 1.94$ Hz.

Because of the dative bound trichloro stannato group, the C_1 symmetric η^2-complex Pt(tdppcyme)Cl($SnCl_3$) (**1e**) shows resonances due to three inequivalent phosphorus nuclei in the ^{31}P{^{1}H}-NMR spectrum. The resonance frequency of the free, uncoordinated phosphorus appears as a singlet at δ 22.7. Both other resonances are each flanked with tin satellites and therefore can be attributed to an AX spin pattern of two platinum bound phosphine groups. The indirect platinum phosphorus coupling of the signal at δ 29 is $^1J_{PtP} = 3601$ Hz. The $^2J_{SnP}$ coupling via the platinum center is 185 Hz. The two tin isotopomers are not resolved herein. Each platinum satellite is also surrounded by these $^2J_{SnP}$ patterns. The signal of the second coordinated phosphorus atom appears at δ 39.2. The observed $^1J_{PtP}$ coupling of 2792 Hz is essentially smaller than the one derived from the other P_{coord}, whereas the tin phosphorus couplings belonging to the isotopomers Sn-117 and Sn-119 $^2J_{SnP} = 4009$ and 4197 Hz, respectively, are about 22 times larger. Beyond this all resonances of the coordinated phosphorus nuclei are split into doublets with $^2J_{PP} = 16.7$ Hz. The magnitude of the platinum satellites, i.e. the $^1J_{PtP}$ coupling, shows a strong dependence on the kind of *trans* positioned ligand to the regarded phosphorus atom, respectively. That P-31 nucleus has a weaker coupling to Pt-195, which is *trans* to a ligand with a stronger *trans* influence (here: P *trans* to $SnCl_3$). Both the observed values of coupling constants and the fact that the P_{coord} with the greater $^1J_{PtP}$ is shifted to higher field are evidence for a *cis* bisphosphine complex in which δ 29.0 can be assigned to P_{coord} *cis* to $SnCl_3$ and δ 39.2 to P_{coord} *trans* to $SnCl_3$, respectively. Further proof of a *cis* isomer is the fact that two distinctively different interactions occur between $^{119/117}$Sn and ^{31}P, depending whether it is a *cis* $^2J_{SnP}$ coupling (185 Hz) or a *trans* $^2J_{SnP}$ coupling (4009/4197 Hz).

The ^{195}Pt chemical shift of **1e** is δ −4752 with a highfield shift of $\Delta\delta = -191$ ppm compared to **1b**. Dependent on its C_1 symmetry the signal pattern is a doublet of doublet. The ^{119}Sn{^{1}H}-NMR spectrum shows a doublet of doublet at δ −46.3. The enormous platinum tin coupling constant of the platinum satellites, $^1J_{PtSn} > 14\,200$ Hz, is remarkable.

For further elucidation of structural properties of the M(η^2-tripod)Cl_2 template an X-ray diffraction analysis was undertaken on a suitable crystal of the ester functionalized complex Ni(tdppcyme)Cl_2 (**3b**). It corroborates and completes the results derived from the NMR measurements of the analogous platinum and palladium complexes investigated so far. The complex **3b** crystallizes in the triclinic space group $P\bar{1}$. The perspective view of **3b** is presented in Fig. 2, together with selected bond lengths and bond angles. Two chlorine atoms and two phosphorus donor groups of the η^2-ligand coordinate *cis* to the nickel metal center in an only slightly distorted square-planar arrangement. The Ni[P]$_2$ fragment forms, together with the three carbon atoms C(1)–C(6)–C(5) of the ligand backbone, a metal-

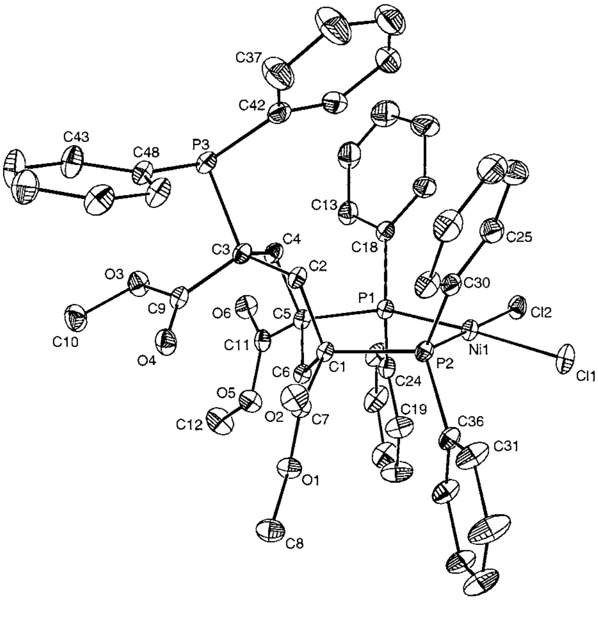


Fig. 2. ORTEP drawing and atom-labeling scheme for Ni(tdppcyme)Cl_2 (**3b**). Selected bond lengths and bond angles are as follows: Ni–Cl(1): 219.4(2); Ni–Cl(2): 220.2(2); Ni–P(1): 218.5(2); Ni–P(2): 218.5(2) pm. P(2)–Ni–P(1): 101.51(7); P(2)–Ni–Cl(1): 84.80(7); Cl(1)–Ni–Cl(2): 91.66(7); P(1)–Ni–Cl(2): 82.27(7); P(1)–Ni–Cl(1): 172.23(7); P(2)–Ni–Cl(2): 175.30(7); C(5)–P(1)–Ni: 118.2(2); C(1)–P(2)–Ni: 116.6(2); C(6)–C(1)–P(2): 109.3(3); C(6)–C(5)–P(1): 108.3(3); C(5)–C(6)–C(1): 115.0(4); C(6)–C(1)–C(2): 113.5(4); C(6)–C(5)–C(4): 113.2(4); C(3)–C(2)–C(1): 113.1(4); C(3)–C(4)–C(5): 113.8(4); C(2)–C(3)–C(4): 108.1(4)°.

ladiphosphacyclohexane unit in the manner of a planar 'envelope', conformation with the squared off edge at carbon C6. The endocyclic angle at the metal center is increased to 101.5°, the angles P(1)–Ni–Cl(2) and P(2)–Ni–Cl(1) are reduced to 82.3 and 84.8°, respectively, whereas Cl(1)–Ni–Cl(2) (91.7°) is close to the ideal right angle. The cyclohexane ring of the tdppcyme backbone shows a boat conformation, likely because of the steric constraint of the free uncoordinated diphenylphosphine group. The carbocyclic bond angles at the methylene carbon atoms only differ by an average of 1.3° from the ideal angle in unsubstituted cyclohexane (111.5°).

The preference of a square-planar coordination over a tetrahedral arrangement of the nickel in the solid state was confirmed by the result of a magnetic measurement of Ni(tdppcyme)Cl_2 (**3b**) in the solid state, where pure diamagnetism was observed. The solid state ^{31}P CP/MAS-NMR spectrum, which is depicted in the lower part of Fig. 1, is in accordance with this. Similar to the above discussed spectrum of the platinum complex **1c** (see Fig. 1), two downfield resonances — in addition to the signal of the free, uncoordinated diphenylphosphine group — of both coordinated, chemically inequivalent phosphorus nuclei occur, which would not be observable in the case of a distinct deviation from the planar geometry and the herewith arising increase in paramagnetism.

In contrast, the high-resolution $^{31}P\{^1H\}$-NMR spectrum of **3b** in the liquid phase at r.t. shows only one singlet at δ 20.8, which is in the range of signals for the uncoordinated phosphorus in the CP/MAS spectrum of **3b** as in the spectra of the homologous ester functionalized platinum and palladium complexes **1b** and **2b**, respectively. If this sample is cooled to a temperature below -34°C (Fig. 3), an additional broad signal arises from the baseline in the downfield region ($\delta \sim 40$), coincident with the coordinated species of the diphenylphosphine groups. Further cooling to -91°C results in a sharp singlet which has an integration ratio of 2:1 to the signal of the uncoordinated phosphorus. In the low-temperature area the high-resolution $^{31}P\{^1H\}$-NMR spectrum is in conformity with the solid state ^{31}P CP/MAS-NMR spectrum. Therefore, a square-planar geometry with diamagnetic behavior can be assigned to this complex in solution for this case also. The broadening and final coalescence of the peak of the coordinated phosphorus nuclei at higher temperatures can be explained as a growing distortion of this coordination geometry in favor of a tetrahedral arrangement, leading to a more rapid relaxation of the metal-bound groups which is caused by the increasing paramagnetism. Above 44°C a considerable broadening of the signal of the uncoordinated phosphorus nucleus also takes place. The resonance begins to coalesce into the baseline at the highest reachable temperature of 91°C. This indicates that an intramolecular chemical exchange process begins to replace the free with the coordinated phosphine groups and vice versa. This is supported by the behavior of the observable peaks of the oxidation product of **3b** in Fig. 3. At elevated temperatures the resonance due to the coordinated phosphorus nuclei disappears, whereas the one for the oxidized noncoordinated diphenylphosphine group remains sharp over the whole temperature range. The latter is no longer able to coordinate to the metal center and therefore cannot participate in a chemical exchange as mentioned above.

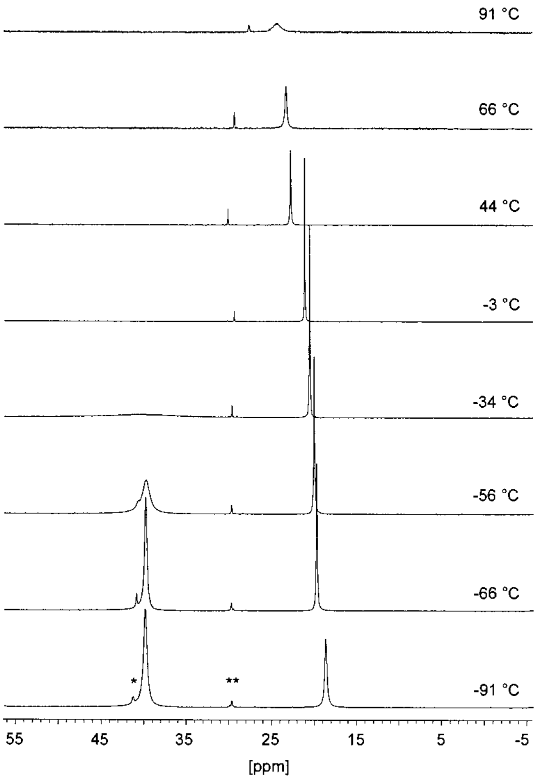


Fig. 3. Variable-temperature $^{31}P\{^1H\}$-NMR spectra of Ni(tdppcyme)Cl_2 (**3b**). (*P_{coord} and **$P_{uncoord}$ of **3b** in which $P_{uncoord}$ is oxidized) (161.98 MHz).

The cyano functionalized nickel complex Ni(tdppcycn)Cl_2 (**3c**) shows a stronger paramagnetism involving a larger distortion of the square-planar structure. No signal of the metal-bound diphenylphosphine groups is observed over the whole temperature range in its variable-temperature $^{31}P\{^1H\}$-NMR spectra.

^1H- and $^{13}C\{^1H\}$-NMR spectroscopic data for the nickel species are listed in the Section 4. Paramagnetism mainly affects the ^1H-NMR spectra. This leads to an enlarged chemical shift range (δ from -3 to $+12$ for **3b**), to a broadening and/or an increased number of signals, which complicates the assignment of the resonances and interpretation of the spectra.

3. Conclusions

The potentially tripodal phosphine ligands **a**–**c** coordinate only in an η^2-fashion to the Ni-, Pd-, Pt-dichlorides, in spite of the high stability of the adamantane-type polyhedron that is formed when all three phosphine arms bind to one metal center. The preferred planarity at the metal sites and the steric constraints of the functional groups at the ligand forces the cyclohexane backbone into the boat conformation. Indications for chemical exchange processes are only observed in the case of the nickel complexes at higher temperatures.

4. Experimental

4.1. General comments

All reactions were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were distilled under Ar; diethyl ether and THF were distilled from Na/Ph_2CO; *n*-pentane was distilled from $LiAlH_4$; dichloromethane and chloroform were distilled from CaH_2. The phosphine ligands *cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxymethyl) cyclohexane (tdppcymome) (**a**) [7], *cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane (tdppcyme) (**b**) [5], *cis,cis*-1,3,5-tricyano-1,3,5-tris(diphenylphosphino)cyclohexane (tdppcycn) (**c**) [6], $Pt(COD)Cl_2$ (**1**) [19], $Pd(COD)Cl_2$ (**2**) [20], dehydrated $NiCl_2$ (**3**) [21], and dehydrated $SnCl_2$ [22] were prepared as described in the literature. ^1H-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker DRX 250 or a Bruker AMX 400 operating at 250.13 or 400.13, 62.90 or 100.62, and 101.26 or 161.98 MHz, respectively, ^{195}Pt- and ^{119}Sn-NMR spectra were recorded on a Bruker DRX 250 operating at 53.77 and 93.28 MHz, respectively. ^1H chemical shifts were referenced to the residual proton peaks of the solvents versus TMS. ^{13}C chemical shifts were calibrated against the deuterated solvent multiplet relative to TMS. ^{31}P chemical shifts were measured relative to external 85% H_3PO_4. ^{119}Sn and ^{195}Pt chemical shifts were measured relative to external 50% $Sn(CH_3)_4$ in $CDCl_3$ and 1.2 M $Na_2PtCl_6\cdot 6H_2O$ in D_2O, respectively. In addition to the $^{13}C\{^1H\}$-NMR spectra ^{13}C-DEPT [23] experiments were routinely performed for each compound. Special assignments were supported by 2D $^1H/^{13}C$ HMQC or 2D $^1H/^{31}P$ HMQC experiments [24] using standard Bruker software. ^1H-, ^{13}C-, and ^{31}P-DNMR experiments were carried out on a Bruker AMX 400 and DRX250 after a thermic equilibration time of ≥20 min. The temperature was measured using the temperature control unit Eurotherm and an external thermocouple (Pt 100). ^{31}P and ^{13}C CP/MAS-NMR spectra were taken on a Bruker MSL 200 or a Bruker ASX 300 operating at 80.0 or 121.49 MHz and at 75.46 MHz, respectively. ^{31}P chemical shifts were measured relative to external $(NH_4)H_2PO_4$ ($\delta = 0.81$). ^{13}C chemical shifts were referenced to TMS or the carbonyl resonance of glycine ($\delta = 107.09$), respectively. Downfield values were always taken as positive and temperature was 298 K unless otherwise noted. The single-crystal X-ray structure determination was carried out with a Siemens P4 diffractometer. IR spectra were recorded on a Bruker IFS 48. Mass spectra (FD) were detected on a Finnigan MAT 711 A modified by AMD; FAB Finnigan MAT TSQ70. Elemental analysis were performed using a Carlo Erba model 1106 elemental analyzer.

4.2. General procedure for the reactions of *1* and *2* with the ligands *a*, *b*, and *c*

An equimolar mixture of 250 μmol of $M(COD)Cl_2$ [M = Pt (**1**), Pd (**2**)] and the ligands **a**, **b**, or **c** was soluted by adding 20 ml of freshly distilled and carefully degassed THF. The solution was stirred at r.t. while some product began to precipitate. After a reaction time of 4 h the solvent was concentrated in volume to 5 ml, and 15 ml of *n*-pentane was added. The resulting off-white (M = Pt) or off-white to yellow precipitates (M = Pd) were filtered by a sintered glass fritt (P4), washed three times with 15 ml of *n*-pentane, and dried under reduced pressure.

4.2.1. *cis-Dichloro[η^2-cis,cis-(1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)cyclohexane]-platinum(II) — cis-Pt(tdppcymome)Cl_2 (**1a**)*

Complex **1** (93.5 mg) was treated with 192.2 mg of **a**. Yield: 233 mg (90%). M.p.: >265°C (dec.). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta = 23.5$ [s, $P_{uncoord}$], 3.2 [s; d, $^1J_{PtP} = 3509$ Hz, P_{coord}]. ^1H-NMR ($CDCl_3$): $\delta = 1.65$–1.82 [m, 2H, CHH_A], 2.04–2.41 [m, 2H, CHH_B, 1H, CHH], 2.57–2.99 [m, 1H, CHH, 2H, $CH_3OCHH_ACP_{coord}$], 2.90 [s, 3H, $CH_3OCH_2CP_{uncoord}$], 2.92 [s, 6H, $CH_3OCH_2CP_{coord}$], 3.04–3.20 [m, 2H, $CH_3OCHH_BCP_{coord}$], 3.19 [d, $^3J_{PH} = 11.9$ Hz, 2H, $CH_3OCH_2CP_{uncoord}$], 7.10–7.99 [m, 30H, C_6H_5]. $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 32.77$–33.47, 34.67–35.27 [m, CH_2], 35.20–36.20 [m, CP_{coord}], 41.00–42.20 [m, $CP_{uncoord}$], 51.86 [s, $CH_3OCH_2CP_{uncoord}$], 58.36 [s, $CH_3OCH_2CP_{coord}$], 76.15–76.32 [m, $CH_3OCH_2CP_{uncoord}$], 78.34 [s, $CH_3OCH_2CP_{coord}$], 127.30–137.70 [m, C_6H_5]. $^{195}Pt\{^1H\}$-NMR ($CDCl_3$): $\delta = -4471.9$ [t, $^1J_{PtP} = 3509$ Hz]. MS (FAB), *m/z*: 1034.2 [M^+], 999.1 [$M^+ - Cl$], 963.2 [$M^+ - 2Cl$]. Calc. for $C_{48}H_{51}Cl_2O_3P_3Pt$ (1034.85): C, 55.71; H, 4.97; Cl, 6.85. Found: C, 55.25; H, 4.92; Cl, 7.20.

4.2.2. *cis-Dichloro[η^2-cis,cis-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane]platinum(II) — cis-Pt(tdppcyme)Cl_2 (**1b**)*

Complex **1** (93.5 mg) was treated with 202.7 mg of **b**. Reaction temperature: 60°C. Yield: 253 mg (94%). M.p. > 254°C (dec.). IR (KBr, cm^{-1}): 1729 $\nu(COOCH_3)$. $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta = 22.2$ [s, $P_{uncoord}$], 33.0 [s; d, $^1J_{PtP} = 3581$ Hz, P_{coord}]. ^1H-NMR ($CDCl_3$): $\delta = 1.40$ [ddd, CHH_A], 2.70 [br. d, 1H, CHH_A], 2.81 [br. d, CHH_B], 3.02 [br. d, CHH_B] [25], 3.02 [s, 3H, $CH_3OOCCP_{uncoord}$], 3.05 [s, 6H, CH_3OOCCP_{coord}], 6.95–8.50 [m, 30H, C_6H_5]. $^{13}C\{^1H\}$-NMR (CD_2Cl_2): $\delta = 35.58$ [t, $^2J_{PC} = 5.16$ Hz, CH_2], 39.50 [br. d, $^2J_{PC} = 19.92$ Hz, CH_2], 42.02–43.00 [m, CP_{coord}], 48.04 [dt, $^1J_{PC} = 30.94$ Hz, $^3J_{PC} = 5.34$ Hz, $CP_{uncoord}$], 51.83 [s, $CH_3OOCCP_{uncoord}$], 52.86 [s, CH_3OOCCP_{coord}], 124.10–139.00 [m, C_6H_5], 173.13 $[A[X]_2$, $N = |^2J_{PC} + {}^4J_{PC}| = 4.62$ Hz, CH_3OOCCP_{coord}], 173.43 [d, $^2J_{PC} = 2.49$ Hz, $CH_3OOCCP_{uncoord}$]. $^{195}Pt\{^1H\}$-NMR ($CDCl_3$): $\delta = -4560.8$ [t, $^1J_{PtP} = 3581$ Hz]. MS (FD), m/z: 1076.4 [M^+]. Calc. for $C_{48}H_{45}Cl_2O_6P_3Pt$ (1076.80): C, 53.54; H, 4.21; Cl, 6.58. Found: C, 53.09; H, 4.33; Cl, 7.00.

4.2.3. *cis-Dichloro[η^2-cis,cis-1,3,5-tris(cyano)-1,3,5-tris(diphenylphosphino)cyclohexane] platinum(II) — cis-Pt(tdppcycn)Cl_2 (**1c**)*

Complex **1** (93.5 mg) and 177.9 mg of **c** were applied. Yield: 235 mg (96%). M.p. > 220°C (dec.). IR (KBr, cm^{-1}): 2235, 2223 $\nu(CN)$. $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta = 19.3$ [s, $P_{uncoord}$], 22.5 [s; d, $^1J_{PtP} = 3491$ Hz, P_{coord}]. ^1H-NMR ($CDCl_3$): $\delta = 1.91$–2.09 [m, 2H, CHH_A], 2.59–2.81 [m, 2H, CHH_B], 3.19–3.65 [m, 2H, CH_2], 7.20–8.02 [m, 30H, C_6H_5]. $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 28.71$–29.65 [m, CP_{coord}], 29.57 [dt, $^1J_{PC} = 32.15$ Hz, $^3J_{PC} = 4.26$ Hz, $CP_{uncoord}$], 31.43–31.72 [m, CH_2], 39.61 $[AM[X]_2$, $^2J_{PC} = 26.73$ Hz, $N = |^2J_{PC} + {}^4J_{PC}| = 6.4$ Hz, CH_2], 119.17 $[A[X]_2$, $N = |^2J_{PC} + {}^4J_{PC}| = 7.35$ Hz, $NCCP_{coord}$], 119.95 [d, $^2J_{PC} = 1.94$ Hz, $NCCP_{uncoord}$], 122.05–125.30 [m, *ipso*-$C_6H_5P_{coord}$], 128.20–135.80 [m, C_6H_5]. $^{195}Pt\{^1H\}$-NMR ($CDCl_3$): $\delta = -4437.3$ [t, $^1J_{PtP} = 3491$ Hz]. MS (FAB), m/z: [n.i.]. $C_{45}H_{36}Cl_2N_3P_3Pt$ (977.72): C, 55.28; H, 3.71; N, 4.30; Cl, 7.25. Found: C, 55.63; H, 3.99; N, 4.14; Cl, 7.25.

4.2.4. *cis-Dichloro[η^2-cis,cis-(1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)cyclohexane]palladium (II) — cis-Pd(tdppcymome)Cl_2 (**2a**)*

Complex **2** (71.4 mg) and 192.2 mg of **a** were used. Yield: 203 mg (86%). M.p. > 195°C (dec.). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): $\delta = 25.5$ [s, $P_{uncoord}$], 54.2 [s, P_{coord}]. ^1H-NMR (CD_2Cl_2): $\delta = 1.60$–3.80 [m, 21H, CH_2, CH_3], 6.90–8.60 [m, 30H, C_6H_5]. $^{13}C\{^1H\}$-NMR (CD_2Cl_2): $\delta = 34.20$–35.00, 35.00–35.90 [m, CH_2], 35.90–37.50 [m, CP], 58.35 [s, CH_3], 76.00–76.70 [m, $CH_3OCH_2CP_{uncoord}$], 78.71 [br. s, $CH_3OCH_2CP_{coord}$], 126.00–140.00 [m, C_6H_5]. MS (FAB), m/z: 946.2 [M^+], 911.2 [$M^+ - Cl$], 874.9 [$M^+ - 2Cl$]. Calc. for $C_{48}H_{51}Cl_2O_3P_3Pd$ (946.159): C, 60.93; H, 5.43; Cl, 7.49.

4.2.5. *cis-Dichloro[η^2-cis,cis-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane]palladium(II) — cis-Pd(tdppcyme)Cl_2 (**2b**)*

Complex **2** (71.4 mg) was treated with 202.7 mg of **b**. Reaction temperature: 60°C. Yield: 225 mg (91%). M.p. > 247°C (dec.). IR (KBr, cm^{-1}): 1729 $\nu(COOCH_3)$. $^{31}P\{^1H\}$-NMR ($C_2D_2Cl_4$): $\delta = 22.2$ [s, $P_{uncoord}$], 51.7 [s, P_{coord}]. ^1H-NMR ($C_2D_2Cl_4$): $\delta = 1.32$ [ddd, 2H, CHH_A] [25], 2.50–3.20 [m, 13H, CH_2, CH_3], 6.92–8.47 [m, 30H, C_6H_5]. $^{13}C\{^1H\}$-NMR ($C_2D_2Cl_4$): $\delta = 34.30$–35.00 [m, CH_2], 39.23 [br. d, $^2J_{PC} = 18.50$ Hz, CH_2], 42.80–43.90 [m, CP_{coord}], 47.77 [dt, $^1J_{PC} = 31.30$ Hz, $^3J_{PC} = 4.98$ Hz, $CP_{uncoord}$], 52.14 [s, $CH_3OOCCP_{uncoord}$], 53.25 [s, CH_3OOCCP_{coord}], 124.70–138.40 [m, C_6H_5], 172.96 $[A[X]_2$, $N = |^2J_{PC} + {}^4J_{PC}| = 4.98$ Hz, CH_3OOCCP_{coord}], 173.41 [d, $^2J_{PC} = 2.84$ Hz, $CH_3OOCCP_{uncoord}$]. MS (FAB), m/z: [not interpretable]. Calc. for $C_{48}H_{45}Cl_2O_6P_3Pd$ (988.109): C, 58.35; H, 4.59; Cl, 7.18. Found: C, 57.93; H, 4.38; Cl, 7.50.

4.2.6. *cis-Dichloro[η^2-cis,cis-1,3,5-tris(cyano)-1,3,5-tris(diphenylphosphino)cyclohexane]palladium(II) — cis-Pd(tdppcycn)Cl_2 (**2c**)*

Complex **2** (71.4 mg) and 177.9 mg of **c** were used. Reaction temperature: 60°C. Yield: 213 mg (96%). M.p. > 226°C (dec.). IR (KBr, cm^{-1}): 2234, 2223 $\nu(CN)$. $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta = 19.5$ [br. s, $P_{uncoord}$], 38.8 [br. s, P_{coord}]. ^1H-NMR ($CDCl_3$): $\delta = 1.93$–2.21 [m, 2H, CHH_A], 2.40–2.72 [m, 2H, CHH_B], 3.10–3.65 [m, 2H, CH_2], 6.90–8.20 [m, 30H, C_6H_5]. $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 29.50$–30.90 [m, CP], 31.20–31.90 [m, CH_2], 39.00–40.20 [m, CH_2], 118.70–119.20 [m, CN], 123.00–126.00 [m, *ipso*-$C_6H_5P_{coord}$], 128.00–136.30 [m, C_6H_5]. MS (FAB), m/z: 854.3 [$M^+ - Cl$]. Calc. for $C_{45}H_{36}Cl_2N_3P_3Pd$ (889.028): C, 60.80; H, 4.08; N, 4.73; Cl, 7.98. Found: C, 60.43; H, 4.48; N, 4.55; Cl, 8.40.

4.3. *cis-Dichloro[η^2-cis,cis-(1,3-bis(diphenylphosphino)-5-diphenylphosphinooxid)-1,3,5-tris(methoxymethyl)cyclohexane]platinum(II) — cis-Pt-(tdppcymome[O])Cl_2 (**1d**)*

To a solution of 103.5 mg (100 μmol) of **1a** in 10 ml of CH_2Cl_2 was added 0.1 ml (1 mmol) of an aqueous solution of H_2O_2 (30%). The reaction mixture was vigorously stirred for 2 h at room temperature (r.t.). The solvent was concentrated in volume to 2 ml, and 15 ml of *n*-pentane was added. The resulting off-white precipitate was filtered by a sintered glass fritt (P4), washed three times with 15 ml of *n*-pentane, and dried under reduced pressure. Yield: 104 mg (99%). M.p. > 265°C (dec.). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta = 31.6$ [s; d,

$^{1}J_{PtP} = 3500$ Hz, P_{coord}], 36.8 [s, PO]. ^{1}H-NMR ($CDCl_3$): $\delta = 1.63–1.80$ [m, 2H, CHH_A], 2.09–2.38 [m, 2H, CHH_B, 1H, CHH], 2.65–2.85 [m, 1H, CHH], 2.82–2.96 [m, 2H, $CH_3OCHH_ACP_{coord}$], 2.89 [s, 6H, $CH_3OCH_2CP_{coord}$], 2.94 [s, 3H, CH_3OCH_2CPO], 3.04–3.17 [m, 2H, $CH_3OCHH_BCP_{coord}$], 3.62 [d, $^{3}J_{PH} =$ 18.83 Hz, 2H, CH_3OCH_2CPO], 7.11–7.97 [m, 30H, C_6H_5]. $^{13}C\{^{1}H\}$-NMR ($CDCl_3$): $\delta = 30.80–31.15$, 32.70–33.05 [m, CH_2], 34.35–35.33 [m, CP_{coord}], 45.32 [dt, $^{1}J_{PC} = 67.14$ Hz, $^{3}J_{PC} = 6.18$ Hz, CPO], 57.95 [s, CH_3OCH_2CPO], 58.33 [s, $CH_3OCH_2CP_{coord}$], 73.34 [br. d, $^{2}J_{PC} = 2.5$ Hz, CH_3OCH_2CPO], 78.07 [s, $CH_3OCH_2CP_{coord}$], 127.30–137.70 [m, C_6H_5]. $^{195}Pt\{^{1}H\}$-NMR ($CDCl_3$): $\delta = -4461.0$ [t, $^{1}J_{PtP} = 3500$ Hz]. MS (FD), *m/z*: 1050.1 [M^+], 1014.1 [$M^+ - Cl$]. Calc. for $C_{48}H_{51}Cl_2O_4P_3Pt$ (1050.85): C, 54.86; H, 4.89; Cl, 6.75.

*4.4. cis-Chloro-trichlorostannato(II)[η^2-cis,cis-1,3,5-tris-(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane]platinum(II) — cis-Pt(tdppcyme)Cl(SnCl$_3$) (**1e**)*

To a solution of 107.7 mg (100 μmol) of **1b** in 10 ml of carefully degassed CH_2Cl_2 in a septum sealed Schlenk tube was added, via syringe, a suspension of 19.0 mg (100 μmol) of dehydrated $SnCl_2$ in 10 ml of CH_2Cl_2. The reaction mixture turned orange in color and was stirred at r.t. until it turned into a clear solution (about 3 h). The solvent was concentrated in volume to 2 ml, and 15 ml of *n*-pentane was added. The resulting light-orange precipitate was filtered by a sintered glass fritt (P4), washed three times with 15 ml of *n*-pentane, and dried under reduced pressure. Yield: 101 mg (80%). M.p. > 165°C (dec.). IR (KBr, cm^{-1}): 1729 $\nu(COOCH_3)$. $^{31}P\{^{1}H\}$-NMR ($CDCl_3$): $\delta = 22.7$ [s, $P_{uncoord}$], 29.0 [d, $^{2}J_{PP} = 16.7$ Hz; dd, $^{1}J_{PtP} = 3601$ Hz, $^{2}J_{PP} = 16.7$ Hz; dd, $^{2}J_{cis\text{-}SnP} = 185.3$ Hz, $^{2}J_{PP} = 16.7$ Hz; ddd, $^{1}J_{PtP} = 3600.7$ Hz, $^{2}J_{cis\text{-}SnP} = 185.3$ Hz, $^{2}J_{PP} = 16.7$ Hz, P *cis* $SnCl_3$], 39.2 [d, $^{2}J_{PP} = 16.7$ Hz; dd, $^{1}J_{PtP} =$ 2792 Hz, $^{2}J_{PP} = 16.7$ Hz; dd, $^{2}J_{trans\text{-}117SnP} = 4008.7$, $^{2}J_{PP} = 16.7$ Hz; dd, $^{2}J_{trans\text{-}119SnP} = 4196.7$, $^{2}J_{PP} = 16.7$ Hz, P *trans* $SnCl_3$]. ^{1}H-NMR ($CDCl_3$): $\delta = 1.35–1.71$ [m, 2H, CHH_A], 2.65–3.00 [m, 4H, CH_2], 3.07 [br. s, 3H, CH_3], 3.13 [br. s, 6H, CH_3], 6.90–8.50 [m, 30H, C_6H_5]. $^{13}C\{^{1}H\}$-NMR ($CDCl_3$): $\delta = 38.40–39.60$ [m, CH_2], 42.40–43.70 [m, CP_{coord}], 47.56 [br. d, $^{1}J_{PC} =$ 32.59 Hz, $CP_{uncoord}$], 51.78 [s, $CH_3OOCCP_{uncoord}$], 52.79 [s, CH_3OOCCP_{coord}], 127.80–138.60 [m, C_6H_5], 172.20–173.60 [m, CH_3OOC]. $^{119}Sn\{^{1}H\}$-NMR ($CDCl_3$): $\delta = -46.3$ [d, $^{1}J_{PtSn} = 14223$ Hz; dd, $^{2}J_{trans\text{-}SnP} = 4197$ Hz, $^{2}J_{cis\text{-}SnP} = 185.3$ Hz]. $^{195}Pt\{^{1}H\}$-NMR ($CDCl_3$): $\delta = -4751.6$ [dd, $^{1}J_{PtP\ (cis\ Sn)} = 3601$ Hz, $^{1}J_{PtP\ (trans\ Sn)} = 2792$ Hz]. MS (FAB), *m/z*: 1040.2 [$M^+ - SnCl_3$]. Calc. for $C_{48}H_{45}Cl_4O_6P_3PtSn$ (1266.39): C, 54.53; H, 3.58; Cl, 11.20.

*4.5. cis-Dichloro[η^2-cis,cis-(1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)cyclohexane]nickel(II) — cis-Ni(tdppcymome)Cl$_2$ (**3a**)*

Following the general procedure for the reaction of **1** and **2** an equimolar mixture of 250 μmol of dehydrated $NiCl_2$ (**3**) and **a** was used. The resulting precipitate was a light-brown powder. Complex **3** (32.4 mg) and 192.2 mg of **a** were used. Yield: 191 mg (85%). M.p. > 180°C (dec.). $^{31}P\{^{1}H\}$-NMR (CD_2Cl_2): $\delta = 29.2$ [br. s, $P_{uncoord}$], 40.3 [br. s, P_{coord}]. ^{1}H-NMR (CD_2Cl_2): $\delta =$ 0.0–8.5 [very broad signals, paramagnetic]. MS (FAB), *m/z*: 861.2 [$M^+ - Cl$]. Calc. for $C_{48}H_{51}Cl_2NiO_3P_3$ (898.458): C, 64.17, H, 5.72, Cl, 7.89.

*4.6. cis-Dichloro[η^2-cis,cis-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane]nickel(II) — cis-Ni(tdppcyme)Cl$_2$ (**3b**)*

According to the general procedure for the reaction of **1** and **2** an equimolar mixture of 250 μmol of **3** and **b** were applied. The reaction temperature was 60°C. The resulting precipitate was a light-brown powder. Deep-red crystals could be obtained by diffusion of diethyl ether into the dark red concentrated reaction solution at r.t. If a brown precipitate occurred during concentrating the solvent was completely removed. The residue was dissolved in chloroform and exposed to diffusion of diethyl ether, and dried under reduced pressure. Yield: 207 mg (88%). M.p. > 218°C (dec.). IR (KBr, cm^{-1}): 1727 $\nu(COOCH_3)$. $^{31}P\{^{1}H\}$-NMR ($CDCl_3$): $\delta = 20.8$ [br. s]. ^{1}H-NMR ($CDCl_3$): $d =$ $-3.1–12.0$ [broad signals in the whole range, paramagnetic]. $^{13}C\{^{1}H\}$-NMR ($C_2D_2Cl_4$): $\delta = 40.0–40.8$ [m, CH_2], 40.2–41.4 [m, CP_{coord}], 46.3 [d, $^{1}J_{PC} = 31.0$ Hz, $CP_{uncoord}$], 49.2–50.5 [m, CH_2], 51.9 [s, $CH_3OOCCP_{uncoord}$], 52.9 [s, CH_3OOCCP_{coord}], 127.8–137.2 [m, C_6H_5], 172.8 [br. s, $COOMe$]. MS (FAB), *m/z*: 904.3 [$M^+ - Cl$]. Calc. for $C_{48}H_{45}Cl_2NiO_6P_3$ (940.409): C, 61.31; H, 4.82; Cl, 7.54. Found: C, 61.09; H, 4.89; Cl, 7.60.

*4.7. cis-Dichloro[η^2-cis,cis-1,3,5-tris(cyano)-1,3,5-tris(diphenylphosphino)cyclohexane]nickel(II) — cis-Ni(tdppcycn)Cl$_2$ (**3c**)*

Following the general procedure for the reaction of **1** and **2** an equimolar mixture of 250 μmol of **3** and **c** was used. The reaction temperature was 70°C. The resulting precipitate was an off-white powder. Complex **3** (32.4 mg) and 177.9 mg of **c** were used. Yield: 196 mg (93%). M.p. > 261°C (dec.). IR (KBr, cm^{-1}): 2319, 2291, 2223 $\nu(CN)$. $^{31}P\{^{1}H\}$-NMR (CD_2Cl_2): $\delta = 23.2$ [br. s]. ^{1}H-NMR (CD_2Cl_2): $\delta = 0.0–7.4$ [very broad signals, paramagnetic]. $^{13}C\{^{1}H\}$-NMR (CD_2Cl_2): $\delta = 31.2–33.0$ [m, CP], 35.2–40.6 [m, CH_2], 119.2 [br. s, CN], 127.0–137.5 [m, C_6H_5]. MS (FAB), *m/z*: [n.i.]. Calc. for

$C_{45}H_{36}Cl_2N_3NiP_3$ (841.328): C, 64.24; H, 4.31; N, 4.99; Cl, 8.43. Found: C, 63.91; H, 4.63; N, 4.81; Cl, 8.01.

4.8. Crystal data for **3b**

The nickel complex $C_{48}H_{45}Cl_2NiO_6P_3\cdot C_4H_8O$ (**3b**) with a formula weight of 1012.46 g mol^{-1} crystallized as bright-red plates after slow diffusion of diethyl ether into a solution of **3b** in THF. The data were collected at −100°C on a Siemens P4 diffractometer (Mo–K_α radiation) by using an oil-coated crystal of approximate dimensions 0.50 × 0.20 × 0.05 mm. The unit cell parameters are: $a = 11.559(5)$, $b = 12.053(6)$, $c = 19.242(9)$ Å; $\alpha = 82.68(4)$, $\beta = 83.14(3)$, $\gamma = 80.20(4)$°; $V = 2607(2)$ Å^3; $D_{\text{calc.}} = 1.290$ (g cm^{-3}). The complex crystallized in the space group $P\bar{1}$ ($Z = 2$). A total of 19176 reflections collected by ω scan ($4 < 2\Theta < 50°$), 9180 were unique. The data were corrected for absorption (psi-scan method) minimum and maximum transmission factors are 0.491 and 0.574, respectively. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. A crystallization solvent molecule (THF) was also detected and included in the refinement. The hydrogen atoms were placed on geometrically calculated positions. Final agreement factors were $R_1 = 0.0593$ [$I \geq 2\sigma(I)$, 3993 reflections] and $wR_2 = 0.1840$ (all data).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 119247. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The support of this research by the Deutsche Forschungsgemeinschaft (Forschergruppe) Bonn/Bad Godesberg, and the Fonds der Chemischen Industrie, Frankfurt/Main is gratefully acknowledged. We thank the DEGUSSA AG for loans of Pt and Pd salts.

References

[1] W. Levason, in: F.R. Hartley, S. Patai (Eds.), The Chemistry of Organophosphorus Compounds, vol. 1, Wiley, New York, 1990, p. 567.

[2] R. Mason, D.W. Meek, Angew. Chem. 90 (1978) 195.

[3] H.A. Mayer, W.C. Kaska, Chem. Rev. 94 (1994) 1239.

[4] H.A. Mayer, H. Otto, H. Kühbauch, R. Fawzi, M. Steimann, J. Organomet. Chem. 472 (1994) 347.

[5] H.A. Mayer, P. Stößel, R. Fawzi, M. Steimann, J. Organomet. Chem. 492 (1995) C1.

[6] H.A. Mayer, P. Stößel, R. Fawzi, M. Steimann, Chem. Ber. 128 (1995) 719.

[7] P. Stößel, H.A. Mayer, C. Maichle-Mössmer, R. Fawzi, M. Steimann, Inorg. Chem. 35 (1996) 5860.

[8] P. Stößel, H.A. Mayer, F. Auer, Eur. J. Inorg. Chem. (1998) 37.

[9] P. Stößel, W. Heins, H.A. Mayer, R. Fawzi, M. Steimann, Organometallics 15 (1996) 3393.

[10] P. Stößel, W. Heins, H.A. Mayer, W. Hörner, T.S. Ertel, H. Bertagnolli, J. Organomet. Chem. 552 (1998) 229.

[11] R. Davis, J.E. Ferguson, Inorg. Chim. Acta 4 (1970) 23.

[12] (a) G.G. Stanley, S.E. Saum, S.A. Laneman, Inorg. Chem. 29 (1990) 5065. (b) G.G. Stanley, M.E. Broussard, B. Juma, S.G. Train, W. Peng, S.A. Laneman, Science 260 (1993) 1784. (c) A.R. Khan, S.M. Socol, D.W. Meek, Inorg. Chim. Acta 221 (1994) 187.

[13] (a) H. Itatani, J.C. Bailor Jr., Ind. Eng. Chem. Prod. Res. Dev. 11 (1972) 146. (b) J.F. Knifton, J. Org. Chem. 41 (1976) 793. (c) J.F. Knifton, J. Catal. 45 (1976) 256. (d) G. Consiglio, P. Pino, Helv. Chim. Acta 59 (1976) 642.

[14] (a) F. Morandini, G. Consiglio, M. Scalone, P. Pino, J. Organomet. Chem. 279 (1985) 193. (b) L. Kollar, J. Bakos, I. Tóth, B. Heil, J. Organomet. Chem. 350 (1988) 277. (c) L. Kollar, T. Kégl, J. Bakos, J. Organomet. Chem. 453 (1993) 155. (d) S. Gladiali, D. Fabbri, L. Kollar, J. Organomet. Chem. 491 (1995) 91.

[15] D.W. Meek, A.R. Khan, S.M. Socol, Inorg. Chim. Acta 221 (1994) 187.

[16] P.S. Pregosin, S.N. Sze, Helv. Chim. Acta 61 (1978) 1848.

[17] L. Kollár, E. Farkas, Organometallics 15 (1996) 1345.

[18] P.S. Pregosin, K.A. Ostoja Starzewski, P-31, Sn-119, Pt-195 NMR studies on platinum–tin homogenous hydrogenation catalysts, in: E.C. Alyea, D.W. Meek (Eds.), Catalytic Aspects of Metal Phosphine Complexes, Advances in Chemistry Series 196, ACS, Washington, D.C., 1982.

[19] D. Drew, J.R. Doyle, Inorg. Synth. XIII (1972) 47.

[20] D. Drew, J.R. Doyle, Inorg. Synth. XIII (1972) 52.

[21] D. Brauer, Handbuch der Präparativen Anorganischen Chemie, Bd. III, F. Enke Verlag, Stuttgart, 1981, 3., umgearb. Auflage, p. 1685f.

[22] D. Brauer, Handbuch der Präparativen Anorganischen Chemie, Bd. II, F. Enke Verlag, Stuttgart, 1981, 3., umgearb. Auflage, p. 753.

[23] R. Benn, H. Günther, Angew. Chem. Int. Engl. Ed. 22 (1983) 350.

[24] A. Bax, R.H. Griffey, B.L. Hawkins, J. Magn. Reson. 55 (1983) 301.

[25] The multiplet finestructure is only recognizable in the 2D-HMQC NMR spectra. A detailed quantitative analysis of the coupling constants was not practicable.