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Inorganica Chimica Acta 343 (2003) 209–216

Inorganica Chimica Acta

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Coordination modes of *cis*-*P*,*P*′-diphenyl-1,4-diphospha-cyclohexane to metal ions of Groups 9 and 10

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Received 28 April 2002; accepted 3 July 2002

Abstract

Complexes of a tertiary diphosphine with cyclic core, *cis*-*P*,*P*′-diphenyl-1,4-diphospha-cyclohexane (dpdpc), with metal ions of Groups 9 and 10 have been prepared and characterised. In neutral M(0) or M(II) (M = Pt, Pd) complexes the diphosphine acts as a bridge affording polynuclear products. Instead, in cationic mononuclear Pt(II) and Pd(II) species a clear preference for chelation of dpdpc is observed. Also the cation $[Ni(dpdpc)_2Cl]^+$ contains the two dpdpc moieties as chelates. The molecular and crystal structure of $[Ni(dpdpc)_2Cl]_2(NiCl_4)$ discloses a significantly small bite angle of the chelate and interaction of near phenyl rings pertaining to opposite dpdpc moieties. Coordination of dpdpc to cobalt prompts its oxidation to the corresponding *P*,*P*′-dioxide.

Keywords: Diphosphine; Crystal structures; Nickel; Palladium; Platinum; Cobalt

1. Introduction

Vicinal diphosphines are a class of ligands, which hardly can be matched in the field of organometallic homogeneous catalysis for their ability to sturdily bind the metal centre [1]. It is to note that, although the use of diphosphines with a single chain skeleton >P–C–C–P< is accordingly quite extended, it appears that no substantial investigation has dealt with the double chain cyclic compounds having a $-P(-C-C-)_2P-$ skeleton. Yet the use in coordination chemistry of the latter compounds as ligands could possibly present some innovative features. For instance, diphosphines with cyclic core, particularly the *P*,*P*′-disubstituted 1,4-diphospha-cyclohexanes, in case act as chelates, can be suited to afford a fairly rigid steric hindrance towards the adjacent ligands within the plane, where the metal and the two phosphorus atoms sit. This feature, which proved to be a source of quite relevant effects in the case of the *N*,*N*′-chelates [2], is hardly attainable by use of the single chain vicinal diphosphines.

For the sake of comparison we remind that nitrogen analogous of the above cited ligands, such as *N*,*N*′-diphenylpiperazine [3] and *N*,*N*′-dimethylpiperazine [4], can act as chelates towards d^8 ions, the latter being responsible of relevant in plane hindrance.

In this work we have examined the coordination behaviour of *P*,*P*′-diphenyl-1,4-diphospha-cyclohexane. The preparation of this compound as the mixture of *cis* and *trans* stereoisomers was described many years ago [5], while more recently the stereoselective synthesis of the *cis* isomer (henceforth 'dpdpc') was attained [6]. We have investigated the behaviour of the *cis* form since this stereoisomer is in principle suitable not only to act as a bridge by binding two metal centers (Fig. 1(a)), but also to chelate one metal atom (Fig. 1(b)). In chelate dpdpc the steric hindrance of the two phenyl groups can be conformationally modulated and it is not likely to cause a forceful constraint, undesired in this initial part of the study.

Here results on the coordination mode(s) of dpdpc in the environment of platinum(0 or II), palladium(0 or II), nickel(II) and cobalt(II) are reported. These ions are

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PII: S0020-1693(02)01211-2

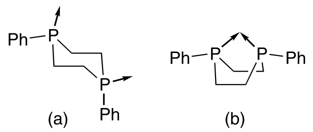

Fig. 1. Formula of *cis*-*P*,*P′*-diphenyl-1,4-diphospha-cyclohexane in the chair conformation (a) and in the boat conformation (b).

known to be particularly suitable to bind open-chain vicinal diphosphines. The molecular and crystal structure of $[Ni(dpdpc)_2Cl]_2(NiCl_4)$ and the molecular structure of a cobalt(II) complex containing the *P*,*P′*-dioxide of *cis*-*P*,*P′*-diphenyl-1,4-diphospha-cyclohexane are also reported.

2. Experimental

All reactions were carried out under a nitrogen atmosphere by using Schlenk techniques. Solvents were dried before use with standard procedures. ^1H NMR spectra were recorded at 298 K with a Gemini 300-MHz spectrometer. $CDCl_3$ and CD_3NO_2 were used as solvents, and $CHCl_3$ ($\delta = 7.26$ ppm) and CHD_2NO_2 ($\delta = 4.33$ ppm) as internal standards. ^{31}P NMR spectra were recorded on an AM 400-MHz Bruker model. The following abbreviations were used for describing NMR multiplicities: no attribute, singlet; d, doublet; t, triplet; q, quartet; dd, double doublet; m, multiplet; br, broad. Conductivity measurements were performed on a Crison Conductimeter model microCM 2200. The complexes $[PtCl_2(SMe_2)_2]$ [7], $[PtCl_2(1,5\text{-COD})]$ [8], $[PtClMe(SMe_2)_2]$ [9], $[PtCl_2(PPh_3)_2]$ [10], $[Pt(norbornene)_3]$ [11], $[PdClMe(1,5\text{-COD})]$ [12] and $[PdCl_2(1,5\text{-COD})]$ [13] were obtained by known methods. Particular care was employed in excluding moisture or air in the synthesis of dpdpc, which was obtained as previously reported [14] from the commercially available 1,2-bis(phenylphosphino)ethane (Aldrich).

2.1. *Attempt to prepare [Pt(dpdpc)(dmf)]*

Solid $[Pt(norbornene)_3]$ (96 mg, 0.20 mmol) was added at room temperature (r.t.) to a solution of dmf (28 mg, 0.20 mmol) in Et_2O (5 ml). After 10 min of stirring the resulting solution was added to a solution of dpdpc (54 mg, 0.20 mmol) in 2.5 ml of Et_2O. The yellow product was collected by filtration after approximately 24 h, washed with Et_2O and dried in vacuo. The yield was approximately 95%. The molecular weight, as determined by osmometric measurements, was 1980 uma. ^1H NMR ($CDCl_3$): 7.6–7.0 (br, 10H); 3.6–1.6 (br, 16H).

2.2. *[PtClMe(μ-dpdpc)]$_3$*

A solution of dpdpc (30 mg, 0.11 mmol) in 1 ml of $CHCl_3$ was added to a stirred solution of $[PtClMe(Me_2S)_2]$ (40 mg, 0.11 mmol) in $CHCl_3$ (1.5 ml). After 4 h the white microcrystalline precipitate was recovered by filtration. The solid was washed with Et_2O (4 ml) and dried in vacuo. Yield: 85%. *Anal.* Calc. for $C_{17}H_{21}ClP_2Pt$: C, 39.44; H, 4.09. Found: C, 39.58; H, 4.11%. ^1H NMR ($CDCl_3$) δ: 7.8–7.3 (m, 10H); 3.6–3.3 (br, 4H); 2.7–2.3 (br, 4H); 0.28 (t, 3H, $^2J_{Pt-H} = 83$ Hz, $^3J_{P-H} = 6.5$ Hz); ^{31}P NMR ($CDCl_3$) δ: 8.0 ($^1J_{Pt-P} = 2588$ Hz).

2.3. *[PtMe(PPh$_3$)(dpdpc)]BF$_4$*

To a stirred solution of triphenylphosphine (26 mg, 0.10 mmol) in $CHCl_3$ (2 ml) was added at r.t. solid $AgBF_4$ (20 mg, 0.10 mmol) and a few drops of nitromethane to obtain complete dissolution. After 5 min the solution was added to a mixture of $[PtClMe(\mu\text{-}dpdpc)]_3$ (51 mg, 0.033 mmol) and 5 ml of $CHCl_3$, and stirring was continued 24 h at r.t. The solvent was removed in vacuo and the residue was extracted with 3 × 2 ml portions of $CHCl_3$. The solution was passed on a small Celite bed and concentrated to a small volume. Addition of Et_2O prompted the precipitation of the white product. The yield was approximately 80%. *Anal.* Calc. for $C_{35}H_{36}BF_4P_3Pt$: C, 50.56; H, 4.36. Found: C, 50.27; H, 4.26%. ^1H NMR ($CDCl_3$) δ: 7.8–7.2 (m, 25H); 2.9–2.5 (br, 8H); 0.32 (app q, 3H, $^2J_{Pt-H} = 66$ Hz); ^{31}P NMR resonances ($CDCl_3$) δ: 48.0 (dd, $^1J_{Pt-P} = 2550$ Hz, $^2J_{P-P}(trans) = 393$ Hz; $^2J_{P-P}(cis) = 69$ Hz); 39.4 (d, $^1J_{Pt-P} = 1398$ Hz); 29.0 (d, $^1J_{Pt-P} = 2915$ Hz). Conductivity in nitromethane at 298 K: 81.2 S mol^{-1} cm^{-1}.

2.4. *[Pt(PPh$_3$)$_2$(dpdpc)](BF$_4$)$_2$*

Solid $AgBF_4$ (49 mg, 0.25 mmol) was added at r.t. to a stirred solution of $[PtCl_2(PPh_3)_2]$ (100 mg, 0.127 mmol) in phenyl cyanide (2 ml). After 24 h the mixture is filtered and the solvent was removed in vacuo. The white residue was dissolved in 6 ml of $CHCl_3$ and a solution of dpdpc (34 mg, 0.125 mmol) in the same solvent (0.5 ml) was added at r.t. After 48 h stirring the solvent was removed in vacuo and the white residue was dissolved in a minimum amount of CH_2Cl_2/nitromethane (9:1). Hexane was added to achieve crystallization of the product in 70% yield. *Anal.* Calc. for $C_{52}H_{48}B_2F_8P_4Pt$: C, 53.59; H, 4.15. Found: C, 53.25; H, 4.24%. ^1H NMR ($CDCl_3$) δ: 7.7–7.4 (br, 32H); 7.2–7.0 (m, 4H); 6.9–6.7 (m, 4H); 3.4–3.2 (br, 4H); 2.8–2.5 (br, 4H); ^{31}P NMR resonances ($CDCl_3$) δ: 50.3 (d, $^1J_{Pt-P} = 2684$ Hz, $^2J_{P-P} = 278$ Hz); 15.5 (d, $^1J_{Pt-P} = 2710$ Hz). Conductivity in nitromethane at 298 K: 175.6 S mol^{-1} cm^{-1}.

2.5. [Pt(dpdpc)$_2$](BF$_4$)$_2$

To a solution of [PtCl$_2$(Me$_2$S)$_2$] (30 mg, 0.077 mmol) in methylene chloride (2 ml) a solution of dpdpc (42 mg, 0.15 mmol) in 1 ml of the same solvent and AgBF$_4$ (30 mg, 0.15 mmol) dissolved in a few drops of nitromethane were added at r.t. After 48 h of stirring a precipitate was filtered off, and the solvent was removed in vacuo to give an oily residue. This crude product was dissolved in a minimum amount of a CHCl$_3$/nitromethane mixture (9:1) and Et$_2$O was added to achieve crystallisation of the product in 75% yield. *Anal.* Calc. for $C_{32}H_{36}B_2F_8P_4Pt$: C, 42.09; H, 3.97. Found: C, 42.30; H, 4.02%. ^{1}H NMR (CD$_3$NO$_2$) δ: 7.25 (m, 4H); 7.15 (br, 8H); 6.98 (m, 8H); 3.10 (app d, 8H); 2.4 (br, 8H); ^{31}P NMR (CD$_3$NO$_2$) δ: 48.8 ($^1J_{Pt-P} = 2410$ Hz). Conductivity in nitromethane at 298 K: 164 S mol^{-1} cm^{-1}.

2.6. [Pt(dpdpc)(1,5-COD)](BF$_4$)$_2$

A solution of [PtCl$_2$(1,5-COD)] (56 mg, 0.15 mmol) in 2 ml of CH$_2$Cl$_2$ was added at r.t. to a stirred solution of dpdpc (41 mg, 0.15 mmol) in the same solvent (2 ml). After 3 h stirring a solution of AgBF$_4$ (60 mg, 0.30 mmol) in a few drops of nitromethane was added to the resulting suspension. After 18 h the white precipitate was removed by filtration and the solvent was eliminated in vacuo to afford an oily residue. This crude product was dissolved in a minimum amount of CHCl$_3$/nitromethane (9:1) and Et$_2$O was added to crystallise the product as a white solid in 75% yield. *Anal.* Calc. for $C_{24}H_{30}B_2F_8P_2Pt$: C, 38.48; H, 4.04. Found: C, 38.55; H, 3.99%. ^{1}H NMR (CD$_3$NO$_2$) δ: 7.9–7.7 (m, 10H); 5.81 (t, 4H, $^2J_{Pt-H} = 50$ Hz); 3.7 (br, 4H); 2.9–2.5 (br, 12H); ^{31}P NMR (CD$_3$NO$_2$) δ: 51.7 ($^1J_{Pt-P} = 3000$ Hz). Conductivity in nitromethane at 298 K: 178 S mol^{-1} cm^{-1}.

2.7. [PdMeCl(dpdpc)]$_3$

A solution of [PdMeCl(1,5-COD)] (40 mg, 0.15 mmol) in 1 ml of methylene chloride was added at r.t. to a stirred solution of dpdpc (41 mg, 0.15 mmol) in 2 ml of the same solvent. After 3 h stirring Et$_2$O (3 ml) was added dropwise in order to increase the amount of the white precipitate. The solid was recovered by filtration, washed with Et$_2$O and dried in vacuo in 85% yield. *Anal.* Calc. for $C_{17}H_{21}ClP_2Pd$: C, 47.58; H, 4.93. Found: C, 47.65; H, 5.02%. ^{1}H NMR (CDCl$_3$) δ: 7.7 (m, 4H); 7.4 (m, 6H); 3.4 (br, 4H); 2.45 (br, 4H); 0.10 (t, 3H, $^3J_{P-H} = 6$ Hz); ^{31}P NMR (CDCl$_3$) δ: 8.8.

2.8. [PdMe(MeCN)(μ-dpdpc)]$_3$(BF$_4$)$_3$

A solution of AgBF$_4$ (20 mg, 0.10 mmol) in methyl cyanide (1 ml) was added at r.t. to a mixture of [PdClMe(μ-dpdpc)]$_3$ (42 mg, 0.033 mmol) and 5 ml of CHCl$_3$, and stirring was continued 24 h at r.t. The solvent was removed in vacuo and the residue extracted with 3 × 2 ml portions of CHCl$_3$. The solution was passed on a small Celite bed and concentrated to a small volume. Addition of Et$_2$O prompted the precipitation of the white product in 80% yield. *Anal.* Calc. for $C_{19}H_{24}BF_4NP_2Pd$: C, 43.76; H, 4.64. Found: C, 43.52; H, 4.51%. ^{1}H NMR (CD$_3$NO$_2$/CDCl$_3$ 1:5) δ: 7.55 (br, 4H); 7.45 (br, 6H); 2.75 (br, 8H); 2.13 (3H); 0.80 (3H, $^3J_{P-H} = 6$ Hz); ^{31}P NMR (CD$_3$NO$_2$/CDCl$_3$ 1:5) δ: 6.6. Conductivity in nitromethane at 298 K: 79 S mol^{-1} cm^{-1}.

2.9. [PdMe(PPh$_3$)(dpdpc)](BF$_4$)

A solution of AgBF$_4$ (19 mg, 0.10 mmol) in 1 ml of nitromethane was added to a stirred mixture of [PdClMe(μ-dpdpc)]$_3$ (42 mg, 0.033 mmol) and triphenylphosphine (26 mg, 0.10 mmol) in 4 ml of CH$_2$Cl$_2$, and stirring was continued 1 h at r.t. The mixture was passed on a small Celite bed and concentrated to a small volume (1 ml). Addition of Et$_2$O prompted the precipitation of the white product in 70% yield. *Anal.* Calc. for $C_{35}H_{36}BF_4P_3Pd$: C, 56.60; H, 4.88. Found: C, 56.80; H, 5.01%. ^{1}H NMR (CDCl$_3$) δ: 7.60–7.20 (br, 20H); 7.15 (t, 1H); 6.95 (t, 2H); 6.70 (t, 2H); 2.7 (br, 8H); 0.25 (t, 3H, $^3J_{P-H} = 6$ Hz); ^{31}P NMR (CDCl$_3$) δ: 47.2 (d, $^2J_{P-P} = 369$ Hz); 34.1 (d); 30.3. Conductivity in nitromethane at 298 K: 85 S mol^{-1} cm^{-1}.

2.10. [Pd(dpdpc)$_2$](BF$_4$)$_2$

To a stirred solution of [PdCl$_2$(1,5-COD)] (29 mg, 0.10 mmol) in methylene chloride (5 ml) a solution of dpdpc (54 mg, 0.20 mmol) in the same solvent (1 ml) and a solution of AgBF$_4$ (39 mg, 0.20 mmol) in nitromethane (1 ml) were added at r.t. After 24 h of stirring the mixture was filtered, and approximately half of the solvent was removed in vacuo. After dropwise addition of approximately 3 ml of Et$_2$O, the white precipitate was recovered by filtration, washed with Et$_2$O and dried in vacuo. Yield: 80%. *Anal.* Calc. for $C_{32}H_{36}B_2F_8P_4Pd$: C, 46.61; H, 4.40. Found: C, 46.73; H, 4.48%. ^{1}H NMR (CD$_3$NO$_2$) δ: 7.25 (m, 2H); 7.15 (m, 4H); 7.0 (m, 4H); 3.15 (d, 4H); 2.35 (br, 4H); ^{31}P NMR (CD$_3$NO$_2$) δ: 57.4. Conductivity in nitromethane at 298 K: 170 S mol^{-1} cm^{-1}.

2.11. [Pd(py)$_2$(dpdpc)](BF$_4$)$_2$

To a stirred solution of [PdCl$_2$(1,5-COD)] (29 mg, 0.10 mmol) in methylene chloride (5 ml) were added a solution of dpdpc (27 mg, 0.10 mmol) in the same solvent (1 ml), pyridine (20 mg, 0.25 mmol), and a solution of AgBF$_4$ (39 mg, 0.20 mmol) in nitromethane (1 ml) at r.t. After 24 h of stirring, the mixture was filtered, and approximately half of the solvent was removed in vacuo. After dropwise addition of approximately 3 ml of Et_2O, the white precipitate was recovered by filtration, washed with Et_2O and dried in vacuo. Yield: 70%. *Anal.* Calc. for $C_{26}H_{28}B_2F_8N_2P_2Pd$: C, 43.95; H, 3.97; N, 3.94. Found: C, 44.09; H, 3.89; N, 3.79%. ^1H NMR ($CDCl_3$) δ: 8.81 (d, 4H), 7.6–7.4 (m, 8H); 7.3 (m, 4H); 7.18 (d, 4H); 3.78 (app t, 4H); 2.37 (app t, 4H). ^{31}P NMR ($CDCl_3$) δ: 66.8. Conductivity in nitromethane at 298 K: 168 S mol^{-1} cm^{-1}.

2.12. [CoCl$_2$(dpdpc-P,P′-dioxide)]$_2$

A solution of $CoCl_2 \cdot 6H_2O$ (30 mg, 0.13 mmol) in isopropanol was added dropwise to a stirred solution of dpdpc (34 mg, 0.13 mmol) in 2.5 ml of the same solvent. A brown microcrystalline precipitate immediately formed, while the solution turned to a turquoise-green color. The precipitate was recovered by filtration, washed with isopropanol and dried in vacuo. Attempt to recrystallise the brown compound from MeOH by addition of Et_2O resulted in the attainment of azure crystals, which were used for an X-ray analysis (see text). *Anal.* Calc. for $C_{32}H_{36}Cl_4Co_2O_4P_4$: C, 44.27; H, 4.18. Found: C, 44.35; H, 4.27%.

2.13. {[NiCl(dpdpc)$_2$]}$_2$[NiCl$_4$]

A solution of $NiCl_2 \cdot 6H_2O$ (24 mg, 0.10 mmol) in EtOH (1 ml) was added dropwise to a stirred solution of dpdpc (27 mg, 0.10 mmol) in 1 ml of methylene chloride. After 1 h standing at r.t. addition of Et_2O gave a red–brown microcrystalline precipitate, which was recovered by filtration, washed with Et_2O and dried in vacuo. Recrystallization from $CHCl_3$ by addition of Et_2O resulted in the attainment of dark-red crystals (yield: 75%). ^1H NMR ($CDCl_3$) δ: 7.4 (br, 4H); 7.25 (t, 2H); 7.16 (t, 4H); 3.24 (d, 4H); 2.02 (d, 4H); ^{31}P NMR ($CDCl_3$) δ: 62.2. *Anal.* Calc. for $C_{64}H_{72}Cl_6Ni_3P_8$: C, 52.01; H, 4.91. Found: C, 52.29; H, 4.89%.

2.14. Crystal structure determination of {[NiCl(dpdpc)$_2$]}$_2$(NiCl$_4$)

Details of the structure analysis are listed in Table 1. The compound was recrystallised from CH_2Cl_2/Et_2O. X-ray data were collected at r.t. on an Enraf–Nonius CAD4-F automatic diffractometer using Mo Kα graphite-monochromated radiation and operating in the ω/θ scan mode. The unit cell parameters were obtained by a least-squares fitting of the setting values of 25 reflections in θ range $14° \leq \theta \geq 12°$. Three monitoring reflections, measured every 500, showed an intensity decay of about 2.37% and a linear correction was applied. In addition to the corrections for Lp factors, an empirical absorption correction based on Fourier analysis of the data was applied. Relative transmission coefficients ranged from 148.966 to 65.106 with an average value of 101.572. The structure was solved by routine application of the Patterson and Fourier techniques and refined by full-matrix least-square procedure minimizing the quantity $\Sigma\, w(|F_o|-|F_c|)^2$ with $w^{-1} = [\sigma^2(F_o)+(0.02F_o)^2+1]$ where σ is derived from counting statistics. All non-hydrogen, but carbon atoms, were refined anisotropically. The H atoms were placed in calculated positions and included but not refined in last refinement cycles with isotropic thermal parameters equal those of the carrier atoms. The final Fourier difference map showed no peaks greater than 0.5 e Å^{-3}.

Table 1
Crystallographic parameters for chloronickel(dpdpc)$_2$ tetrachloronickelate

Formula weight	$C_{64}H_{72}Cl_6Ni_3P_8$
Temperature (K)	295±1
System	triclinic
Space group	#2 $P\bar{1}$
Crystal color	blue
Crystal shape	needles
Corrections	Lorentz-polarization linear decay (from 0.988 to 1.000 on *I*) reflection averaging (agreement on *I* = 3.2%) empirical absorption (from 1.536 to 0.671 on *I*)
a (Å)	10.878 (1)
b (Å)	17.794 (1)
c (Å)	20.294 (1)
α (°)	106.36 (1)
β (°)	105.58 (2)
γ (°)	107.82 (1)
V (Å^3)	3306.8
Z	2
D_{calc} (g cm^{-3})	1.48
Radiation	Cu Kα (1.54184 Å)
μ (cm^{-1})	54.4
F(000)	1528
Crystal dimensions (mm)	0.25 × 0.01 × 0.01
Maximum 2θ (°)	77.4
Reflections measured	7082 total, 7048 unique
Number unobserved data	3274
Reflections included	3774 with $F_o^2 > 3.0\sigma(F_o^2)$
Parameters refined	410
Unweighted agreement factor	0.059
Weighted agreement factor	0.068
Factor including unobserved data	0.198
Esd of observed of unit weight	1.35
Convergence, largest shift	0.01σ
Refinement	full-matrix least-squares
Minimization function	$\Sigma\, w(\lvert F_o\rvert-\lvert F_c\rvert)^2$
Least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
High peak in final difference map (e Å^{-3})	0.48 (9)
Low peak in final difference map (e Å^{-3})	0.39 (9)

All calculations were performed by using the Enraf–Nonius SDP set of programs [15].

3. Results and discussion

3.1. Platinum complexes

Attempts to isolate monomeric Pt(0) complexes of chelate dpdpc of the more common type known for single chain diphosphines [16], i.e. [Pt(*P*,*P*′-chelate)(ol)] (ol = electron-poor olefin) failed. In fact, the reaction of Pt(norbornene)$_3$ with dpdpc in presence of dimethylfumarate (‘dmf’) or fumarodinitrile (‘fdn’) gave poorly soluble products with scarcely significant broad ^{1}H NMR spectra. The only fairly reliable molecular weight determination pointed to the formula [Pt$_3$(dpdpc)$_3$(dmf)$_3$].

Also the nature of the products obtained from PtCl$_2$L$_2$ (L = Me$_2$S or L$_2$ = 1,5-COD) and dpdpc could not be satisfactorily understood, due to their very poor solubility.

A fairly poor solubility was displayed also by the white microcrystalline air stable solid obtained by reacting [PtClMeL$_2$] (L = Me$_2$S or L$_2$ = 1,5-COD) with the diphosphine. Although also in this case neither single crystal suitable for X-ray analysis nor a reliable molecular weight determination could be obtained, at least the NMR spectra at room temperature gave useful information. Only one signal is observed in the ^{31}P NMR spectrum, at 8.0 ppm ($^1J_{P-Pt} = 2588$ Hz), which discloses the equivalence of the two phosphorous atoms. Thus, the compound should not be a mononuclear one. In the ^{1}H NMR spectrum the Pt–Me signal is a triplet centred at 0.28 ppm ($^3J_{P-H} = 6.5$ Hz) and has satellites due to coupling with ^{195}Pt ($^2J_{Pt-H} = 83$ Hz). The former coupling is in keeping with a *cis* Me–Pt–P arrangement. Measurement of low temperature spectra was not permitted by the low solubility.

As for the molecular complexity of the product, we note: (i) the compound is not an electrolyte, thus ruling out an A-frame dimer of the type invoked for the related bisdiphenylphosphinomethane derivative [17,18]; (ii) the FAB mass spectrum only allows to rule out a monomeric structure. On consideration of the molecular complexity of the above reported dmf derivative we tentatively assume a trinuclear cyclic structure [PtMeCl(μ-dpdpc)]$_3$ [17,18]. Similarly, we will indicate as [PtCl$_2$(μ-dpdpc)]$_3$ the above mentioned dichloro derivative.

A simple mononuclear dpdpc complex of formula [PtMe(PPh$_3$)(dpdpc)]BF$_4$ could be isolated by reaction of the putative neutral trinuclear species with silver tetrafluoroborate in presence of triphenylphosphine, according to Eq. (1).

$$[\mathrm{PtClMe}(\mu\text{-dpdpc})]_3 + 3\mathrm{AgBF}_4 + 3\mathrm{PPh}_3 = 3[\mathrm{PtMe}(\mathrm{PPh}_3)(\mathrm{dpdpc})]\mathrm{BF}_4 + 3\mathrm{AgCl} \quad (1)$$

Relevant NMR features for the structure assignment are the following ones: (i) one doublet in the ^{31}P NMR spectrum at 39.4 ppm ($^1J_{Pt-P} = 1398$ Hz, $^2J_{P-P}(cis) = 69$ Hz), diagnostic [18] of a phosphorus atom *trans* to Me; (ii) two more signals at 48.0 ppm (double doublet, $^1J_{Pt-P} = 2550$ Hz, $^2J_{P-P}(trans) = 393$ Hz; $^2J_{P-P}(cis) = 69$ Hz) and at 29.0 ppm ($^1J_{Pt-P} = 2915$ Hz, $^2J_{P-P}(trans) = 393$ Hz). It is noteworthy the large low-field shift of the ^{31}P signal observed on comparing this spectrum and that pertaining to the parent compound. Conductivity measurements [19] and elemental analyses support the above structure.

Also mononuclear cationic dipositive complexes of general formula [PtL$_2$(dpdpc)](BF$_4$)$_2$, (L$_2$ = dpdpc or 1,5-COD or 2·PPh$_3$) could be isolated. The first one was prepared according to Eq. (2).

$$[\mathrm{PtCl}_2(\mathrm{Me}_2\mathrm{S})_2] + 2\mathrm{AgBF}_4 + 2\mathrm{dpdpc} = [\mathrm{Pt}(\mathrm{dpdpc})_2](\mathrm{BF}_4)_2 + 2\mathrm{AgCl} + 2\mathrm{Me}_2\mathrm{S} \quad (2)$$

The presence of only one signal at 48.8 ppm ($^1J_{Pt-P} = 2410$ Hz) in the ^{31}P NMR support the above formula, which is in keeping with conductivity measurements and elemental analyses.

The 1,5-COD derivative has been obtained according to Eq. (3).

$$[\mathrm{PtCl}_2(1,5\text{-COD})] + \mathrm{dpdpc} + 2\mathrm{AgBF}_4 = [\mathrm{Pt}(\mathrm{dpdpc})(1,5\text{-COD})](\mathrm{BF}_4)_2 + 2\mathrm{AgCl} \quad (3)$$

The ^{1}H NMR spectrum of the product discloses the presence of the diolefin through the signal of olefin protons (δ 5.81, $^2J_{Pt-H} = 50$ Hz). The single signal at 51.7 ppm in the ^{31}P NMR spectrum ($^1J_{P-Pt} = 3000$ Hz) is in agreement with the equivalence of the two phosphorus atoms.

The triphenyl phoshine dipositive cation could be obtained by preparing in situ [Pt(PPh$_3$)$_2$(PhCN)$_2$](BF$_4$)$_2$, and by exchanging the two phenylcyanide ligands with dpdpc (Eqs. (4) and (5)).

$$[\mathrm{PtCl}_2(\mathrm{PPh}_3)_2] + 2\mathrm{AgBF}_4 + 2\mathrm{PhCN} = [\mathrm{Pt}(\mathrm{PPh}_3)_2(\mathrm{PhCN})_2](\mathrm{BF}_4)_2 + 2\mathrm{AgCl} \quad (4)$$

$$[\mathrm{Pt}(\mathrm{PPh}_3)_2(\mathrm{PhCN})_2](\mathrm{BF}_4)_2 + \mathrm{dpdpc} = [\mathrm{Pt}(\mathrm{PPh}_3)_2(\mathrm{dpdpc})](\mathrm{BF}_4)_2 + 2\mathrm{PhCN} \quad (5)$$

The doublet at 15.5 ppm ($^2J_{P-P}(trans) = 278$ Hz) can be attributed to the equivalent phosphorous atoms of the two triphenylphosphines, while the donor atoms of dpdpc resonate at 50.3 ppm.

3.2. Palladium complexes of dpdpc

A close similarity is observed on comparing the above results concerning platinum with the behaviour of dpdpc in palladium environments. Attempts to obtain a simple mononuclear organometallic derivative [20] of the type [Pd(dpdpc)(ol)] from Pd(dba)$_2$ and an electron poor olefin failed. The products were possibly polynuclear species similar to the proposed platinum species.

The product from [PdCl$_2$(1,5-COD)] and dpdpc was poorly soluble and also its structure, possibly polynuclear, could not be unambiguously determined.

Also in this case, the fairly soluble Pd(II) chloro/methyl derivative displayed well resolved ^{1}H and ^{31}P NMR spectra. The former exhibits a triplet at 0.10 ppm ($^3J_{P-H} = 6.0$ Hz). In the latter one only one signal is observed at 8.8 ppm, pointing to the equivalence of the two P atoms. Thus, a mononuclear species should be ruled out. Unfortunately, the solubility was not sufficient for a molecular weight determination in solution. By analogy with the corresponding platinum complex we will denote this product as [PdClMe(μ-dpdpc)]$_3$.

Again, a cationic complex could be obtained by reaction of the putative neutral trinuclear species with silver tetrafluoroborate in presence of MeCN (Eq. (6)).

$$\begin{aligned}&[\mathrm{PdClMe}(\mu\text{-dpdpc})]_3 + 3\mathrm{AgBF_4} + 3\mathrm{MeCN}\\&\quad = [\mathrm{PdMe(MeCN)}(\mu\text{-dpdpc})]_3(\mathrm{BF_4})_3 + 3\mathrm{AgCl}\end{aligned} \tag{6}$$

The following NMR data are in keeping with the structure assigned to the complex: (i) a triplet in the ^{1}H NMR spectrum, centred at 0.80 ppm, ($^3J_{P-H} = 6$ Hz); (ii) only one signal in the ^{31}P NMR spectrum at 6.6 ppm. On consideration that lowering the temperature at 243 K does not affect significantly the proton spectrum and of the minor shift of the ^{31}P resonance with respect to the starting complex it appears that the polynuclear structure is retained in the cation.

Also for palladium a simple mononuclear complex of formula [PdMe(PPh$_3$)(dpdpc)]BF$_4$ could be prepared according to Eq. (7).

$$\begin{aligned}&[\mathrm{PdClMe}(\mu\text{-dpdpc})]_3 + 3\mathrm{AgBF_4} + 3\mathrm{PPh_3}\\&\quad = 3[\mathrm{PdMe(PPh_3)(dpdpc)}]\mathrm{BF_4} + 3\mathrm{AgCl}\end{aligned} \tag{7}$$

Three phosphorous signals are present in the ^{31}P spectrum. The singlet at δ 30.3 is attributable to the phosphorus atom of dpdpc *trans* to Me, while the doublets at 34.1 and 47.2 ppm ($^2J_{P-P}(trans) = 369$ Hz) pertain to the mutually *trans* phosphorous nuclei. Also in this case the large low field shift of the signals of dpdpc is in support for its chelation to the metal centre with formation of a mononuclear compound.

The mononuclear dipositive complexes [Pd(dpdpc)$_2$](BF$_4$)$_2$ and [Pd(py)$_2$(dpdpc)](BF$_4$)$_2$ were obtained according to Eqs. (8) and (9).

$$\begin{aligned}&[\mathrm{PdCl_2(1,5\text{-}COD)}] + 2\mathrm{AgBF_4} + 2\mathrm{dpdpc}\\&\quad = [\mathrm{Pd(dpdpc)_2}](\mathrm{BF_4})_2 + 2\mathrm{AgCl} + 1,5\text{-}\mathrm{COD}\end{aligned} \tag{8}$$

$$\begin{aligned}&[\mathrm{PdCl_2(1,5\text{-}COD)}] + 2\mathrm{AgBF_4} + \mathrm{dpdpc} + 2\mathrm{py}\\&\quad = [\mathrm{Pd(py)_2(dpdpc)}](\mathrm{BF_4})_2 + 2\mathrm{AgCl} + 1,5\text{-}\mathrm{COD}\end{aligned} \tag{9}$$

In the ^{31}P spectrum of the former complex the 4 equiv. phosphorous atoms resonate at 57.4 ppm, while in the spectrum of the latter one a singlet is observed at 66.8 ppm. Both conductivity measurements and elemental analyses support the proposed structures.

3.3. Nickel complex of dpdpc

Given the ability of nickel(II) to give complexes with vicinal diphosphines, we attempted the preparation of a dpdpc derivative by reacting the ligand with NiCl$_2$·6H$_2$O in ethanol/methylene chloride. The reaction can be described by Eq. (10).

$$\begin{aligned}&3\mathrm{NiCl_2\cdot 6H_2O} + 4\mathrm{dpdpc}\\&\quad = \{[\mathrm{NiCl(dpdpc)_2}]\}_2(\mathrm{NiCl_4}) + 18\mathrm{H_2O}\end{aligned} \tag{10}$$

The chelated phosphorous atoms of the brick colored product resonate at 62.2 ppm in the ^{31}P NMR spectrum. Crystals suited for X-ray analyses were grown from chloroform/diethyl ether (see before).

3.4. Cobalt complex of the dpdpc-*P*,*P′*-dioxide

The attempt to react CoCl$_2$·6H$_2$O with dpdpc afforded a brown microcrystalline material, which appeared very sensitive to air and turned to a blue–green microcrystalline stable compound also in presence of traces of oxygen. In spite of several crystallisation attempts, the last product could be obtained only as very small single crystals, on which an X-ray analysis was attempted. Although the molecular structure resolution was unsatisfactory, the general stereogeometry was unequivocally determined and is shown in Fig. 3. The compound is a binuclear derivative with two bridging *cis*-chair dpdpc-*P*,*P′*-dioxide moieties. Unfortunately, the standard errors of the structure model are quite high and not useful for a comparative discussion.

3.5. Molecular structure of chloronickel(dpdpc)$_2$ tetrachloronickelate

The molecular structure of the complex, together with the atom-labelling scheme, is shown in Fig. 2. Selected bond distances and angles are listed in Table 2. In the cation, displaying typical [21] square planar pyramidal geometry, the nickel atom is coordinated to four phosphorus atoms of two chelate dpdpc molecules and to one apical chlorine atom. The Ni–Cl distance is approximately 0.3 Å longer that the sum of atomic radii. The phenyl groups are perpendicular to the pyramid base and face each other. This arrangement should be caused both by mutual dipolar interactions in each pair of rings, and by the need of minimising steric contacts [22]. The Ni–P distances are in the range 2.19–2.20 Å, i.e. are in keeping with normal values for similar

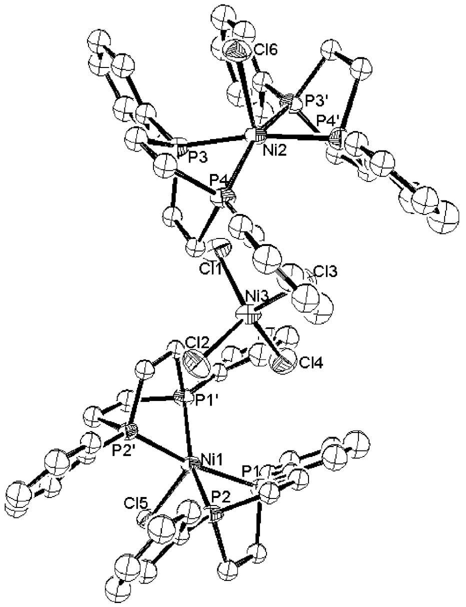

Fig. 2. Molecular structure of $\{[NiCl(dpdpc)_2]\}_2[NiCl_4]$ as determined through X-ray diffraction.

Table 2
Selected bond distances (Å) and angles (°) for chloronickel(dpdpc)$_2$ tetrachloronickelate

Bond distances	
Ni(1)–Cl(5)	2.469(3)
Ni(1)–P(1′)	2.207(3)
Ni(1)–P(1)	2.189(6)
Ni(1)–P(2)	2.191(3)
Ni(1)–P(2′)	2.183(5)
Ni(1)–Ni(3)	5.640(2)
Ni(2)–Cl(6)	2.463(4)
Ni(2)–P(3)	2.185(5)
Ni(2)–P(3′)	2.199(4)
Ni(2)–P(4)	2.201(4)
Ni(2)–P(4′)	2.195(5)
Ni(2)–Ni(3)	5.643(2)
Bond angles	
Cl(5)–Ni(1)–P(1′)	101.6(1)
Cl(5)–Ni(1)–P(1)	97.7(2)
Cl(5)–Ni(1)–P(2)	101.1(1)
Cl(5)–Ni(1)–P(2′)	94.6(2)
P(1′)–Ni(1)–P(1)	103.3(2)
P(1′)–Ni(1)–P(2)	157.2(1)
P(1′)–Ni(1)–P(2′)	75.0(2)
P(1)–Ni(1)–P(2)	75.4(2)
P(1)–Ni(1)–P(2′)	167.6(1)
P(2)–Ni(1)–P(2′)	101.3(2)
Cl(6)–Ni(2)–P(3)	94.8(2)
Cl(6)–Ni(2)–P(3′)	101.3(1)
Cl(6)–Ni(2)–P(4)	101.4(1)
Cl(6)–Ni(2)–P(4′)	97.6(1)
P(3)–Ni(2)–P(3′)	101.4(1)
P(3)–Ni(2)–P(4)	75.0(1)
P(3)–Ni(2)–P(4′)	167.6(2)
P(3′)–Ni(2)–P(4)	157.2(1)
P(3′)–Ni(2)–P(4′)	75.1(2)
P(4)–Ni(2)–P(4′)	103.5(2)

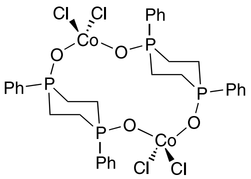

Fig. 3. Structure of $[CoCl_2(dpdpc\text{-}P,P'\text{-dioxide})]_2$.

complexes [23,24]. Noticeably, the bite angle P–Ni–P is nearly 75°, which is smaller than the values commonly exhibited by chelate open chain vicinal diphosphines in comparable environment [23]. The angles Ni–P–C$_{phenyl}$ are 130°, thus indicating that the tetrahedral geometry around P is significantly distorted. This can be explained on consideration that smaller values of the angles should accompany both to a diminished distance of facing rings, with increase of steric hindrance, and to a loss of the their parallelism, with decrease of the dipolar attraction. Within the dpdpc ring the C–P–C angles are approximately 100°, as for free *trans*-dpdpc [6]. As for the anions, they lie nearly halfway (Ni1–Ni3 = 5.641, Ni2–Ni3 = 5.643 Å) between two cations.

4. Conclusions

Complexes of dpdpc with platinum, palladium, nickel and cobalt have been prepared and characterised. The results indicate that a cyclic diphosphine like dpdpc can behave not only as bridge between metal centers, but also can chelate to one metal atom, affording a tough and enduring contribution, with uncommon stereochemistry, to the coordination environment. From our data it appears that a main feature prompting the attainment of chelation is the presence of a positive charge on the complex.

5. Supplementary material

Supplementary data have been deposited with the Cambridge Crystallographic Centre, CCDC No. 192717. 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

We thank Professor Federico Giordano, Università di Napoli ‘Federico II’, for helpful discussion, the MURST (Cofinanziamento 2000–2001) for financial support and the Centro Interdipartimentale di Metodologie Chimico-Fisiche, Università di Napoli ‘Federico II’ for NMR and X-ray facilities.

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