

# Synthesis and characterization of new homo-heterobinuclear platinum(II) complexes with dimethylphosphonate as bridging ligands. Crystal structure of $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2(\mu\text{-I})\text{PtMe}_3]$

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Received 29 April 1996; revised 19 June 1996

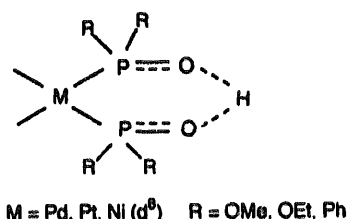
## Abstract

The preparation of the new neutral complex  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2]$  (1) (dppm = 1,1-bis(diphenylphosphino) methane) and its behaviour as a chelate (O,O)-donor ligand is described. This ligand reacts with  $[\text{Me}_3\text{PtI}]_4$  to give the homobimetallic complex  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2(\mu\text{-I})\text{PtMe}_3]$  (2), which in turn reacts with  $\text{AgPF}_6$  in the presence of  $\text{PPh}_3$  to yield the new cationic complex  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2(\text{PtMe}_3(\text{PPh}_3))]\text{PF}_6$  (3). In contrast, the treatment of binuclear complexes  $[\{\text{Pd}(\mu\text{-Cl})(2\text{-MeC}_3\text{H}_4)\}_2]$  and  $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$  with silver perchlorate in the presence of the bidentate ligand 1 yields the heterobinuclear compounds  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2\text{Pd}(\eta^3\text{MeC}_3\text{H}_4)]\text{ClO}_4$  (4) and  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2\text{Rh}(\text{cod})]\text{ClO}_4$  (5). Complex 5 reacts with an atmosphere of CO at room temperature yielding the *cis*-dicarbonyl complex  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2\text{Rh}(\text{CO})_2]\text{ClO}_4$  (6). The structure of complex  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2(\mu\text{-I})\text{PtMe}_3]$  has been determined by single crystal X-ray diffraction methods.

**Keywords:** Platinum; Trimechylplatinum(IV) complex; Phosphonate; Diphosphine; Crystal structure

## 1. Introduction

A variety of  $d^8$  transition metal compounds containing disubstituted phosphinites or phosphonates and disubstituted phosphinous acid or phosphite as ligands have been described [1–6].



These metal compounds contain a hydrogen-bonded proton symmetrically bonded to the oxygen atoms of the phosphonate or phosphinite groups. This proton can easily be removed by bases to form an anionic complex which can act as a bidentate chelating ligand through the oxygens.

In contrast, neutral bis(phosphonate)platinum(II) complexes of the type  $[(\eta^2\text{L}_n)\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2]$ , where  $\text{L}_n = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$  (dppe) or *o*-phenylen-bis(dimethylarsine) (diars), can act as oxygen donor ligands in reactions with main-group or transition metals in normal oxidation states to form trimetallic derivatives [3,7,8].

In this paper we describe the preparation of the new compound  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2]$  and its behaviour as a chelate (O,O)-donor ligand in reaction with the organometallic fragments  $\{\text{PtMe}_3\}$ ,  $\{\text{Pd}(\text{MeC}_3\text{H}_4)\}^+$  and  $\{\text{Rh}(\text{cod})\}^+$ . The crystal structure of the homobinuclear complex  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2(\mu\text{-I})\text{PtMe}_3]$  has been determined by X-ray diffraction.

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## 2. Experimental details

Elemental analyses were made with a Heraeus Mikro Standard microanalyser. IR spectra were recorded on a Perkin–Elmer 567 spectrophotometer (over the range 4000–200 cm<sup>-1</sup>) using KBr pellets. Conductivities were measured in ca. 5 × 10<sup>-4</sup> M acetone solutions using a WTW LF-521 conductimeter. <sup>1</sup>H (200 MHz) and <sup>31</sup>P{<sup>1</sup>H} (81 MHz) NMR spectra were recorded on a Bruker AC-200P spectrometer and the chemical shifts are reported relative to Me<sub>4</sub>Si and 85% H<sub>3</sub>PO<sub>4</sub> in D<sub>2</sub>O respectively (positive shifts downfield).

All reactions were carried out by Schlenk techniques under purified nitrogen. Reagent-grade solvents were dried, distilled, and stored under a nitrogen atmosphere. The starting complexes [Pt{P(O)(OMe)<sub>2</sub>}<sub>2</sub>{P(OH)(OMe)<sub>2</sub>}] [4], [PtMe<sub>3</sub>]<sub>4</sub> [9], [Rh(μ-Cl)(cod)]<sub>2</sub> [10], and [Pd(μ-Cl)(2-MeC<sub>3</sub>H<sub>4</sub>)<sub>2</sub>] [11] were prepared by published procedures.

### 2.1. Synthesis of [Pt(η<sup>2</sup>dppm)Pt{P(O)(OMe)<sub>2</sub>}] (1)

To a solution of the platinum complex [Pt{P(O)(OMe)<sub>2</sub>}<sub>2</sub>{P(OH)(OMe)<sub>2</sub>}] (1.2 g; 1.9 mmol) in benzene (120 cm<sup>3</sup>) the stoichiometric amount of dppm was added (0.728 g; 1.9 mmol). After stirring the solution for 48 h, a white solid was formed, which was filtered and washed with cold benzene. The complex crystallized from dichloromethane–*n*-hexane as air-stable white crystals. Yield 1.21 g (81%). Found: C, 43.8; H, 4.2. C<sub>29</sub>H<sub>34</sub>O<sub>6</sub>P<sub>4</sub>Pt. Calc.: C, 43.7; H, 4.3%. IR (KBr): ν(PO) = 1104 cm<sup>-1</sup>.

### 2.2. Synthesis of [Pt(η<sup>2</sup>-dppm)Pt{μ-P(O)(OMe)<sub>2</sub>}(μ-IPtMe<sub>3</sub>)] (2)

Complex 1 (263 mg; 0.33 mmol) dissolved in chloroform (20 cm<sup>3</sup>) was added to a solution of the complex [PtMe<sub>3</sub>]<sub>4</sub> (120 mg; 0.327 mmol) in chloroform (10 cm<sup>3</sup>). The mixture was boiled under reflux for 6 h and then evaporated to a small volume. Orange crystals were obtained by addition of *n*-hexane and cooling at -20°C. Yield 303 mg (80%). Found: C, 33.0; H, 4.0. C<sub>32</sub>H<sub>43</sub>IO<sub>6</sub>P<sub>4</sub>Pt<sub>2</sub>. Calc.: C, 33.0; H, 3.7%. IR (KBr): ν(PO) = 1104 cm<sup>-1</sup>.

### 2.3. Synthesis of [Pt(η<sup>2</sup>dppm)Pt{μ-P(O)(OMe)<sub>2</sub>}(μ-PtMe<sub>3</sub>(PPh<sub>3</sub>))PF<sub>6</sub>] (3)

A solution of complex 2 (85 mg; 0.073 mmol) in chloroform (5 cm<sup>3</sup>) was treated with a solution of AgPF<sub>6</sub> (19 mg; 0.075 mmol) dissolved in acetone (5 cm<sup>3</sup>). After stirring at room temperature for 30 min, the mixture was filtered through cellulose to remove the AgCl formed. To the resulting solution PPh<sub>3</sub> (19.2 mg; 0.075 mmol) was added and then stirred again for 1 h. The solution

was concentrated and the addition of *n*-hexane gave a white precipitate which was filtered off, washed with *n*-hexane and dried in vacuo. Crystallization at -20°C from chloroform–*n*-hexane gave colourless crystals. Yield 89 mg (84%). Found: C, 42.24; H, 4.23. C<sub>51</sub>H<sub>56</sub>O<sub>6</sub>P<sub>6</sub>F<sub>6</sub>Pt<sub>2</sub>. Calc.: C, 42.1; H, 3.88%. IR (KBr): ν(PO) = 1095 cm<sup>-1</sup>; ν(PF<sub>6</sub><sup>-</sup>) = 840 and 560 cm<sup>-1</sup>. Λ<sub>M</sub> = 136 cm<sup>2</sup> mol<sup>-1</sup> Ω<sup>-1</sup> (acetone).

### 2.4. Synthesis of [Pt(η<sup>2</sup>dppm)Pt{μ-P(O)(OMe)<sub>2</sub>}(μ-Pd(η<sup>3</sup>MeC<sub>3</sub>H<sub>4</sub>))ClO<sub>4</sub>] (4)

A solution of complex [Pd(μ-Cl)(2-MeC<sub>3</sub>H<sub>4</sub>)<sub>2</sub>] (30 mg; 0.075 mmol) in tetrahydrofuran (20 cm<sup>3</sup>) was treated with AgClO<sub>4</sub> (31.2 mg; 0.15 mmol). After stirring at room temperature for 1 h, the mixture was filtered through cellulose to remove the AgCl formed. To the resulting solution complex 1 (120 mg; 0.15 mmol) dissolved in tetrahydrofuran (10 cm<sup>3</sup>) was added. The white precipitate formed was filtered off, washed with tetrahydrofuran and dried in vacuo. The complex was recrystallized from chloroform–*n*-hexane at low temperature (-20°C). Yield 93 mg (59%). Found: C, 37.2; H, 4.4. C<sub>33</sub>H<sub>41</sub>ClO<sub>10</sub>P<sub>4</sub>PdPt. Calc.: C, 37.4; H, 3.9%. IR (KBr): ν(PO) = 1090; ν(ClO<sub>4</sub><sup>-</sup>) = 1100 and 625 cm<sup>-1</sup>. Λ<sub>M</sub> = 138 cm<sup>2</sup> mol<sup>-1</sup> Ω<sup>-1</sup> (acetone).

### 2.5. Synthesis of [Pt(η<sup>2</sup>dppm)Pt{μ-P(O)(OMe)<sub>2</sub>}(μ-Rh(cod))ClO<sub>4</sub>] (5)

A solution of complex [Rh(μ-Cl)(cod)]<sub>2</sub> (125 mg; 0.253 mmol) in dichloromethane (10 cm<sup>3</sup>) was treated with a solution of AgClO<sub>4</sub> (105.2 mg; 0.506 mmol) dissolved in acetone (15 cm<sup>3</sup>). After stirring at room temperature for 15 min, the mixture was filtered through cellulose to remove the AgCl formed. To the resulting solution complex 1 (403.6 mg; 0.506 mmol) dissolved in acetone (10 cm<sup>3</sup>) was added. After 30 min, the solution was concentrated and the addition of diethyl ether gave yellow-orange crystals. Yield 481 mg (86%). Found: C, 40.6; H, 4.4. C<sub>37</sub>H<sub>46</sub>ClO<sub>10</sub>P<sub>4</sub>PtRh. Calc.: C, 40.1; H, 4.2%. IR (KBr): ν(PO) = 1085 cm<sup>-1</sup>; ν(ClO<sub>4</sub><sup>-</sup>) = 1100 and 620 cm<sup>-1</sup>. Λ<sub>M</sub> = 159 cm<sup>2</sup> mol<sup>-1</sup> Ω<sup>-1</sup> (acetone).

### 2.6. Synthesis of [Pt(η<sup>2</sup>dppm)Pt{μ-P(O)(OMe)<sub>2</sub>}(μ-Rh(CO)<sub>2</sub>)ClO<sub>4</sub>] (6)

CO (1 atm) was bubbled for 20 min through an acetone solution of complex 3 (200 mg; 0.180 mmol). The solution was evaporated to dryness, the solid residue dissolved in acetone, and CO was bubbled again for 10 min. The careful addition of diethyl ether led to the formation of yellow crystals, which were washed with cold diethyl ether and dried in vacuo. Yield 157 mg (82%). Found: C, 35.2; H, 3.4. C<sub>31</sub>H<sub>34</sub>ClO<sub>12</sub>P<sub>4</sub>PtRh. Calc.: C, 35.3; H, 3.2%. <sup>1</sup>H NMR(CDCl<sub>3</sub>): δ 5.43

(tb,CH<sub>2</sub>, <sup>2</sup>J<sub>PH</sub> = 11 Hz), 3.46 ppm (d,OMe,<sup>3</sup>J<sub>PH</sub> = 12 Hz). IR (KBr): ν(PO) = 1070; ν(CO) = 2075 and 1995 cm<sup>-1</sup>. IR (Me<sub>2</sub>CO): ν(CO) = 2060 and 1970 cm<sup>-1</sup>. A<sub>M</sub> = 128 cm<sup>2</sup> mol<sup>-1</sup> Ω<sup>-1</sup> (acetone).

### 2.7. Crystal structure determination of complex 2

A deep-orange, polyhedron-shaped crystal, of average dimension 0.56 × 0.42 × 0.60 mm<sup>3</sup>, obtained from a slow diffusion of *n*-hexane into a chloroform solution of complex 2, was selected for structure determination by X-ray diffraction. Intensity data were collected on a Siemens R3m/V four-circle diffractometer, in ω-scan mode, using graphite-monochromated Mo Kα radiation. Cell parameters were refined by least squares fit of 50 reflections with 15 ≤ 2θ ≤ 30°. A total of 8967 reflections were collected, with 3.0 ≤ 2θ ≤ 45°, for structure solution and refinement, and merged to give 5018 unique reflections, of which 3609 had I > 2σ(I). Intensities were corrected for Lorentz and polarization effects.

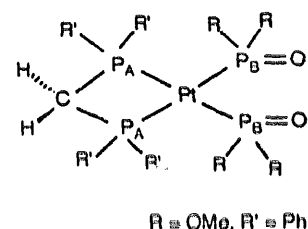
Table 1  
Crystallographic data for [(η<sup>2</sup>-dppm)Pt(μ-P(O)OMe)<sub>2</sub>](μ-PtMe<sub>3</sub>) (2)

Empirical formula	C <sub>32</sub> H <sub>43</sub> O <sub>6</sub> P <sub>4</sub> Pt <sub>2</sub>
Formula weight	1164.62
Temperature (K)	297(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	
<i>a</i> (Å)	27.458(7)
<i>b</i> (Å)	14.204(3)
<i>c</i> (Å)	21.567(5)
α (deg)	90
β (deg)	114.31(2)
γ (deg)	90
Volume (Å <sup>3</sup> )	7666(3)
Z	8
Density (calc.) (Mg m <sup>-3</sup> )	2.018
Absorption coefficient (mm <sup>-1</sup> )	8.303
<i>F</i> (000)	4416
Index ranges	0 ≤ <i>h</i> ≤ 29, 0 ≤ <i>k</i> ≤ 15, -23 ≤ <i>l</i> ≤ 21
Reflections collected	8967
Independent reflections	5018 ( <i>R</i> <sub>int</sub> = 0.0788)
Absorption correction	Semi-empirical
Max. and min. transmission	1.0000 and 0.3862
Refinement method	Full-matrix least squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	5017/0/407
Goodness-of-fit of <i>F</i> <sup>2</sup>	0.986
Final <i>R</i> indices ( <i>I</i> > 2σ( <i>I</i> ))	<i>R</i> ( <i>F</i> ) = 0.0500, <i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.1224
<i>R</i> indices (all data)	<i>R</i> ( <i>F</i> ) = 0.0676, <i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.1288
Extinction coefficient	χ = 0.00033(3), where <i>F</i> <sub>c</sub> <sup>*</sup> = <i>kF</i> <sub>c</sub> (1 + 0.001 χ <i>F</i> <sub>c</sub> <sup>2</sup> λ <sup>3</sup> / sin 2θ) <sup>-1/4</sup>
Weighting scheme	<i>w</i> <sup>-1</sup> = σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + [0.0691( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3] <sup>2</sup>
Largest diff. peak and hole (e Å <sup>-3</sup> )	1.885 and -2.592 in the vicinity of heavy atoms

Semi-empirical corrections, via psi-scans, were applied for absorption. The structure was solved by direct methods and refined on *F*<sup>2</sup>, using all reflections, by full-matrix least squares with anisotropic thermal parameters for non-H atoms. A riding model was applied to hydrogen atoms placed geometrically at idealized positions, with C–H distances of 0.96 Å and isotropic *U* = 1.0 *U*<sub>eq</sub> of their parent C atoms. Refinement converged to final *R* = 0.050 for *I* > 2σ(*I*) [12]. Calculations were performed with SHELXTL-PLUS software programs, and refinements with the SHELXL93 program [13]. Crystal data and relevant refinement parameters are summarized in Table 1.

### 3. Results and discussion

The neutral platinum(II) complex [Pt(P(O)OMe)<sub>2</sub>]<sub>2</sub>(P(OH)OMe)<sub>2</sub> reacts with 1,1-bis(diphenylphosphine)methane (dppm) in benzene solution to give the neutral complex [Pt(P(O)OMe)<sub>2</sub>]<sub>2</sub>(η<sup>2</sup>-dppm) (1) (hereafter abbreviated as L).



This compound was isolated as a stable white solid and its IR spectrum in KBr pellet shows the characteristic strong absorption of ν(PO) at 1104 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> exhibits the expected doublet resonance at δ 3.46 ppm (<sup>3</sup>J<sub>PH</sub> = 12 Hz) for the methyl groups of the phosphonate ligands and a broad triplet signal centred at δ 4.53 ppm (<sup>2</sup>J<sub>PH</sub> = 10 Hz) for the methylene protons of the dppm ligand. The pattern of this signal is due to the proton coupling with <sup>31</sup>P and <sup>195</sup>Pt, and also to the virtual coupling <sup>2</sup>J<sub>(PPtP)</sub> [8,14,15]. All chemical shifts and coupling constants are summarized in Table 2. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows two doublet resonances at δ -39.52 and 66.71 ppm corresponding to the P<sub>A</sub> atoms of the dppm and P<sub>B</sub> atoms of the phosphonate ligands respectively. This spectrum has been analysed as an AA'BB' spin system for isotopes of Pt (spin inactive (*I* = 0); 66.3% abundance) and as an AA'BB'X spin system for isotope <sup>195</sup>Pt (spin active (*I* = 1/2); 33.7% abundance) where δ<sub>PA</sub> = δ<sub>PA'</sub>, δ<sub>PB</sub> = δ<sub>PB'</sub>, and *J*<sub>AA'}</sub>, *J*<sub>AB}</sub>, *J*<sub>A'B'}</sub> and *J*<sub>BB'}</sub> are not resolved, and *J*<sub>AB'}</sub> = *J*<sub>A'B}</sub> = 539 Hz.

L (1) reacts with the tetramer compound  $[(\text{PtIme}_3)_4]$  in chloroform solution at reflux temperature by cleavage of the iodine bridges to form the neutral homobinuclear complex  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2\text{PtIme}_3]$  (2). The IR spectrum of the orange solid obtained shows that the  $\nu(\text{PO})$  absorption band does not change with respect to that of the free ligand L ( $1104\text{ cm}^{-1}$ ). The  $^1\text{H}$  NMR spectrum shows two multiplet resonances at  $\delta$  4.18 and 5.07 ppm indicating the presence of two non-equivalent methylene protons,  $\text{H}_a$  and  $\text{H}_b$ . The proton endo to the iodine atom is labelled  $\text{H}_a$  and is tentatively assigned to the highest field resonance on the basis of results obtained for the coordinated dppm ligand in platinum(II) and ruthenium(II) complexes [16]. Moreover, the spectrum shows two doublet resonances at  $\delta$  3.08 and 3.56 ppm corresponding to non-equivalent methoxy protons of the bridged phosphonate ligands. These signals appear at higher and lower field with respect to the signals of the free ligand L. These shifts are probably due to a conformational modification on the dppm moiety of the ligand L which changes the spatial orientation of its phenyl groups, which in turn causes a differentiation of the methoxy phosphonate groups [14,17,18]. Also, the spectrum shows two broad singlet signals due to the resonances of methyl bonded to platinum (intensity relation of 2:1), with the corresponding satellites due to  $^{195}\text{Pt-H}$  coupling, at  $\delta$  1.40 ppm ( $^2J_{\text{Pt-H}} = 80\text{ Hz}$ ), assigned to the methyl group trans to the oxygen atoms of ligand L and at  $\delta$  1.38 ppm ( $^2J_{\text{Pt-H}} = 72\text{ Hz}$ ), attributed to the methyl group trans to iodide atom.

These results suggest that in complex 2 the non-

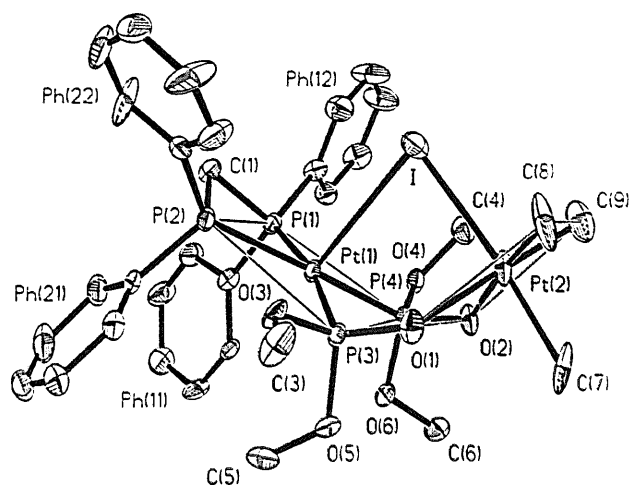


Fig. 1. ORTEP plot of complex 2 with thermal ellipsoids at 25% probability level. Best planes of platinum coordination indicated with full lines. H atoms omitted for clarity.

equivalence of the protons of the dppm ligand is due to some interaction with the iodide ligand of the  $(\text{PtIme}_3)$  moiety. In order to confirm this interaction and to determine the detailed geometry, an X-ray structural determination of complex 2 was undertaken. Fig. 1 shows an ORTEP representation of the complex, including the atom numbering scheme. Tables 3 and 4 list atomic coordinates with equivalent isotropic thermal parameters of non-H atoms, and relevant bond distances and angles respectively. The compound is a homobinuclear neutral complex with two platinum atoms in different oxidation states (Pt(1): oxidation state II; Pt(2):

Table 2  
NMR chemical shifts ( $\delta$  ppm)<sup>a</sup> and coupling constants ( $J$  Hz) of the homo- and heterobinuclear complexes

Complex	$^1\text{H}$ NMR			$^{31}\text{P}\{^1\text{H}\}$ NMR				
	P(OMe) <sub>2</sub>	CH <sub>2</sub> (dppm)	Other signals	P <sub>A</sub>	P <sub>B</sub>	$^2J_{\text{P}_A-\text{P}_B}$	$^1J_{\text{Pt}-\text{P}_A}$	$^1J_{\text{Pt}-\text{P}_B}$
L (1)	3.46(d) $^3J_{\text{PH}} = 12$	4.53(bt) $^2J_{\text{PH}} = 10$	—	-39.52(d)	66.71(d)	539	1607	4397
(2)	3.08(d) $^3J_{\text{PH}} = 11$ 3.56(d) $^3J_{\text{PH}} = 12$	4.18(m, H <sub>A</sub> ) 5.07(m, H <sub>B</sub> )	1.38(s, CH <sub>3</sub> ) <sup>b</sup> $^2J_{\text{Pt-H}} = 72.0$ 1.40(s, CH <sub>3</sub> ) <sup>c</sup> $^2J_{\text{Pt-H}} = 80.0$	-51.57(d)	78.25(d)	537	1897	4474
(3) <sup>d</sup>	3.02(d) $^3J_{\text{PH}} = 13.1$ 3.20(d) $^3J_{\text{PH}} = 11.1$	4.80(bt) $^2J_{\text{PH}} = 10.5$	1.02(d, CH <sub>3</sub> ) <sup>c</sup> $^2J_{\text{PH}} = 77.0$ 1.50(d, CH <sub>3</sub> ) <sup>f</sup> $^2J_{\text{PH}} = 56.9$	-37.40(d)	76.07(d)	523	1694	4176
(4)	3.41(vt) $^3J_{\text{PH}} = 11.8$	5.06(bt) $^2J_{\text{PH}} = 10.7$	2.13(s, CH <sub>3</sub> ) 2.71(s, anti) 3.69(s, syn)	-39.18(d)	78.02(d)	525	1690	4175
(5)	3.30(d) $^3J_{\text{PH}} = 12.0$	5.11(bt) $^2J_{\text{PH}} = 11.0$	1.75(bd, CH <sub>2</sub> ) 2.49(bs, CH <sub>2</sub> ) 3.98(bs, CH)	-38.59(d)	78.56(d)	517	1708	4132

<sup>a</sup> Measured in CDCl<sub>3</sub> at room temperature. Chemical shifts relative to Me<sub>4</sub>Si and H<sub>3</sub>PO<sub>4</sub> (85%) as standards: s = singlet, bs = broad singlet, d = doublet, bd = broad doublet, bt = broad triplet, vt = virtual triplet, q = quartet, m = multiplet. All complexes show multiplets in the region corresponding to phenyl groups of the ligands. <sup>b</sup>  $^2J_{\text{Pt-H}}$  corresponded to methyl group trans to I. <sup>c</sup>  $^2J_{\text{Pt-H}}$  corresponded to two methyl groups trans to oxygen atoms of the ligand L. <sup>d</sup>  $\delta_{\text{P}_C} = 10.74\text{ ppm}$ ;  $^1J_{\text{Pt}-\text{P}_C} = 1088\text{ Hz}$ ;  $\delta_{\text{P}_A} = -145\text{ ppm}$ . <sup>e</sup>  $^2J_{\text{Pt-H}}$  corresponded to methyl groups trans to oxygen atoms of the ligand L;  $^3J_{\text{P}_C-\text{H}(\text{cis})} = 7.7\text{ Hz}$ . <sup>f</sup>  $^2J_{\text{Pt-H}}$  corresponded to methyl group trans to P<sub>C</sub> of the ligand PPh<sub>3</sub>;  $^3J_{\text{P}_C-\text{H}(\text{trans})} = 8.0\text{ Hz}$ .

Table 3

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ) for 2

	x	y	z	$U_{eq}^a$
Pt(1)	1345(1)	1534(1)	6082(1)	30(1)
Pt(2)	1094(1)	3978(1)	5066(1)	51(1)
I	1895(1)	3549(1)	6368(1)	60(1)
P(1)	1341(1)	1078(2)	7111(2)	33(1)
P(2)	2100(1)	582(2)	6654(2)	33(1)
P(3)	1373(1)	1700(2)	5038(2)	30(1)
P(4)	552(1)	2315(2)	5685(2)	31(1)
O(1)	1319(4)	2662(6)	4720(4)	52(2)
O(2)	494(3)	3189(6)	5263(5)	45(2)
O(3)	1919(3)	1226(7)	5093(4)	45(2)
O(4)	379(3)	2582(6)	6287(4)	38(2)
O(5)	929(3)	1103(7)	4449(4)	44(2)
O(6)	77(3)	1607(6)	5274(4)	41(2)
C(1)	2046(5)	689(10)	7467(6)	41(3)
C(3)	2076(7)	1286(14)	4539(8)	81(6)
C(4)	454(6)	3512(10)	6567(8)	57(4)
C(5)	865(7)	111(12)	4542(8)	83(6)
C(6)	-451(5)	2023(11)	4965(7)	61(4)
C(7)	496(6)	4185(11)	4102(8)	72(6)
C(8)	1602(7)	4733(11)	4811(13)	110(8)
C(9)	874(6)	5148(12)	5356(10)	85(6)
C(111)	975(5)	33(10)	7093(6)	37(3)
C(112)	600(5)	-343(9)	6482(6)	37(3)
C(113)	330(5)	-1161(11)	6464(8)	54(4)
C(114)	420(6)	-1629(12)	7066(8)	64(4)
C(115)	787(6)	-1239(12)	7680(8)	71(5)
C(116)	1063(6)	-460(11)	7696(7)	58(4)
C(121)	1245(5)	1845(10)	7728(6)	40(3)
C(122)	795(5)	1734(10)	7873(7)	48(4)
C(123)	719(6)	2340(12)	8326(7)	62(5)
C(124)	1067(7)	3079(15)	8622(9)	86(6)
C(125)	1500(7)	3154(16)	8488(10)	94(7)
C(126)	1589(6)	2576(12)	8038(8)	65(5)
C(211)	2025(5)	-641(9)	6407(7)	38(3)
C(212)	2098(6)	-883(11)	5837(7)	58(4)
C(213)	2024(8)	-1823(14)	5617(10)	85(6)
C(214)	1880(7)	-2506(14)	5973(13)	93(7)
C(215)	1807(6)	-2260(13)	6515(13)	91(7)
C(216)	1890(6)	-1321(10)	6761(9)	59(4)
C(221)	2802(5)	848(9)	6851(6)	37(3)
C(222)	2964(6)	1448(13)	6501(8)	75(5)
C(223)	3493(79)	1582(15)	6649(10)	105(8)
C(224)	3866(6)	1187(12)	7199(9)	71(5)
C(225)	3708(6)	576(13)	7525(11)	88(7)
C(226)	3198(6)	430(13)	7386(13)	95(7)

<sup>a</sup>  $U_{eq}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

oxidation state IV), linked by a pair of P–O bridges and an iodide bridge. The Pt(1)–Pt(2) separation of 4.009(1) Å excludes any significant intermetallic interaction. The two phosphorus atoms of a dpmm ligand and the three carbon atoms of the methyl groups complete the coordination spheres of the Pt(1) and Pt(2) atoms respectively.

The Pt(1) centre has a distorted five-coordinate square-pyramidal geometry with the iodide bridging ligand at the apical site and the four phosphorus atoms, P(1), P(2), P(3) and P(4), forming the basal plane with

an r.m.s. deviation of 0.036 Å from their least squares plane (max. dev. 0.040(2) Å; min. dev. 0.032(1) Å). Pt(1) is raised 0.127(2) Å above this plane towards the iodide atom. The Pt(1)–I axis deviates by an angle of 11.7° from the ideal apical position. The Pt(2) centre exhibits a distorted octahedral geometry. Atoms O(1), O(2), C(8) and C(9), define the equatorial plane with an r.m.s. deviation of 0.030 Å from their least squares plane (max. dev. 0.031(9) Å; min. dev. 0.028(8) Å). The Pt(2) atom is raised 0.054(9) Å from this plane and the vector Pt(2)–I deviates 4.0° from the ideal axial position. The bond angle Pt(1)–I–Pt(2) is 83.55(3)°. The angle between the basal plane of the square-pyramidal geometry of Pt(1) and the equatorial plane of the octahedral geometry of Pt(2) is 110.4(3)°. This angle is smaller than that between the mean square planes in the binuclear complex [(dppe)Pt(μ-SMe)<sub>2</sub>PtClMe<sub>3</sub>] (154°) which only exhibits thiolate bridges [19].

The Pt(2)–C distances (2.072(15), 1.956(16) and 2.009(15) Å), as well as the Pt(2)–O bond lengths (2.173(8) and 2.194(9) Å), compare well with those found in the complex [(C<sub>5</sub>H<sub>5</sub>)Co(μ-PO(OEt)<sub>2</sub>)<sub>2</sub>PtMe<sub>3</sub>] (Pt–C: average 2.004(8); Pt–O: average 2.196(4) Å) [20]. The Pt(2)–I distance (2.829(2) Å) is similar to that found in the mononuclear complexes for terminal Pt–I bonds, [PtMe<sub>3</sub>(pz)<sub>2</sub>CHMe] (2.807(1) Å) and [PtMe<sub>3</sub>(3,5-Me<sub>2</sub>pz)<sub>2</sub>CH<sub>2</sub>] (2.842(1) Å) [21]. The Pt(1)–P(dpmm) distances (2.353(3) and 2.318(3) Å) are slightly greater than those found in the complex [Pt<sub>2</sub>(μ-I)<sub>2</sub>(dpmm)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (2.240(2) and 2.243(2) Å) [22] and the Pt(1)–P(phosphonate) distances (2.295(3) and 2.273(3) Å) are similar to those found in the complex [Cl(Et<sub>3</sub>P)Pt(μ-POPh<sub>2</sub>)<sub>2</sub>Pt(PEt<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (2.294(4) and 2.233(4) Å) [1]. The Pt(1)–I distance is very long (3.176(1) Å), greater than the Pt–I distances found in the binuclear complex [Pt<sub>2</sub>(μ-I)<sub>2</sub>(dpmm)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (Pt–I: 2.662(1) and 2.669(1) Å) [22] and in the five-coordinated complex [Pt(C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe(CH<sub>2</sub>)<sub>7</sub>MeNCH<sub>2</sub>)<sub>2</sub>)-2,6(η<sup>1</sup>-I<sub>2</sub>)] (Pt–I: 2.747(2) and Pt–I–I: 2.968(2) Å) [23].

The bridging phosphoryl P–O bond distances (1.510(9) and 1.509(9) Å) are shorter than the P–O bonds found in the related binuclear complex [Cl(Et<sub>3</sub>P)Pt(μ-POPh<sub>2</sub>)<sub>2</sub>Pt(PEt<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (1.541(11) and 1.539(11) Å) [1] and are similar to reported uncoordinated P=O bonds (average 1.507(5) Å) [24]. This result indicates that the bridging groups maintain a clear double bond character upon coordination.

Previous <sup>31</sup>P{<sup>1</sup>H} NMR studies performed on related complexes of platinum(II) indicate that the coupling constant (<sup>1</sup>J<sub>Pt–P</sub>) would decrease with decreasing covalency of the Pt–P bond. Moreover, the value of <sup>1</sup>J<sub>Pt–P</sub> is also dependent on the nature of the ligand bonded in trans position to the phosphorus atom, and to the steric and electronic effects of the ligand bonded in cis position to the phosphorus atom [17,25–27].

Table 4  
Selected bond distances (Å) and bond angles (deg) for 2

Pt(1)–I	3.176(1)	Pt(2)–I	2.829(2)
Pt(1)–P(1)	2.318(3)	Pt(2)–O(1)	2.194(9)
Pt(1)–P(2)	2.353(3)	Pt(2)–O(2)	2.173(8)
Pt(1)–P(3)	2.295(3)	Pt(2)–C(7)	2.072(15)
Pt(1)–P(4)	2.273(3)	Pt(2)–C(8)	2.009(15)
P(1)–C(1)	1.849(12)	Pt(2)–C(9)	1.956(16)
P(1)–C(111)	1.784(13)	P(3)–O(1)	1.509(9)
P(1)–C(121)	1.821(13)	P(3)–O(3)	1.602(9)
P(2)–C(1)	1.826(12)	P(3)–O(5)	1.595(9)
P(2)–C(211)	1.804(14)	P(4)–O(2)	1.510(9)
P(2)–C(221)	1.835(13)	P(4)–O(4)	1.601(8)
O(3)–C(3)	1.431(16)	P(4)–O(6)	1.596(9)
O(4)–C(4)	1.430(16)	O(6)–C(6)	1.449(15)
O(5)–C(5)	1.445(19)		
Pt(1)–I–Pt(2)	83.55(3)	I–Pt(2)–O(1)	86.6(2)
I–Pt(1)–P(1)	104.8(1)	I–Pt(2)–O(2)	92.2(2)
I–Pt(1)–P(2)	99.8(1)	I–Pt(2)–C(7)	175.8(5)
I–Pt(1)–P(3)	83.9(1)	I–Pt(2)–C(8)	92.4(7)
I–Pt(1)–P(4)	86.5(1)	I–Pt(2)–C(9)	94.7(6)
P(1)–Pt(1)–P(2)	71.8(1)	O(1)–Pt(2)–O(2)	88.3(3)
P(1)–Pt(1)–P(3)	169.5(1)	O(1)–Pt(2)–C(7)	89.8(5)
P(1)–Pt(1)–P(4)	96.6(1)	O(1)–Pt(2)–C(8)	92.1(6)
P(2)–Pt(1)–P(3)	101.3(1)	O(1)–Pt(2)–C(9)	178.5(5)
P(2)–Pt(1)–P(4)	167.8(1)	O(2)–Pt(2)–C(7)	85.3(5)
P(3)–Pt(1)–P(4)	89.7(1)	O(2)–Pt(2)–C(8)	175.4(7)
Pt(1)–P(1)–C(1)	93.7(4)	O(2)–Pt(2)–C(9)	91.0(5)
Pt(1)–P(1)–C(111)	115.9(4)	C(7)–Pt(2)–C(8)	90.1(8)
Pt(1)–P(1)–C(121)	126.3(5)	C(7)–Pt(2)–C(9)	88.8(7)
C(1)–P(1)–C(111)	104.1(6)	C(8)–Pt(2)–C(9)	88.5(7)
C(1)–P(1)–C(121)	108.5(6)	O(1)–P(3)–O(3)	109.2(5)
C(111)–P(1)–C(121)	105.3(6)	O(1)–P(3)–O(5)	102.6(5)
Pt(1)–P(2)–C(1)	93.1(4)	O(3)–P(3)–O(5)	102.7(5)
Pt(1)–P(2)–C(211)	115.5(4)	O(2)–P(4)–O(4)	107.5(5)
Pt(1)–P(2)–C(221)	128.1(4)	O(2)–P(4)–O(6)	108.9(5)
C(1)–P(2)–C(221)	108.6(7)	O(4)–P(4)–O(6)	98.8(5)
C(1)–P(2)–C(211)	104.7(6)	Pt(2)–O(1)–P(3)	127.3(5)
C(211)–P(2)–C(221)	104.3(6)	Pt(2)–O(2)–P(4)	129.9(5)
Pt(1)–P(3)–O(1)	120.1(4)	C(3)–O(3)–P(3)	120.5(8)
Pt(1)–P(3)–O(3)	107.0(3)	C(5)–O(5)–P(3)	120.3(9)
Pt(1)–P(3)–O(5)	113.8(4)	C(4)–O(4)–P(4)	121.4(8)
Pt(1)–P(4)–O(4)	118.3(3)	C(6)–O(6)–P(4)	115.6(8)
Pt(1)–P(4)–O(6)	111.7(3)	P(1)–C(1)–P(2)	96.4(6)
Pt(1)–P(4)–O(6)	109.8(3)		

The  $^1\text{P}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{CDCl}_3$  shows two doublet signals at  $\delta = 51.57$  and  $78.25$  ppm, assigned to  $\text{P}_A$  and  $\text{P}_B$  respectively. The unusually high field value of the  $\text{P}_A$  chemical shift of the dppm ligand is associated with the formation of the four-membered ring and with the trans influence of the  $\text{P}_B$  atoms [12,28]. On the contrary, the contact of the iodide atom with the platinum(II) centre produces an additional electronic contribution on this metal which, in turn, increases of the electronic density on the phosphorus atoms  $\text{P}_A$  of dppm. These factors cause an increase of the  $\sigma$  character in the  $\text{Pt}-\text{P}_A$  bond, and an increase of the coupling  $\text{Pt}-\text{P}_A$  ( $^1J_{\text{Pt}-\text{P}_A} = 1897$  Hz) with respect to the free ligand **L** ( $^1J_{\text{Pt}-\text{P}_A} = 1607$  Hz), possibly due to strain in the chelate ring and to the distortion of the

angles  $\text{P}-\text{Pt}-\text{P}$  and  $\text{Pt}-\text{P}-\text{CH}_2$  [12,28,29]. Consequently, a large deshielding of the  $\text{P}_B$  atoms of the phosphonate ligands, which was observed ( $\delta = 78.85$  ppm), synergistically increases the  $\sigma$  donation of the  $\text{Pt}-\text{P}_B$  bond, which in turn, causes an increase of the  $^1J_{\text{Pt}-\text{P}_B}$  value ( $^1J_{\text{Pt}-\text{P}_B} = 4474$  Hz) with respect to that of the free ligand **L** ( $^1J_{\text{Pt}-\text{P}_B} = 4397$  Hz) [8,17,18].

Complex **2** reacts with  $\text{AgPF}_6$  in chloroform–acetone solution in the presence of  $\text{PPh}_3$  to give  $\text{AgI}$  and the cationic complex  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2\text{PtMe}_3(\text{PPh}_3)]\text{PF}_6$  (**3**). Interestingly, the  $^1\text{H}$  NMR spectrum shows only a broad triplet resonance centred at  $\delta 4.80$  ppm, indicating that the methylene protons of dppm are equivalent. This result confirms that the non-equivalence of the dppm protons of complex **2** in

chloroform solution is due to the presence of the iodide ligand and suggests that the contact Pt(II)–I is maintained in solution.

Moreover, the  $^1\text{H}$  NMR spectrum of **3** shows two doublet resonances at  $\delta$  3.02 and 3.20 ppm corresponding to the non-equivalent methoxy protons of the phosphonate groups and two doublet signals (intensity relation of 2:1) at  $\delta$  1.02 ( $^2J_{\text{Pt-H}} = 77$  Hz;  $^3J_{\text{Pc-H(cis)}} = 7.7$  Hz) and 1.50 ppm ( $^2J_{\text{Pt-H}} = 57$  Hz;  $^3J_{\text{Pc-H(trans)}} = 8.0$  Hz) assigned to methyl protons of the organometallic moiety  $\{\text{PtMe}_3(\text{PPh}_3)\}^+$ , trans to the oxygen atoms of ligand L and trans to the  $\text{PPh}_3$  ligand respectively.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the cationic complex  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2\text{PtMe}_3(\text{PPh}_3)]\text{PF}_6$  (**3**) shows two doublet signals at  $\delta$  –37.40 and 76.07 ppm attributed to the  $\text{P}_\text{A}$  atoms of dppm and the  $\text{P}_\text{B}$  atoms of the phosphonate ligands respectively. The large shift to lower field of the  $\text{P}_\text{A}$  resonances compared with those of complex **2** indicates that no interaction between the triphenylphosphine ligand and the  $[(\eta^2\text{dppm})\text{Pt}\{\text{PO}(\text{OMe})_2\}_2]$  moiety was produced. Also, a decrease in the  $\sigma$  donation of the Pt– $\text{P}_\text{A}$  bond, and consequently a decrease in the  $^1J_{\text{Pt-P}_\text{A}}$  value, are observed. In contrast, a slight shift of the  $\text{P}_\text{B}$  resonances to high field and, simultaneously, a large decrease of the coupling value with respect to the starting complex was observed ( $^1J_{\text{Pt-P}_\text{B}} = 4176$  Hz (**3**);  $^1J_{\text{Pt-P}_\text{B}} = 4474$  Hz (**2**)). These results imply that a decrease of the  $\sigma$  character of Pt– $\text{P}_\text{B}$  bond was produced. Moreover, complex **3** exhibits a singlet resonance at  $\sigma$  10.74 ppm due to  $\text{P}_\text{C}$  of the triphenylphosphine ligand, with the corresponding satellites due to  $^{195}\text{Pt}$ – $^{31}\text{P}$  coupling ( $^1J_{\text{Pt-P}_\text{C}} = 1088$  Hz).

L (**1**) does not react directly with complexes  $[\{\text{Pd}(\mu\text{-Cl})(2\text{-MeC}_3\text{H}_4)\}_2]$  and  $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ . Consequently, in order to obtain the corresponding heterobinuclear complexes, it is necessary to treat the starting binuclear complexes with silver perchlorate, forming solvate intermediate species, which react immediately with the bidentate ligand L to yield the compounds  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2\text{Pd}(\eta^3\text{MeC}_3\text{H}_4)]\text{ClO}_4$  (**4**) and  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2\text{Rh}(\text{cod})]\text{ClO}_4$ . Treatment of complex **5** with an atmosphere of CO in acetone solution at room temperature caused the displacement of the coordinated cod ligand by the CO groups with formation of complex  $[(\eta^2\text{dppm})\text{Pt}\{\mu\text{-P}(\text{O})(\text{OMe})_2\}_2\text{Rh}(\text{CO})_2]\text{ClO}_4$  (**6**).

All cationic complexes (**3**–**6**) were isolated as stable solids and behave as 1:1 electrolytes in acetone solution. In all cases, the solid-state IR spectra (KBr) showed the presence of uncoordinated anions ( $\text{ClO}_4^-$ : ca. 1100 and  $620\text{ cm}^{-1}$ ;  $\text{PF}_6^-$ : ca. 840 and  $560\text{ cm}^{-1}$ ) together with the absorption band corresponding to P=O bond. For these compounds the  $\nu(\text{PO})$  stretching vibrations are shifted to lower frequency ( $1070$ – $1095\text{ cm}^{-1}$ ) relative to those of the free ligand ( $1104\text{ cm}^{-1}$ ), indicating that the organometallic fragments  $\{\text{PtMe}_3(\text{PPh}_3)\}$ ,

$\{\text{Pd}(\text{Me-allyl})\}$ ,  $\{\text{Rh}(\text{cod})\}$  and  $\{\text{Rh}(\text{CO})_2\}$  are stronger acids in comparison with the neutral moiety  $\{\text{Pt}(\text{Me}_3)\}$ . Moreover, the spectrum of complex **6** shows two strong bands at  $2075$  and  $1995\text{ cm}^{-1}$  (KBr) ( $\nu(\text{CO}) = 2060$ ,  $1970\text{ cm}^{-1}$  ( $\text{Me}_2\text{CO}$ )), characteristic of *cis*-(dicarbonyl) derivatives.

As expected, the  $^1\text{H}$  NMR spectra of cationic heterobimetallic complexes **4**–**6** show the signals of the ancillary ligands together with a broad triplet and doublet resonances corresponding to equivalent methylene protons of dppm and methoxy groups of phosphonate ligands respectively. Their  $^1\text{H}$  decoupled  $^{31}\text{P}$  NMR spectra exhibit the corresponding doublet resonances for  $\text{P}_\text{A}$  and  $\text{P}_\text{B}$  at similar chemical shifts and coupling constants of the cationic complex **3**.

#### 4. Supplementary material available

Observed and calculated structure factors, full list of bond distances and angles, anisotropic displacement coefficients, and H-atom coordinates have been deposited with the Cambridge Crystallographic Data Centre.

#### Acknowledgements

We thank the ‘‘Fondo de Desarrollo Científico y Tecnológico’’, Chile (Grant N° 460/93) and ‘‘Fundación Andes’’ for financial support. We thank MSc. S. Alegría for recording the NMR spectra.

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