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# Bicyclic dinuclear *tris*-(ditopic diphosphane) complexes of zerovalent group 10 metals†

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Selective formation of bimetallic group 10 complexes using the  $C_s$  symmetric, bicyclic diphosphane  $P_2C_{12}H_{20}$  is reported herein. With its eclipsed lone pairs disposed at a relative angle of *ca.*  $45^\circ$ , the diphosphane framework is ideally suited to form multiple bridges between two metal centers. The complexes contain  $\{M_2P_6\}$  cages with three diphosphane bridges and a pair of *trans*-axial ligands such as  $EPh_3$  ( $E = P, As, Sb$ ) or  $\eta^1-P_2C_{12}H_{20}$ . X-Ray crystallography experiments revealed that the cages have a pseudo- $D_{3h}$  symmetry, with metal–metal distances in the 3.9–4.1 Å range. The complexes were isolated in 48–91% yield as crystalline, bright yellow or orange powders. Substitution of the axial ligands with the  $\{M_2P_6\}$  cages remaining intact was also observed.

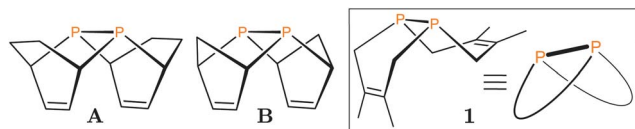
## Introduction

Since the first synthesis of bi- and tetracyclic diphosphanes by effective sequential Diels–Alder addition of two 1,3-dienes to  $P_2$ ,<sup>1</sup> we have been eager to explore the coordination chemistry of the resulting ditopic diphosphanes (illustrated in Chart 1). In particular, we were interested in how the fixed bidentate coordination angle of the two adjacent phosphorus atoms would influence the binding modes and the electronic properties of coordinated metals. Limiting our efforts in this regard was a low-yielding, multi-step procedure requiring an elaborate niobium complex as a stoichiometric source of  $P_2$ .<sup>1</sup> The recent one-step photochemical synthesis directly from  $P_4$  (white phosphorus) of bicyclic diphosphanes,<sup>2</sup> now available in gram quantities (see ESI†), makes possible a systematic investigation of the complexation chemistry of such diphosphanes.

The sole example of a commercially available tetra-organo diphosphane, namely  $P_2Ph_4$ , has been shown to exhibit a wide range of chemical reactivity. Like other diphosphanes,<sup>3</sup>  $P_2Ph_4$

commonly undergoes P–P bond-cleavage reactions assisted by radicals,<sup>4</sup> Lewis acids,<sup>5</sup> cations,<sup>6</sup> organohalogens,<sup>7</sup> alkynes,<sup>8</sup>  $S_4N_4$ ,<sup>9</sup> metal-complex catalysts,<sup>10,11</sup> and photolysis.<sup>12</sup> When the P–P bond remains intact, this diphosphane can bind to one or two metal centers in an  $\eta^1$ ,<sup>13,14</sup>  $\eta^2$ ,<sup>15</sup> or  $\mu, \eta^{1:1}$  fashion, respectively.<sup>13,16,17</sup> The syntheses of a number of bimetallic complexes containing two diphosphane bridges have been reported since 1964.<sup>18</sup> However, very few complexes containing multiple diphosphane bridges (illustrated in Chart 2) have been characterized crystallographically.<sup>17,19–21</sup> In all these cases, the  $\{M_2P_4\}$  six-membered rings exhibit a chair conformation, with M–P–P–M dihedral angles ranging from  $33^\circ$  to  $78^\circ$ .<sup>17,20,21</sup> Boat conformations are observed only when a third bridge is present and require a significant decrease in dihedral angle, such as from  $53^\circ$  to  $22^\circ$  with  $P_2Me_4$ .<sup>17</sup> Thus, the formation of bicyclic bimetallic systems having three diphosphane bridges requires a small dihedral angle to be readily accessible. The only reported case of a triply bridged bimetallic compound with a diphosphane-based  $\{M_2P_6\}$  cage occurs in  $(OC)_3Mo(G)_3Mo(CO)_3$ , with a decrease in the M–P–P–M dihedral angle with diphosphane **G** from  $33^\circ$  to  $25^\circ$ .<sup>19,21,22</sup> There is also a report of P–P triple bridges with  $[P_4(SiMe_2)_3]$  ligands between two  $Cr(CO)_3$  units where the dihedral angle is  $0^\circ$ .<sup>23</sup>

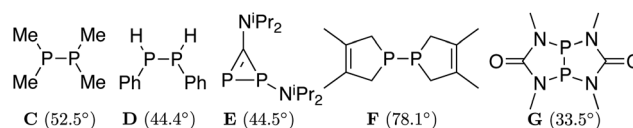
Multimetallic platforms have received a surge in interest due to their increased catalytic potential resulting from the interactions



**Chart 1** Examples of known, free or  $W(CO)_5$ -bound bicyclic and tetracyclic diphosphanes.<sup>1,2</sup>

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† Electronic supplementary information (ESI) available: For full synthetic, spectroscopic, X-ray crystallography details and crystallographic data in CIF format see DOI: 10.1039/c2sc20559a. CCDC reference numbers 863743–863747.



**Chart 2** Examples of diphosphanes which form two bridges in bimetallic systems with their M–P–P–M dihedral angles listed in parentheses.<sup>17,20,21</sup>

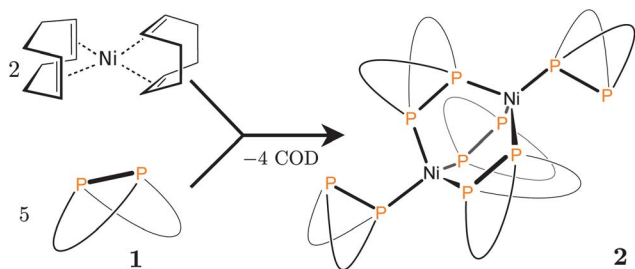
between metallic centers.<sup>24</sup> Such complexes containing multiple bridging ligands are conferred increased stability against dissociation into monomeric units.<sup>24</sup> The bicyclic nature of the diphosphane  $P_2C_{12}H_{20}$  molecule (**1**) results in an eclipsed conformation and a dihedral angle between the two phosphorus lone pairs close to  $0^\circ$ .<sup>2</sup> This pre-configuration positions the diphosphane **1** to form six-membered rings that can create higher-order bridges between metal centers.

## Results and discussion

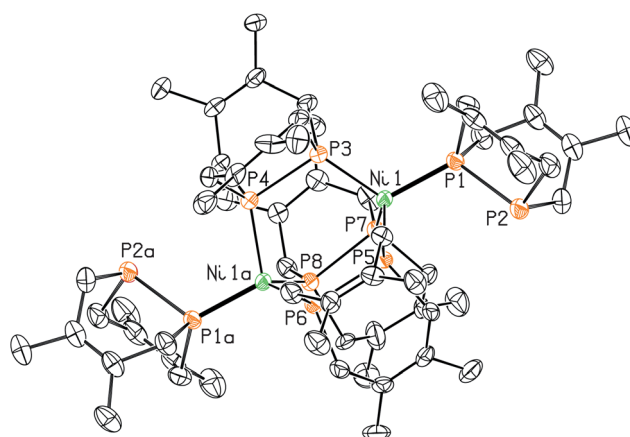
Treatment of  $Ni(cod)_2$  ( $cod = 1,5$ -cyclooctadiene) with 1–2 equiv. of diphosphane **1** yields a single phosphorus-containing, major product: a bimetallic complex with three  $\mu, \eta^1: \eta^1$ -bound diphosphanes and two  $\eta^1$ -terminally bound diphosphane units (Scheme 1). Its molecular formula,  $(\eta^1-1)Ni(\mu, \eta^1: \eta^1-1)_3Ni(\eta^1-1)$  (**2**), was determined by single crystal X-ray diffraction (Fig. 1). Using a 2 : 5 ratio of  $Ni(cod)_2$  to diphosphane **1**, the reaction proceeds stoichiometrically, yielding bright orange solutions. On a preparative scale, analytically pure complex **2** was isolated in 48% yield as a soluble, bright yellow powder after recrystallizing from THF (tetrahydrofuran) at  $-35^\circ C$ . It is interesting to note that complex **2** is obtained in only two steps starting from white phosphorus, 2,3-dimethylbutadiene, and a nickel(0) source.

Bimetallic complexes of palladium and platinum were obtained in an analogous fashion. Treatment of diphosphane **1** with  $Pd(PPh_3)_4$  or  $Pt(PPh_3)_4$  led to the formation of a single, new product in both cases:  $(Ph_3P)M(\mu-1)_3M(PPh_3)$  (**3-Pd** and **3-Pt**; Scheme 2). These bimetallic complexes have very similar  $\{M(1)_3M\}$  units (Fig. 2) with respect to that found in complex **2**. No traces of monometallic or lower-order bridging complexes were observed by  $^{31}P$  NMR spectroscopy even when excess  $M(PPh_3)_4$  was used. From toluene mixtures containing 2 : 3 metal reagent to diphosphane **1**, complexes **3-Pt** and **3-Pd** were isolated as yellow powders in 91% and 65% yield, respectively, after layering the solutions with pentane and storing them at  $-35^\circ C$ .

The nickel analogue was then targeted by adding a 3 : 2 mixture of diphosphane **1** and  $PPh_3$  to solutions of  $Ni(cod)_2$ . Complex  $(Ph_3P)Ni(\mu-1)_3Ni(PPh_3)$  (**3-Ni**) was successfully formed, and isolated as a bright orange powder in 89% yield (Scheme 2). Furthermore, heavier group 15 analogues could be used as axial ligands by replacing  $PPh_3$  with either  $AsPh_3$  or  $SbPh_3$ . The complexes  $(Ph_3E)Ni(\mu-1)_3Ni(EPh_3)$  (**4** for  $E = As$ ; **5** for  $E = Sb$ ) were isolated from toluene–pentane mixtures stored at  $-35^\circ C$  as yellow powders in 88% and 87% yield, respectively.



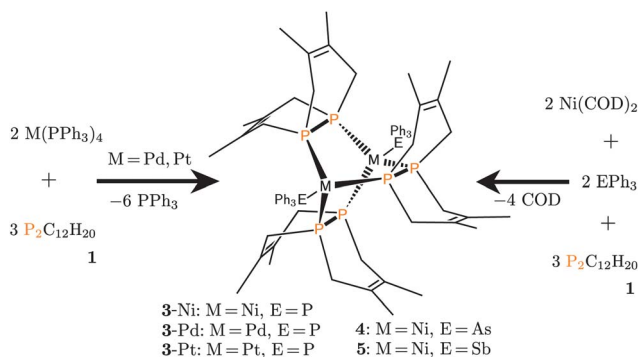
**Scheme 1** Formation of the dinickel complex **2** incorporating three bridging and two axial, monodentate diphosphane ligands.



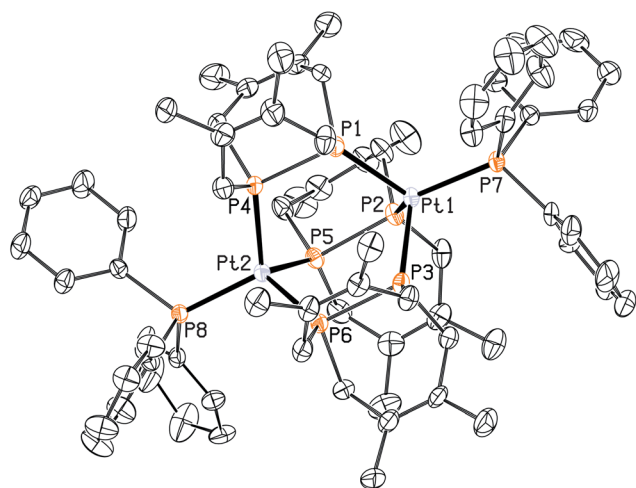
**Fig. 1** Molecular structure of dinickel complex **2**, with hydrogen atoms and solvent molecules removed for clarity. Selected interatomic distances [Å] and angles [°]: Ni1–Ni1a 3.9085(5), P1–P2 2.2239(8), P3–P4 2.2280(14), P5–P6 2.2262(14), P7–P8 2.2241(14); P1–Ni1–Ni1a 180; Ni1–P3–P4–Ni1a 7.09(8), Ni1–P5–P6–Ni1a 5.89(8), Ni1–P7–P8–Ni1a 9.06(9).<sup>28</sup>

Replacing  $PPh_3$  with  $BiPh_3$  led to the formation of only complex **2**, indicating the bismuthane's inability to serve as an adequate axial ligand. Similarly, only complex **2** was observed to form when the reaction was carried out in the presence of a large excess of N-donor solvent molecules such as acetonitrile or pyridine.

Contrasting results were observed when, for purposes of comparison, the reactivity of  $P_2Ph_4$  with the same group 10 metal precursors was investigated. Treatment of  $Ni(cod)_2$  with  $P_2Ph_4$  in benzene led to a gradual color change from yellow to orange to green, and eventually to dark brown. NMR spectroscopy revealed release of 1,5-cyclooctadiene without the appearance of any other NMR-active species. A few dark-green crystals of the previously reported  $Ni(HPPH_2)_4$ <sup>25</sup> were obtained after the reaction mixture had aged for several days. Since 1,5-cyclooctadiene is known to be a competent H-atom donor,<sup>26</sup> it is perhaps the source of the phosphine hydrogen atom in the crystalline nickel product. Treatment of  $Pd(PPh_3)_4$  with  $P_2Ph_4$  in benzene produced a complex reaction mixture which included free  $PPh_3$  and  $P_2Ph_4$ , but no  $^{31}P$ – $^{31}P$  coupled multiplets in the  $^{31}P$  NMR spectrum. In the presence of  $O_2$  and  $H_2O$ ,  $P_2Ph_4$  adds oxidatively



**Scheme 2** Formation of the bimetallic complexes **3-M**, **4** and **5** incorporating three bridging diphosphane molecules **1** and two axial  $EPh_3$  ligands ( $E = P, As, \text{ or } Sb$ ).



**Fig. 2** Molecular structure of diplatinum complex **3-Pt**, with hydrogen atoms and solvent molecules removed for clarity. Selected interatomic distances [Å] and angles [°]: Pt1–Pt2 4.0846(3), P1–P4 2.2219(15), P2–P5 2.2222(15), P3–P6 2.2204(15); P7–Pt1–Pt2 176.11(3), Pt1–Pt2–P8 179.87(3); Pt1–P1–P4–Pt2 5.09(8), Pt1–P2–P5–Pt2 3.94(8), Pt1–P3–P6–Pt2 1.48(8).<sup>28</sup>

to palladium.<sup>10</sup> No reactivity in benzene was observed between Pt(PPh<sub>3</sub>)<sub>4</sub> and P<sub>2</sub>Ph<sub>4</sub>. Although the P–P bond is a relatively strong bond,<sup>27</sup> diphosphanes are commonly susceptible to P–P bond cleavage.<sup>3</sup> The above observations suggest that diphosphane **1** is stabilized with respect to P–P bond-cleavage—compared to P<sub>2</sub>Ph<sub>4</sub>—by the rigid framework of the fused six-membered rings in ligand **1**.

A high degree of thermal stability is observed for complexes **2–5**. As solids, they do not decompose under an inert atmosphere until *ca.* 200 °C. This is only slightly below the decomposition temperature of free diphosphane **1**, *ca.* 220 °C. The complexes are also stable in solution, as only complexes **4** and **5** showed decomposition with conversion into complex **2** and free EPh<sub>3</sub> (by NMR spectroscopy) upon heating to 80 °C for a day. Although the complexes can be synthesized in concentrated reaction mixtures, they crystallize out of solution very easily.

In the solid state, complex **2** has the nickel atoms and the terminal η<sup>1</sup> diphosphanes related by a crystallographically imposed inversion center. This forces the bridging diphosphanes to be disordered over two symmetry-related sites, as the whole {Ni(1)<sub>3</sub>Ni} central fragment is close to having a three-fold symmetry axis. Complexes **3-M** and **4** are isostructural in the solid state (Fig. 2), but only **3-Ni** and **4** are rigorously C<sub>3v</sub>-symmetric. Aside from the change in the axial ligands, the molecular structures of complexes **2–4** are closely related (Table 1). The P–P distances are less than 0.01 Å longer than the value measured in free diphosphane **1** (2.2218(5) Å<sup>2</sup>). The diphosphane binding angle (P–P–M) is in the 112–114° range, while the angles at the metal positions (P–M–P) are in the 104–106° range. The tetrahedral geometry at the metal centers ensures that the fourth, axial ligand forms P–M–E angles in the 112–114° range. The M–M–E angles are very close to 180° for **3-Pd** and **3-Pt**, while for the nickel complexes (**2**, **3-Ni** and **4**), the axial pnictogen atoms are rigorously collinear with the metal centers. Overall, the {M(μ-1)<sub>3</sub>M} units are nearly D<sub>3h</sub> symmetric in all

complexes. The lack of a σ symmetry plane through the P–P bond midpoints perpendicular to the M–M axis stems from a slight deviation from 0° in the M–P–P–M dihedral angles, to between 3° and 9°. These values are much smaller than those of the multiple diphosphane bridges reported in the literature.<sup>17,20–22</sup> The angle formed between the phosphorus lone pairs of the diphosphane (θ in Table 1) can be estimated to be in the 44–48° range, with a mean value of 46°.

The M–M distances increase in the **3-Ni** < **3-Pd** < **3-Pt** order, from 3.9607(6) Å, to 4.0577(6) Å, and 4.0846(3) Å respectively. The latter two values are in contrast with the longer M–P distances in **3-Pd** than in **3-Pt**, and this results from slight variations in binding angles across complexes **3-M**. Changing the axial ligand from PPh<sub>3</sub> to η<sup>1</sup>-**1** produces a slight shortening to 3.9085(5) in complex **2** as compared with that in **3-Ni**, together with a contraction in the axial ligand–metal distance. The latter observation is consistent with the more electron-donating character of the diphosphane but is not correlated with a significant elongation in the cage M–P distances. Only when switching to AsPh<sub>3</sub> in complex **4** is the electronic environment perturbed sufficiently to result in a 0.01 Å diminution in the cage M–P distances and a larger decrease of the Ni–Ni distance to 3.8532(4) Å.

Tripodal ligands play an important role in many branches of modern chemistry, and among those based upon phosphorus, the archetype is *triphos* (*triphos* = MeC(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>).<sup>29</sup> The complexes **2–5** can be regarded as having two such ligands merged together to bind two metal centers, with a {LM(1)<sub>3</sub>} fragment being equivalent to one *triphos* ligand. Complexes **3-Ni** and **4** compare well to monometallic analogues supported by the *triphos* framework, (*triphos*)Ni(L) (L = PPh<sub>3</sub>, AsPh<sub>3</sub>).<sup>30</sup> They exhibit similar Ni–P and Ni–E distances, with P–Ni–E and P–Ni–P angles close to 113° and 105° respectively, compared to *ca.* 120° and 97° respectively for the *triphos* complexes.<sup>30</sup> Complex **3-Pt** compares well to (*triphos*)Pt(*p*-C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub>, which has P–Pt–E and P–Pt–P angles of *ca.* 123° and 94°, respectively.<sup>31</sup> Similar coordination angles to **3-Pd** were reported for (FSi(CH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>)<sub>3</sub>)Pd(PPh<sub>3</sub>).<sup>32</sup>

The {M<sub>2</sub>P<sub>6</sub>} cages exhibit interesting <sup>31</sup>P NMR spectroscopic features. Complexes **4** and **5** manifest a single, sharp resonance for the six phosphorus atoms (Table 2). The <sup>31</sup>P NMR spectra of complexes **3-M** are interpreted as A<sub>2</sub>X<sub>6</sub> coupled spin systems in the Pople nomenclature.<sup>33</sup> Here, the strong coupling between the two phosphorus atoms of the diphosphane bridges results in a virtual coupling,<sup>34</sup> where the PPh<sub>3</sub> resonance is a triplet and the diphosphane is a septuplet. The <sup>31</sup>P NMR signals in complex **2** split even further to an A<sub>2</sub>M<sub>2</sub>X<sub>6</sub> spin system, with large <sup>31</sup>P–<sup>31</sup>P coupling across the terminal diphosphane ligands measured at 344 Hz (Fig. 3). Large one-bond <sup>195</sup>Pt–<sup>31</sup>P coupling constants were observed for complex **3-Pt** (Fig. 4), constants which are comparable in magnitude to those mentioned for the (*triphos*)Pt(PPh<sub>3</sub>) complex.<sup>35</sup>

Uniquely among the complexes reported herein, in the case of **4** and **5** there is evidence of axial ligand lability in both the <sup>1</sup>H and <sup>31</sup>P NMR spectra. <sup>1</sup>H NMR resonances consistent with free EPh<sub>3</sub> (E = As or Sb) and <sup>31</sup>P NMR multiplets consistent with either [Ni(μ-1)<sub>3</sub>Ni(EPh<sub>3</sub>)] or [(solvent)Ni(μ-1)<sub>3</sub>Ni(EPh<sub>3</sub>)] structures were observed. This implied EPh<sub>3</sub> dissociation is correlated with an increased solubility of **4** and **5** when compared to that of **3-Ni**.

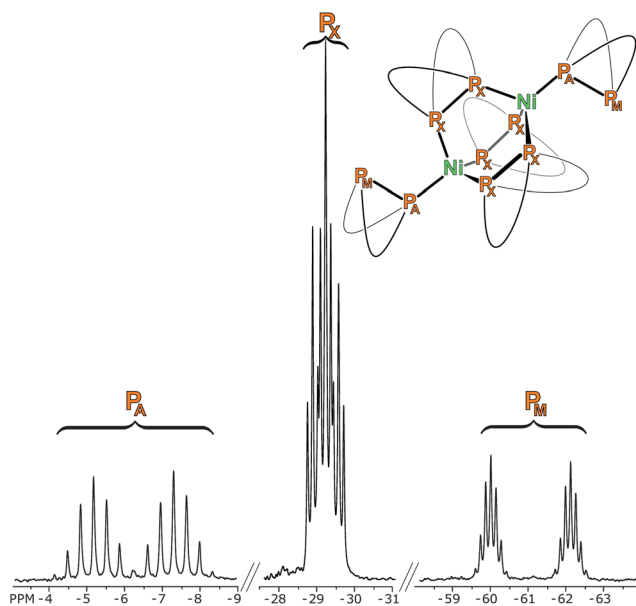
**Table 1** Average interatomic distances [Å] and angles [°] for the {M<sub>2</sub>P<sub>6</sub>} clusters<sup>28,a</sup>

	M–M	P–P	M–P	M–E <sup>b</sup>	P–P–M	P–M–P	P–M–E <sup>b</sup>	M–M–E <sup>b</sup>	M–P–P–M	θ <sup>c</sup>
<b>1</b>	—	2.2218(5)	—	—	—	—	—	—	0.4 <sup>d</sup>	45.9 <sup>d</sup>
<b>2</b>	3.9085(5)	2.226 <sup>e</sup>	2.171	2.1425(6)	112.7 <sup>e</sup>	105.6	112.8	180(0)	7.3	45.4
<b>3-Pt</b>	4.0846(3)	2.222	2.303	2.259	113.8	104.7	113.9	178.0	3.5	47.6
<b>3-Pd</b>	4.0577(6)	2.224	2.351	2.294	112.7	105.6	113.1	174.4	8.9	45.4
<b>3-Ni</b>	3.9607(6)	2.2274(6)	2.173	2.153	113.4	105.1	113.6	180(0)	6.13(4)	46.9
<b>4</b>	3.8532(4)	2.2258(4)	2.160	2.263	112.1	106.6	112.2	180(0)	5.38(3)	44.1

<sup>a</sup> Standard deviations are listed only for directly measured values; remaining values represent arithmetic averages of values fully listed in the ESI. <sup>†</sup> E denotes the pnictogen atom of axial ligands (*i.e.*: P, As, or Sb). <sup>c</sup> Diphosphane lone pair angle, which can be calculated as  $\theta = 2 \times ([\angle M-P-P] - 90^\circ)$  in the metal complexes. <sup>d</sup> Dihedral angle between the lone pairs in **1** is inferred from the average C–P–P–C angle in the reported crystal structure,<sup>2</sup> while the lone pair angle is estimated as the average of  $\theta$  in **2–4**. <sup>e</sup> The P–P and P–P–Ni values for the η<sup>1</sup>-bound diphosphane are 2.2239(8) Å and 114.54(3)°, respectively.

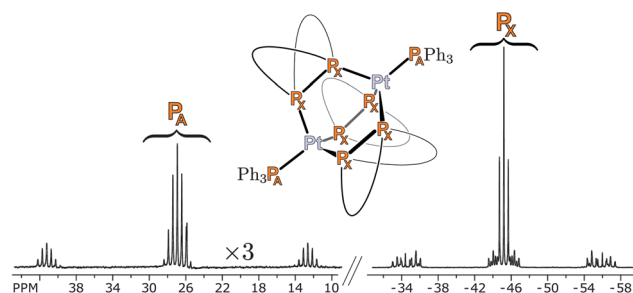
**Table 2** <sup>31</sup>P NMR chemical shifts [ppm] and <sup>31</sup>P–<sup>31</sup>P bond coupling constants [Hz] between the axial ligands (P<sub>A</sub>) and the diphosphane bridges (P<sub>X</sub>)

	δ <sub>P<sub>X</sub></sub>	δ <sub>P<sub>A</sub></sub>	J <sub>P<sub>A</sub>P<sub>X</sub></sub>
<b>1</b>	–53.6	—	—
<b>3-Pt</b>	–45.3	+26.8	79.3
<b>3-Pd</b>	–33.7	+31.2	56.2
<b>3-Ni</b>	–31.6	+36.7	48.4
<b>2</b>	–30.2	–7.3	55.9
<b>4</b>	–28.2	—	—
<b>5</b>	–21.6	—	—



**Fig. 3** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of dinickel complex **2** (C<sub>6</sub>D<sub>6</sub>, 20 °C, 162 MHz) corresponding to an A<sub>2</sub>M<sub>2</sub>X<sub>6</sub> spin system with three 1 : 3 : 1 resonances at –7.3 (dvsept, P<sub>A</sub>), –30.2 (tt, P<sub>X</sub>) and –62.1 (dvsept, P<sub>M</sub>) ppm. Coupling constants [Hz]: <sup>1</sup>J<sub>P<sub>A</sub>P<sub>M</sub></sub> = 344; J<sub>P<sub>A</sub>P<sub>X</sub></sub> = 55.9; J<sub>P<sub>M</sub>P<sub>X</sub></sub> = 22.1.

The “naked” [(triphos)Ni] complex has been proposed several times as an intermediate.<sup>36</sup> Although no such “naked”, tripodal nickel(0) complexes have been characterized crystallographically, the related (N(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>)Pd complex has been.<sup>19,37</sup> Axial ligand lability was confirmed by treating complexes **4** and **5**



**Fig. 4** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the diplatinum complex **3-Pt** (C<sub>6</sub>D<sub>6</sub>, 20 °C, 162 MHz) corresponding to an A<sub>2</sub>X<sub>6</sub> spin system with resonances at +26.8 (vsept, P<sub>A</sub>, displayed with a three-fold magnification in intensity) and –45.3 (vt, P<sub>X</sub>) ppm. Coupling constants [Hz]: J<sub>P<sub>A</sub>P<sub>X</sub></sub> = 79.3; <sup>1</sup>J<sub>195PtP<sub>A</sub></sub> = 4650; <sup>1</sup>J<sub>195PtP<sub>X</sub></sub> = 3510; <sup>2</sup>J<sub>195PtP<sub>X</sub></sub> = 379.

with PPh<sub>3</sub>, a stronger-binding ligand than either AsPh<sub>3</sub> or SbPh<sub>3</sub>. Indeed, the clean formation of the bimetallic complex **3-Ni** and release of EPh<sub>3</sub> was observed in both cases, with the bimetallic cage remaining intact. Furthermore, treatment of complex **3-Ni** with equimolar amounts of either **4** or **5** leads to <sup>31</sup>P NMR spectroscopic evidence of partial conversion to mixed-ligand bimetallic complexes of the type (Ph<sub>3</sub>P)Ni(μ-**1**)<sub>3</sub>Ni(EPh<sub>3</sub>).

## Concluding remarks

The syntheses of complexes **2–5** show that the diphosphane **1** offers an enhanced stability of the P–P bond and an essentially fixed dihedral angle between the two phosphorus lone pairs that is appropriate for forming bimetallic complexes. Group 10 bimetallic complexes of the type reported herein are now available *via* a concise synthesis, for further investigation of applications in catalysis or, *via* axial ligand exchange, as potential components of coordination polymers and supramolecular structures.

## Acknowledgements

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