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°/$C_{14}$, 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 $E$-Ph$_3$ ($E = P, As, Sb$) or $h_1$-$P_2C_{12}H_{20}$. 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 $P_2$, 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 $P_2$. The recent one-step photochemical synthesis directly from $P_4$ (white phosphorus), 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, $P_2Ph_4$ commonly undergoes $P$–$P$ bond-cleavage reactions assisted by radicals, Lewis acids, organohalogenes, alkynes, $S_4N_4$, metal-complex catalysts, and photolysis. When the $P$–$P$ bond remains intact, this diphosphane can bind to one or two metal centers in an $h_1, h_2, m$, or $h_1:1$ fashion, respectively. The syntheses of a number of bimetallic complexes containing two diphosphane bridges have been reported since 1964. However, very few complexes containing multiple diphosphane bridges (illustrated in Chart 2) have been characterized crystallographically. In all these cases, the $\{M_3P_4\}$ six-membered rings exhibit a chair conformation, with $M$–$P$–$P$–$M$ dihedral angles ranging from 33° to 78°. Boat conformations are observed only when a third bridge is present and require a significant decrease in dihedral angle, such as from 53° to 22° with $P_2Me_4$. 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 $\{M_3P_6\}$ cage occurs in $(OC)_2Mo(G)Mo(CO)_3$, with a decrease in the $M$–$P$–$P$–$M$ dihedral angle with diphosphane G from 33° to 25°. 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°.

Multimetallic platforms have received a surge in interest due to their increased catalytic potential resulting from the interactions...
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 μ-η$^1$-bound diphosphanes and two η$^1$-terminally bound diphosphane units (Scheme 1). Its molecular formula, (η$^1$-1)Ni(μ-η$^1$-1)$_2$Ni(η$^1$-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 °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$_3$)$_3$ or Pt(PPh$_3$)$_3$, led to the formation of a single, new product in both cases: (Ph$_3$P)Pt(η$^1$-1)$_2$Pt(η$^1$-1) (3-Pt) and 3-Pt; Scheme 2). These bimetallic complexes have very similar [M(1)M]$_3$ 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 °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$_3$P)Ni(η$^1$-1)$_2$Ni(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$_3$E)Ni(η$^1$-1)$_2$Ni(EPh$_3$) (4 for E = As; 5 for E = Sb) were isolated from toluene–pentane mixtures stored at −35 °C as yellow powders in 88% and 87% yield, respectively.

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$_2$Ph$_4$ with the same group 10 metal precursors was investigated. Treatment of Ni(cod)$_2$ with P$_2$Ph$_4$ 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(HPPPh$_2$)$_2$ were obtained after the reaction mixture had aged for several days. Since 1,5-cyclooctadiene is known to be a competent H-atom donor, it is perhaps the source of the phosphine hydrogen atom in the crystalline nickel product. Treatment of Pd(PPh$_3$)$_3$ with P$_2$Ph$_4$ in benzene produced a complex reaction mixture which included free PPh$_3$ and P$_2$Ph$_4$, but no $^31$P–$^31$P coupled multiplets in the $^31$P NMR spectrum. In the presence of O$_2$ and H$_2$O, P$_2$Ph$_4$ adds oxidatively.

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).

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![Scheme 1](image1.png)  
**Scheme 1** Formation of the dinickel complex 2 incorporating three bridging and two axial, monodentate diphosphane ligands.

![Scheme 2](image2.png)  
**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, or Sb).
...decomposition with conversion into complex D–Pd, compared to D–Pt, by the rigid framework of the fused six-membered rings in ligand L. 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 EPh3 (by NMR spectroscopy) upon heating to 80 °C for a day. Although the complexes can be synthesized in concentrated reaction mixtures, they crystalize out of solution very easily.

In the solid state, complex 2 has the nickel atoms and the terminal η1 diphosphane related by a crystallographically imposed inversion center. This forces the bridging diphosphanes to be disordered over two symmetry-related sites, as the whole \(\{\text{Ni(1)Ni}\} \) central fragment is close to having a three-fold symmetry axis. Complexes 3–M and 4 are isomorphous in the solid state (Fig. 2), but only 3–Ni and 4 are rigorously C3-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). The diphosphane binding angle (P–P–M) is in the 112–114° 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 \(\{\text{M(I–I)M}\} \) units are nearly D3h 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. 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) A, to 4.0577(6) A, and 4.0846(3) A respectively. The latter two values are in contrast with the larger 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 PPh3 to η1–I 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–P distances. Only when switching to AsPh3 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(PhPPh2)3). The complexes 2–5 can be regarded as having two such ligands merged together to bind two metal centers, with a \(\{\text{LM(1)}\} \) 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 = PPh3, AsPh3). 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. Complex 3–Pt compares well to (triphos)Pt(P(η1–C6H4F)3), which has P–Pt–E and P–Pt–P angles of ca. 123° and 94°, respectively. Similar coordination angles to 3–Pd were reported for (FSi(CH3)2H2PMe2)3Pd(PPh3)3.

The \(\{\text{M}3\} \) cages exhibit interesting 31P NMR spectroscopic features. Complexes 4 and 5 manifest a single, sharp resonance for the six phosphorus atoms (Table 2). The 31P NMR spectra of complexes 3–M are interpreted as \(\text{A}2\text{X}6\) coupled spin systems in the Pople nomenclature. The strong 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. 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°.

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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–P2 176.11(3), P1–P2–P8 179.87(3); P1–P1–P4–Pt2 5.09(8), P1–P2–P5–Pt2 3.94(8), P1–P3–P6–Pt2 1.48(8).
The "naked" \((\text{triphos})\text{Ni}\) complex has been proposed several times as an intermediate.\(^{36}\) Although no such "naked", tripodal nickel(0) complexes have been characterized crystallographically, the related \((\text{N(CH}_2\text{CH}_2\text{PPh}_2)_3\)Pd complex has been.\(^{19,37}\) Axial ligand lability was confirmed by treating complexes 4 and 5 with \(\text{PPh}_3\), a stronger-binding ligand than either \(\text{AsPh}_3\) or \(\text{SbPh}_3\). Indeed, the clean formation of the bimetallic complex 3-Ni and release of \(\text{EPh}_3\) 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 \(^{31}\text{P} NMR\) spectroscopic evidence of partial conversion to mixed-ligand bimetallic complexes of the type \((\text{Ph}_3\text{P})\text{Ni}(\mu-1)\text{Ni}(\text{EPh}_3)\).

### 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 \(\text{via a concise synthesis, for further investigation of applications in catalysis or, via axial ligand exchange, as potential components of coordination polymers and supramolecular structures.}\)

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