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The Versatile Reactivity of *cyclo*-$(P_5tBu_4)^-$ with Complexes of the Nickel Triad

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Abstract: Na[*cyclo*-(P_5tBu_4)] (**1**) reacts with $[NiCl_2(PEt_3)_2]$ and $[PdCl_2(PMe_2Ph)_2]$ with elimination of *t*BuCl and formation of the corresponding metal(0) cyclopentaphosphene complexes [Ni{*cyclo*-(P_5tBu_3)}$(PEt_3)_2$] (**2**) and [Pd{*cyclo*-(P_5tBu_3)}$(PMe_2Ph)_2$] (**3**). In contrast, complexes with the more labile triphenylphosphane ligand, such as $[MCl_2(PPh_3)_2]$ (M = Ni, Pd), react with **1** with formation of [NiCl{*cyclo*-(P_5tBu_4)}(PPh_3)] (**4**) and [Pd{*cyclo*-(P_5tBu_4)}$_2$] (**5**), respectively, in which the *cyclo*-(P_5tBu_4) ligand is intact. In the case of palladium, the cyclopentaphosphene complex [Pd{*cyclo*-(P_5tBu_3)}$(PPh_3)_2$] (**6**) in trace amounts is also formed. However, [Ni{*cyclo*-(P_5tBu_4)}$_2$] (**7**) is easily obtained by reaction of two equivalents of **1** and one equivalent of $[NiCl_2(bipy)]$ at room temperature. Complex **7** rearranges on heating in *n*-hexane or toluene to the previously unknown [Ni{*cyclo*-(P_5tBu_4)P*t*Bu}{*cyclo*-(P_4tBu_3)}] (**8**), which presumably is formed via the intermediate [Ni{*cyclo*-(P_5tBu_4)}{*cyclo*-(P_4tBu_3)P*t*Bu}], which, after an unexpected and unprecedented phosphanediide migration, gives **8**, but always as an inseparable mixture with **7**. In the reaction of **1** with $[PtCl_2(PPh_3)_2]$, ring contraction and formation of [PtCl{*cyclo*-(P_4tBu_3)P*t*Bu}(PMe_2Ph)] (**9**) is observed. Complexes **3**–**5** and **7**–**9** were characterised by ^{31}P NMR spectroscopy, and X-ray structures were obtained for **5**–**9**.

Keywords: nickel · palladium · phosphorus · platinum · rearrangement

Introduction

Cyclooligophosphanes *cyclo*-$(PR)_n$,[1] which are isolobal with cycloalkanes, have attracted the interest of chemists for a long time. While the first example of this class of compounds, *cyclo*-$(PPh)_5$, was synthesised as early as 1877,[2] the first cyclooligophosphanide anions *cyclo*-$(P_nR_{n-1})^-$ were reported only about 100 years later.[3,4] Even today, the number of readily accessible, pure compounds is still small.[5] Thus, the alkali metal compounds K[*cyclo*-(P_3tBu_2)],[3] K[*cyclo*-(P_5Ph_4)][5] and Li[*cyclo*-(P_ntBu_{n-1})] (n = 3–5)[6,7] were obtained only in inseparable mixtures, and characterised by ^{31}P NMR spectroscopy. Recently we reported the targeted high-yield synthesis of Na[*cyclo*-(P_5tBu_4)] and preliminary results on its use in coordination chemistry[8,9] and main group chemistry.[10]

Different reactivity patterns are observed in reactions with **1**. While the *cyclo*-(P_5tBu_4) ligand stays intact in the reaction of **1** with Et_2AlCl[10] or $[RhCl(PPh_3)_3]$,[9] elimination of *t*BuCl with formation of a nickel(0) cyclopentaphosphene complex is observed in the reaction with $[NiCl_2(PEt_3)_2]$.[8] With $SnCl_2$, $PbCl_2$ or $BiCl_3$, a redox reaction occurs with formation of the two structural isomers {*cyclo*-(P_5tBu_4)}$_2$ and {*cyclo*-(P_4tBu_3)P*t*Bu}$_2$ (besides other cyclic phosphanes) and elemental metal.[10]

We have now observed that the reaction of **1** with phosphane complexes of the nickel triad is markedly dependent on the nature of the co-ligand and the transition metal. Thus, complexes are obtained in which: 1) the *cyclo*-(P_5tBu_4) ligand stays intact; 2) *t*BuCl is eliminated with formation of a metal(0) cyclopentaphosphene complex; 3) ring contraction with formation of a metal-{*cyclo*-(P_4tBu_3)P*t*Bu} group occurs; and even 4) complexes in which migration of a phosphanediide group gives the novel {*cyclo*-(P_5tBu_4)P*t*Bu} ligand.

Results and Discussion

Reactions of 1 with $[NiCl_2(PR_3)_2]$ ($PR_3 = PEt_3$, PPh_3), $[NiCl_2(bipy)]$ (bipy = 2,2′-bipyridine), $[PdCl_2(PR_3)_2]$ ($PR_3 = PMe_2Ph$, PPh_3) and $[PtCl_2(PPh_3)_2]$: The reaction of Na-

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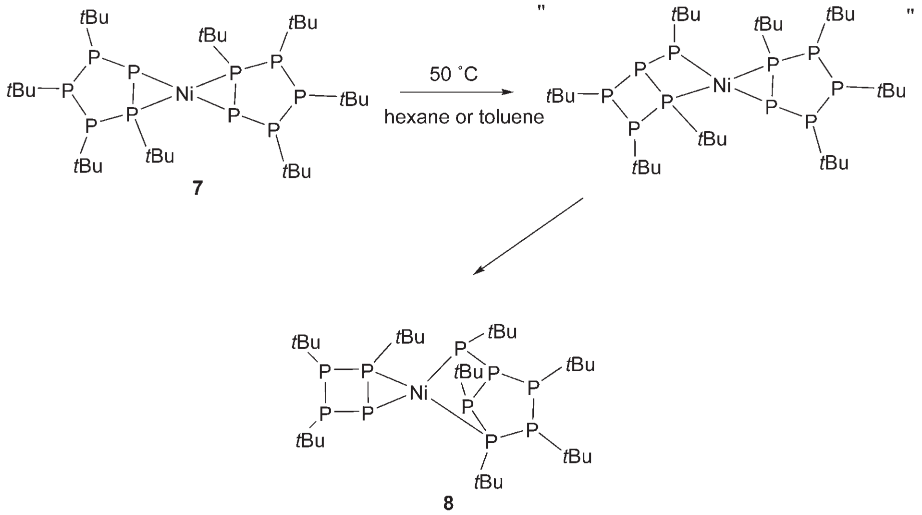
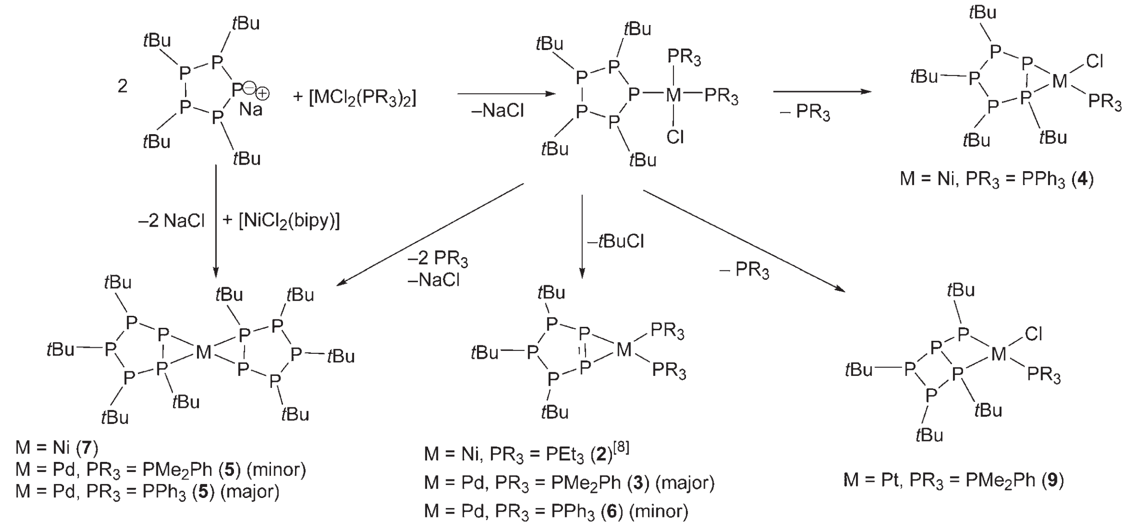
[*cyclo*-(P_5tBu_4)][8] with phosphane complexes of the nickel triad is markedly dependent on the nature of the starting material and the transition metal.

Thus, complexes with alkylphosphanes, such as [$NiCl_2(PEt_3)_2$][11] and [$PdCl_2(PMe_2Ph)_2$],[12] react with **1** with elimination of *t*BuCl and formation of the corresponding metal(0) cyclopentaphosphene complexes [Ni{*cyclo*-(P_5tBu_3)}(PEt_3)$_2$] (**2**)[8] and [Pd{*cyclo*-(P_5tBu_3)}(PMe_2Ph)$_2$] (**3**; Scheme 1). The formation of *cyclo*-(P_5tBu_4H),[13] which results from the reaction of **1** and *t*BuCl, is also observed in these reactions.[8] The Pd complex **3** is unstable in solution and decomposes slowly, even at −27 °C, over 12 months with formation of black palladium metal and {*cyclo*-(P_4tBu_3)P*t*Bu}$_2$. Similarly, reductive elimination is observed in the reactions of $SnCl_2$, $PbCl_2$ and $BiCl_3$ with **1**.[10]

In contrast, complexes with the more labile triphenylphosphane ligand, such as [$MCl_2(PPh_3)_2$] (M = Ni, Pd),[14] react with **1** (1:2) with formation of [NiCl{*cyclo*-(P_5tBu_4)}(PPh_3)] (**4**) and [Pd{*cyclo*-(P_5tBu_4)}$_2$] (**5**), in which the *cyclo*-(P_5tBu_4) ligand is intact (Scheme 1). Accordingly, the cyclopentaphosphene complex [Pd{*cyclo*-(P_5tBu_3)}(PPh_3)$_2$] (**6**) is also formed in the reaction of [$PdCl_2(PPh_3)_2$] with **1**, but this complex was only obtained in trace amounts and could only be analysed by X-ray diffraction studies but not by other characterisation techniques. Compound **5** was obtained, although in very low yield, as well as **3** in the reaction of [$PdCl_2(PMe_2Ph)_2$] with **1** (1:2).



Scheme 2.



Scheme 1.

Only when the more labile nickel(II) bipy complex [$NiCl_2$(bipy)][15] was employed in the reaction with **1** (1:2) was the analogous homoleptic nickel complex [Ni{*cyclo*-(P_5tBu_4)}$_2$] (**7**) formed in high yield, while nickel(II) phosphane complexes gave either **2** or **4** but never **7**. After a dilute solution of **7** in *n*-hexane had been heated for 30 min, a very small amount of the rearranged complex [Ni{*cyclo*-(P_5tBu_4)P*t*Bu}{*cyclo*-(P_4tBu_3)}] (**8**) was formed (Scheme 2). Complex **8** could not be isolated in pure form and was obtained only as a mixture with **7**. To improve the yield, the reaction was carried out at different temperatures, with different solvents and reaction times. While no decomposition products were observed, only a small quantity (less than about 10 %) of **8** was formed. The proposed mechanism of this reaction could include the formation of [Ni{*cyclo*-(P_5tBu_4)}{*cyclo*-(P_4tBu_3)P*t*Bu}] as an intermediate (Scheme 2), followed by migration of the exocyclic phosphanediide group of rearranged *cyclo*-(P_4tBu_3)P*t*Bu to give **8**, which exhibits a *cyclo*-($P_4t Bu_3$) and a *cyclo*-($P_5t Bu_4$)P*t*Bu ligand.

This mechanism seems to be plausible because of the results obtained in the reaction of **1** with [$PtCl_2(PPh_3)_2$],[16] in which ring contraction occurs giving [PtCl{*cyclo*-($P_4t Bu_3$)P*t*Bu}-(PMe_2Ph)] (**9**; Scheme 1), in which the novel {*cyclo*-($P_4t Bu_3$)P*t*Bu} ligand (identical to that proposed for the intermediate in the reaction of **7** to give **8**) is formed via rearrangement of the *cyclo*-($P_5t Bu_4$) ligand.

^{31}P NMR spectroscopy: ^{31}P NMR spectroscopy is a very powerful tool for characterising phosphorus-rich compounds in solution.

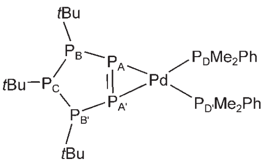
The $^{31}P\{^1H\}$ NMR spectrum of **3**, which is very similar to that reported for **2**,[8] shows a higher-order AA′BB′CDD′ spin system. The chemical shifts and coupling constants were calculated by using the simulation program SpinWorks[17] (Table 1). The observed and calculated coupling patterns are in very good agreement and indicate that a *cyclo*-($P_5t Bu_3$) is present. Due to line broadening (approximately 10 Hz), the ^3J(P,P) and ^4J(P,P) coupling constants were not observed.

The large (absolute) coupling constant ^1J(A,A′) of −472.3(7) Hz indicates multiple-bond character between these P atoms,[18,19] while the smaller ^1J(P,P) coupling constants (−371.1(1) and −336.6(1) Hz) are in a range such as would be expected for P−P single bonds. This indicates that P_C deviates from the plane formed by the P_B-P_A-$P_{A'}$-$P_{B'}$ fragment and should therefore form the tip of the envelope conformation.

The high-resolution $^{31}P\{^1H\}$ NMR spectrum of **4** shows five multiplets for the

Table 1. $^{31}P\{^1H\}$ NMR data δ [ppm] and *J* [Hz]of **3**, **4**, **5**, **7**, **8** and **9** at 25 °C

[Pd{*cyclo*-($P_5t Bu_3$)}(PMe_2Ph)$_2$] (**3**) (AA′BB′CDD′ spin system, C_6D_6)

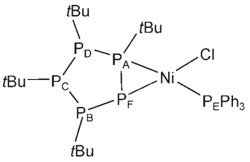


$\delta_{A,A'} = +73.7(1)$ (m)
$\delta_{B,B'} = +101.77(1)$ (m)
$\delta_C = +83.4(1)$ (m)
$\delta_{D,D'} = -17.8(1)$ (m)
rms = 0.25 %

$^1J(A,A') = -472.3(7)$
$^1J(A,B) = -371.1(1) = {}^1J(A',B)$
$^1J(B,C) = -336.6(1) = {}^1J(B',C)$
$^2J(A,B') = +18.1(3) = {}^2J(A',B)$

$^2J(C,A) = -13.1(1) = {}^2J(C,A')$
$^2J(A,D) = +8.2(5) = {}^2J(A',D')$
$^2J(A,D') = +45.9(7) = {}^2J(A',D)$
$^2J(D,D') = +10.6(1)$
$^2J(B,B') = -27.4(7)$

[NiCl{*cyclo*-($P_5t Bu_4$)}(PPh_3)] (**4**) (ABCDEF spin system, C_7D_8)

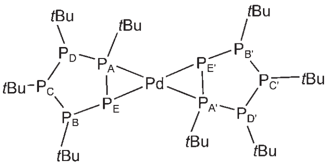


$\delta_A = +88.8(1)$ (m)
$\delta_B = +77.5(1)$ (m)
$\delta_C = +52.1(1)$ (m)
$\delta_D = +47.9(1)$ (m)
$\delta_E = +23.9(1)$ (m)
$\delta_F = -17.1(1)$ (m)
rms = 34.4 %

$^1J(A,D) = -393.8(1)$
$^1J(A,F) = -470.2(2)$
$^1J(B,C) = -332.4(1)$
$^1J(B,F) = -422.9(1)$
$^1J(C,D) = -322.5(1)$
$^2J(A,E) = -172.1(2)$
$^2J(A,C) = -16.4(1)$
$^2J(B,D) = -10.4(1)$

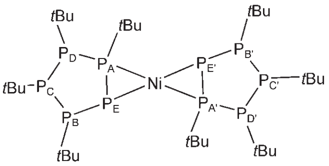
$^2J(A,B) = 0$
$^2J(D,F) = +22.5(1)$
$^2J(E,F) = +36.8(2)$
$^2J(C,F) = -0.3(1)$
$^3J(B,E) = 0$
$^3J(D,E) = +0.2(1)$
$^4J(C,E) = 0$

[Pd{*cyclo*-($P_5t Bu_4$)}$_2$] (**5**) (AA′BB′CC′DD′EE′ spin system, THF)[a]



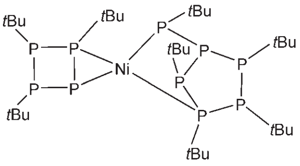
$\delta_A = +103$ (m)
$\delta_D = +55$ (m)
$\delta_B = +87$ (m)
$\delta_E = -30$ (m)
$\delta_C = +63$ (m)

[Ni{*cyclo*-($P_5t Bu_4$)}$_2$] (**7**) (AA′BB′CC′DD′EE′ spin system, C_6D_6)[a]



$\delta_A = +98$ (m)
$\delta_D = +52$ (m)
$\delta_B = +88$ (m)
$\delta_E = -65$ (m)
$\delta_C = +64$ (m)

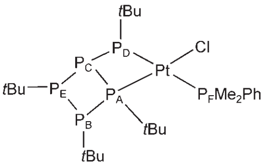
[Ni{*cyclo*-($P_5t Bu_4$)P*t*Bu}{*cyclo*-($P_4t Bu_3$)}] (**8**) (ABCDEFGHIX spin system, C_6D_6)[b]



δ = +163 (m)
δ = +13 (m)
δ = −41 (m)
δ = −103 (m)
δ = +148 (m)
δ = −6 (m)
δ = −49 (m)
δ = +30 (m)
δ = −21 (m)
δ = −75 (m)

Table 1. (Continued)

$[PtCl\{cyclo\text{-}(P_4tBu_3)PtBu\}(PMe_2Ph)]$ (**9**) (ABCDEF spin system, C_6D_6)



$\delta_A = -124.97(2)$ (m)	$^1J(A,Pt) = \pm 1899(1)$	$^1J(A,B) = \pm 196.7(1)$
$\delta_B = +14.61(2)$ (m)	$^1J(D,Pt) = -892(1)$	$^1J(A,C) = -75.4(1)$
$\delta_C = -13.07(2)$ (m)	$^1J(F,Pt) = -2403(1)$	$^1J(B,E) = \pm 150.3(1)$
$\delta_D = -23.57(2)$ (m)	$^1J(C,E) = \pm 150.5(1)$	$^1J(C,D) = \pm 159.8(1)$
$\delta_E = -50.50(2)$ (m)	$^2J(B,C) = -2.8(1)$	$^2J(D,E) = -230.8(1)$
$\delta_F = -8.81(2)$, m	$^2J(D,F) = -12.2(1)$	$^2J(B,Pt) = -59$
	$^2J(C,Pt) = \pm 41$	$^2J(A,E) = -6.5(1)$
	$^2J(A,D) = -45.5(1)$	$^2J(A,F) = -450.6(1)$
	$^3J(B,D) = \pm 0.1(1)$	$^3J(C,F) = \pm 7.5(1)$
rms = 10.6 %	$^4J(B,F) = \pm 2.9(1)$	$^4J(E,F) = \pm 0.02(1)$

[a] Signals corresponding to the predominant isomer; due to the presence of a second isomer (presumably the *cis* isomer) and strongly overlapping signals, the ^{31}P NMR spectrum with its 25 coupling constants could not be analysed unambiguously. [b] The chemical shifts found in the ^{31}P NMR spectrum are reported without any assignment or analysis of the coupling constants, due to the presence of a mixture of isomers of **7** and **8** (ratio ca. 9:1).

ABCDEF spin system (ratio 1:1:2:1:1; see Table 1). Due to similar chemical shifts of the nuclei P_C and P_D ($|(\nu_C - \nu_D)|/J(C,D) < 10$) a higher-order spectrum is observed.[20,21] In the proton-coupled ^{31}P NMR spectrum, only P_A, P_B, P_C and P_D show coupling to *tert*-butyl protons, while P_F and P_E do not. The connectivities of the P atoms were obtained from a two-dimensional $^{31}P,^{31}P$ COSY45 NMR spectrum, and the chemical shifts and coupling constants were calculated by using the simulation program SpinWorks[17] (Table 1). The observed and calculated coupling patterns are in very good agreement and indicate that the *cyclo*-(P_5tBu_4) unit is retained (Figure 1).

The fragment P_D-P_A-P_F-P_B has the largest absolute values for the $^1J(P,P)$ coupling constants (−394 to −470 Hz), which are indicative of multiple-bond character between these P atoms,[18,19] while P_C shows smaller $^1J(P,P)$ coupling constants ($^1J(B,C) = -332$ Hz, $^1J(C,D) = -322$ Hz), as would be expected for P–P single bonds. This indicates that P_C deviates from the plane formed by the P_D-P_A-P_F-P_B fragment and should therefore form the tip of the envelope conformation.

The *trans* effect is also observed here and allows an unambiguous assignment of the P atoms around nickel, as the geminal P-Ni-P coupling constants $^2J(P,P)$ are rather different.[22] Thus, the absolute value of $^2J(A,E)_{trans}$ (−172.1(2) Hz) is much greater than the corresponding value of $^2J(E,F)_{cis}$ (+36.8(2) Hz).[23,24]

The $^{31}P\{^1H\}$ NMR spectra of **5** and **7** show five multiplets for the AA′BB′CC′DD′EE′ spin system at $\delta \approx 103$, 87, 63, 55 and −30 ppm for **5**, and $\delta \approx 98$, 88, 64, 52 and −65 ppm for **7** (ratio 1:1:1:1:1; see Table 1). Apparently, more than one isomer (*cis* and *trans*) is present in solution (Figure 2). Due to overlap of the signals of the two isomers, a full analysis of the spectra and calculation of all 25 coupling constants were not possible; only the $^1J(P,P)$ coupling constants could be obtained (range ≈ −320 to −430 Hz). As the phosphorus atoms A, A′ are chiral in the *trans* and *cis* isomers, different diastereomers are also feasible. For the *trans* isomer, *meso* ($A_SA'_R/A_RA'_S$, containing an inversion centre or a mirror plane) and *racemic* ($A_SA'_S/A_RA'_R$, containing a C_2 axis) diastereomers could be formed. For the *cis* isomer, only the *rac* form seems feasible, due to steric interaction of the *t*Bu groups at P_A and $P_{A'}$. In addition, several conformational isomers could also be present due to the different conformations of the two P_5 envelopes.

In the $^{31}P\{^1H\}$ NMR spectrum of the inseparable mixture of **7** and **8**, the signals of **7** are observed as well as some other signals, corresponding to **8**, in which all the phosphorus atoms are magnetically inequivalent, and thus form a very complicated ABCDEFGHIX spin system with ten different signals. However, as the

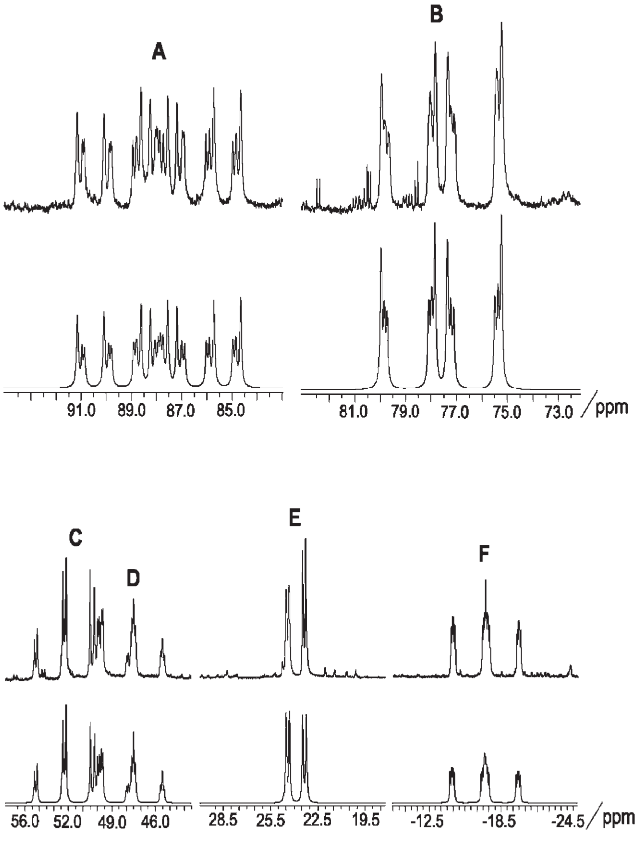


Figure 1. $^{31}P\{^1H\}$ NMR spectra of **4**: P_A (upper left), P_B (upper right), $P_{C,D}$ (bottom left), P_E (centre) and P_F (bottom right). In each case the experimental spectrum is shown above the simulated one.

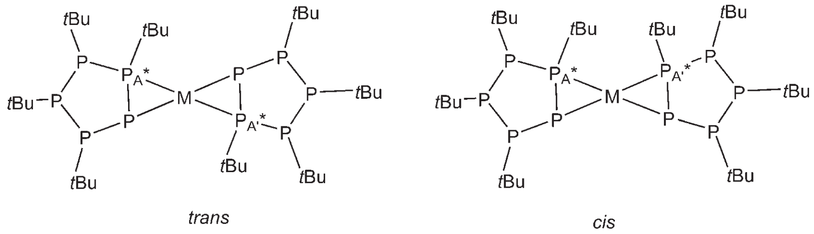


Figure 2. Two potential *trans*/*cis* isomers of [M{*cyclo*-(P_5tBu$_4$)}$_2$] (M = Ni (**7**), Pd (**5**)).

amount of this compound was always very small compared with that of **7**, full analysis of the spectrum and calculation of all the chemical shifts and coupling constants were not possible.

The spectrum of **9** shows a typical first-order ABCDEF spin system with 132 lines. Phosphorus atom A appears at $\delta = -124.9$ ppm, in the high-field range, possibly due to the “small-ring effect” which shifts all the signals to higher field. The connectivities of the P atoms were obtained from a two-dimensional $^{31}P,^{31}P$ COSY45 NMR spectrum, and the coupling constants and chemical shifts are summarised in Table 1.

Mass spectra: In the mass spectra of **3**–**9**, molecular ion peaks are observed (see Experimental Section) as well as fragments of the phosphorus-rich ligands and organyl-free fragments, such as $[PdP_5]^+$ and $[PdP_4]^+$ (for **3** and **5**), $[NiClP_6]^+$ and $[NiP_5]^+$ (for **4**), $[PdP_6]^+$, $[PdP_5]^+$ and $[PdP_4]^+$ (for **6**), $[NiP_5]^+$ and $[NiP_6]^+$ (for **7** and **8**) and $[PtP_5]^+$ (for **9**); this indicates that these complexes could be suitable precursors for the formation of binary metal phosphides.

X-Ray diffraction studies: Compounds **5** and **7** crystallise in the triclinic space group $P\bar{1}$ with one molecule in the unit cell. Selected bond lengths and angles of **5**–**9** are summarised in Table 2.

The molecules lie on a crystallographic inversion centre. Thus, in the solid state only the *meso* form of the *trans* conformation of the *cyclo*-(P_5tBu$_4$) ligand is observed for complexes **5** and **7**. In agreement with the NMR data, the X-ray structures of **5** (Figure 3) and **7** (Figure 4) show an all-*trans* arrangement of the *t*Bu groups and an envelope conformation of the P_5 ring, in which the tip (P4) deviates from the P_4 plane by −43.8(2) pm (**5**) and 23.6(2) pm (**7**). The metal atom in **5** and **7** is located on an inversion centre, resulting in a perfectly planar arrangement of the phosphorus atoms P1, P1′, P2 and P2′ and the nickel or palladium atom. The M–P1 (the P atom of the phosphanido group) distances are 243.4(1) pm for **5** and 229.30(9) pm for **7**, and the M–P2 bond lengths are 229.2(1) pm for **5** and 217.47(9) pm for **7**, which are even shorter than those corresponding to a metal–phosphanido bond. The P2–P3, P3–P4, P4–P5 and P5–P1 bond lengths in the P_5 ring are between 219.6(2) and 222.6(1) pm, which is typical for P–P single bonds; however, the shorter P1–P2 bond length in both complexes (212.3(2) pm for **5** and 212.2(1) pm for **7**) indicates multiple-bond character.

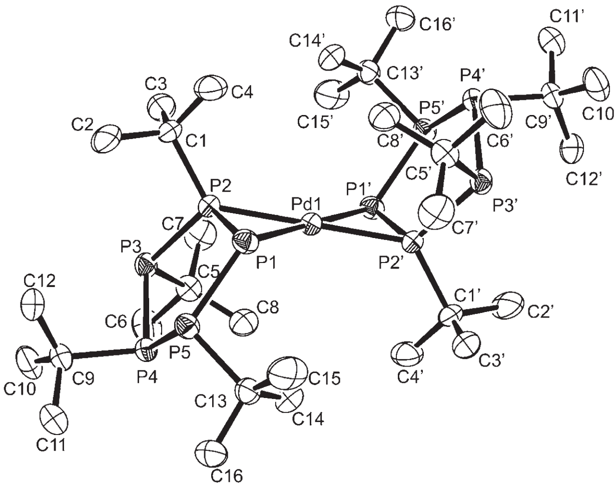


Figure 3. Molecular structure of [Pd{*cyclo*-(P_5tBu$_4$)}$_2$] (**5**).

Table 2. Selected bond lengths [pm] and angles [°] for **5**–**9**.

	5	**6**	**7**	**8**	**9**
P1–P2	212.3(2)	219.7(5)	212.2(1)	225.51(9)	225.0(2)
P2–P3	219.6(2)	219.7(5)	220.3(1)	221.58(9)	221.9(2)
P3–P4	220.2(2)	220.1(5)	220.7(1)	219.93(9)	222.7(2)
P4–P5	222.5(2)	219.7(5)	222.6(1)	–	221.2(2)
P1–P5	219.9(2)	213.7(5)	220.1(1)	–	–
P1–P4	–	–	–	215.53(9)	–
M–P1	243.4(1)	235.4(3)	229.30(9)	227.19(8)	232.7(1)
M–P2	229.2(1)	–	217.47(9)	–	–
M–P5	–	239.5(3)	–	222.13(8)	230.1(1)
M–P6	–	235.0(3)	–	218.58(8)	231.0(1)
M–P7	–	235.9(3)	–	–	–
P1-P2-P3	114.87(7)	107.7(2)	114.33(5)	88.37(3)	95.30(8)
P2-P3-P4	103.37(7)	106.8(2)	103.43(5)	85.79(3)	89.28(7)
P3-P4-P5	105.38(7)	107.1(2)	104.79(5)	–	87.00(7)
P1-M-P2	53.29(4)	–	56.63(3)	–	–
P1-M-P5	–	53.5(1)	–	165.70(2)	79.98(5)

Complex **6** crystallises in the triclinic space group $P\bar{1}$ with two molecules in the unit cell (Figure 5). The P_5 ring shows an all-*trans* arrangement of the *t*Bu groups and an envelope conformation in which P3 deviates by 23.4(5) pm from the

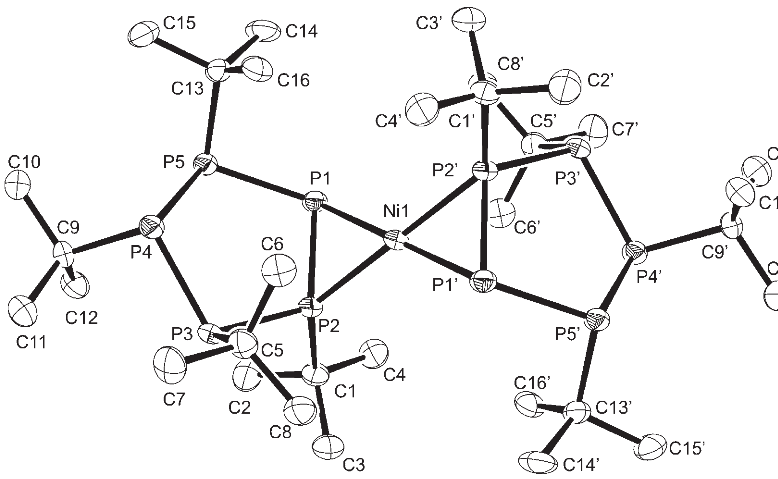


Figure 4. Molecular structure of [Ni{*cyclo*-(P_5tBu$_4$)}$_2$] (**7**).

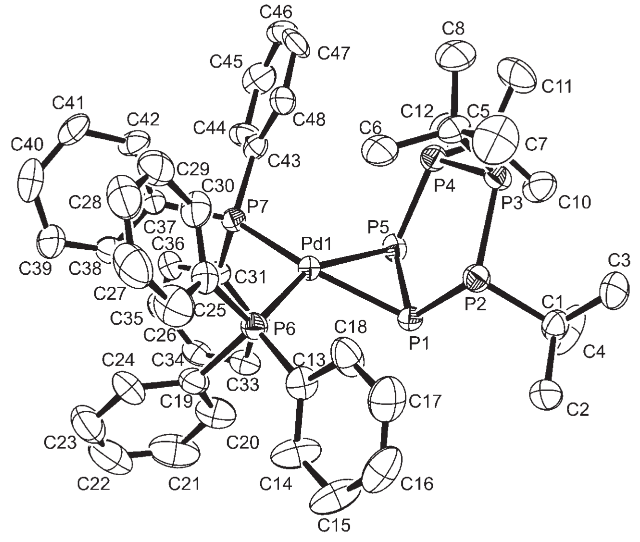


Figure 5. Molecular structure of [Pd{*cyclo*-(P_5tBu$_3$)}(PPh$_3$)$_2$] (**6**).

best plane formed by P1-P2-P4-P5. Again, four of the five P–P bond lengths in the P_5 ring (P1–P2, P2–P3, P3–P4 and P4–P5) are close to 220 pm, in the range of P–P single bonds, but the P1–P5 distance of 213.7(5) pm is typical, albeit somewhat long, for a P–P double bond. The palladium atom is in a highly distorted square-planar geometry in which the best plane is defined by P1-P5-P6-P7, from which the palladium atom deviates by about 24.3 pm. Three of the Pd–P distances are about 235.5 pm; the Pd1–P5 distance (239.5(3) pm) is slightly longer.

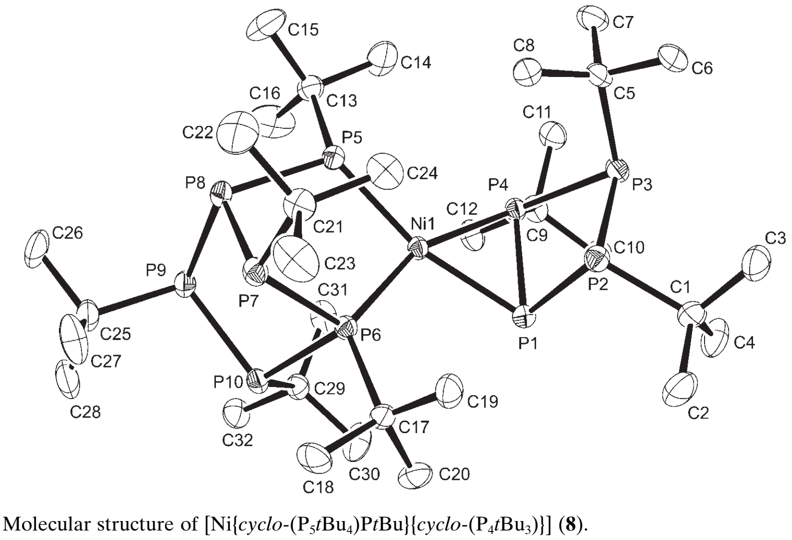


Figure 6. Molecular structure of [Ni{*cyclo*-(P_5tBu$_4$)P*t*Bu}{*cyclo*-(P_4tBu$_3$)}] (**8**).

Complex **8** crystallises in the monoclinic space group *I*2a with eight molecules in the unit cell. The complex has a distorted square-planar geometry in which P1 deviates by about 11.8 pm from the best plane defined by Ni1-P4-P5-P6 (Figure 6). The Ni1–P1 bond length of 227.19(8) pm is slightly greater than the other Ni–P(phosphane) bond lengths (Ni1–P4 222.28(9) pm and Ni1–P6 218.58(8) pm), which is unexpected for a nickel–phosphanido bond, while the Ni1–P5 bond length of 222.13(8) pm is comparable with those of the phosphane groups. The P–P bond lengths in the *cyclo*-(P_4tBu$_3$) ring are P1–P2 225.51(9) pm, P2–P3 221.58(9) pm, P3–P4 219.93(9) pm and P1–P4 215.53(9) pm, which is slightly shorter than the others and thus indicative of multiple-bond character. The P-P-P bond angles in this ring are between 85.87(3)° and 91.38(3)°. The four-membered ring is in a butterfly conformation (distances from each phosphorus atom to the best plane through P1-P2-P3-P4 are 21.4, −20.7, 21.3 and −22.0 pm). The atoms Ni1-P5-P8-P7-P6 form a five-membered metallacycle in an envelope conformation in which the best plane is defined by Ni1-P5-P8-P6, and P7 deviates from this plane by about 45.8 pm. The atoms P6, P7 and P8 are also members of a P_5 ring which is completed by P9 and P10 and which also displays an envelope conformation with the best plane formed by P6-P8-P9-P10 (P7 deviates by 69.1 pm). This arrangement could be considered to be a seven-membered metallabicycle. The angle between the best planes containing the atoms Ni1-P5-P6-P8 and P6-P8-P9-

P10 is 62.9°, and P7 deviates from these planes by 112.3 and 143.0 pm, respectively. The P–P bond lengths in this metallabicycle of between 217.49(9) pm for P7–P8 and 225.19(9) pm for P6–P10 indicate P–P single bonds; the P6–P7 (225.1(1) pm) and P6–P10 (225.19(9) pm) bonds are slightly longer, perhaps due to torsion of the ring. The bond angles in the norbornane-like bicycle of 91.12(3) to 114.81(3)° indicate some distortion (Figure 7).

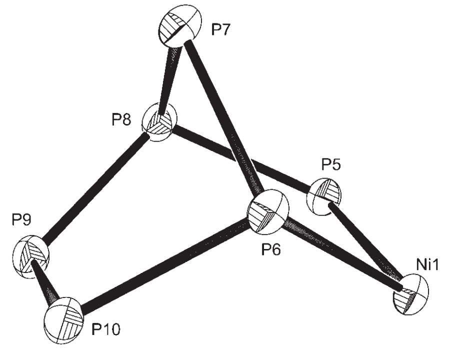


Figure 7. Section of the bicyclic moiety in the molecular structure of [Ni{*cyclo*-(P_5*t*Bu_4)P*t*Bu}{*cyclo*-(P_4*t*Bu_3)}] (**8**).

Platinum complex **9** crystallises in the monoclinic space group *P*2_1/*c* with four molecules in the unit cell (Figure 8). The platinum(II) complex has a square-planar geometry in which the four donor atoms are P1, P5, P6 and Cl1, and the P–P bond lengths in the ligand *cyclo*-(P_4*t*Bu_3)P*t*Bu are in the range of P–P single bonds; the P1–P5 distance of 297.4 pm is too long for us to propose a chemical bond between these atoms. The P5-P2-P1 bond angle of 83.94(7)° is slightly larger than the P5-Pt1-P1 bond angle (79.98(5)°). This geometry is comparable with that described by Fenske and coworkers for the complex [Pt(P_3*t*Bu_3)(PPh_3)$_2$].[25] The phosphorus atoms P1-P2-P5 of the *cyclo*-(P_4*t*Bu_3)P*t*Bu ligand and the palladium atom form an almost planar four-membered metallacycle. P6 deviates by −39.2(2) pm from the plane formed by P1-P5-Pt1-Cl1. The dihedral angle between the planes P1-P2-P5-Pt1 and P2-P3-P4-P5 is 71.72(4)°.

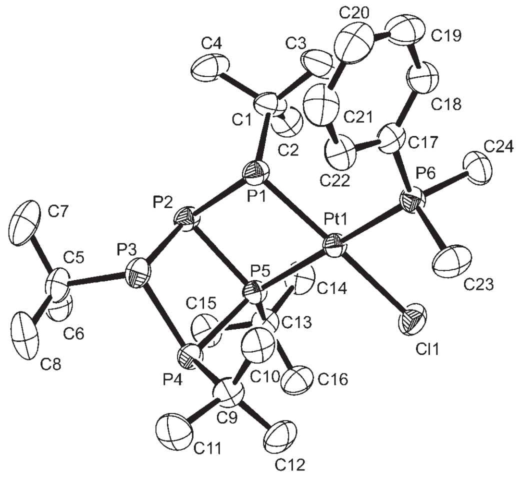


Figure 8. Molecular structure of [PtCl{*cyclo*-(P_4*t*Bu_3)P*t*Bu}(PMe_2Ph)] (**9**).

The P-P-P bond angles in the P_4 ring are between 87.00(7)° and 90.22(7)°, indicating that this four-membered ring adopts an almost ideal planar conformation, whereas the angles are more constrained for the four-membered ring P1-P2-P5-Pt1, being between 79.98(5)° and 98.69(6)°. The distances of the phosphorus atoms to the best plane formed by P2-P3-P4-P5 are 17.9(1), −17.7(1), 17.8(1) and −18.0(1) pm, and for the metallacycle the distances to the best plane are 7.1(1), −7.0(1), 7.5(1) and −7.4(1) pm for P1, Pt1, P2 and P5, respectively. Again, the *t*Bu groups of the *cyclo*-(P_4*t*Bu_3) adopt the all-*trans* conformation.

Conclusion

We have shown the versatility of *cyclo*-(P_5*t*Bu_4)$^-$ in reactions with group 10 metal complexes. The synthesis and characterisation of some novel nickel, palladium and platinum complexes were reported. The results obtained show that the P_5*t*Bu_4 ligand can rearrange to *cyclo*-(P_5*t*Bu_3) or to *cyclo*-(P_4*t*Bu_3)P*t*Bu or it can stay intact, depending on the starting materials. At elevated temperature [Ni{*cyclo*-(P_5*t*Bu_4)}$_2$] (**7**) rearranges to give, albeit in only low yield, [Ni{*cyclo*-(P_5*t*Bu_4)P*t*Bu}{*cyclo*-(P_4*t*Bu_3)}] (**8**), which exhibits the previously unknown *cyclo*-(P_5*t*Bu_4)P*t*Bu and *cyclo*-(P_4*t*Bu_3) ligands.

Experimental Section

General methods: All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques.

The NMR spectra were recorded at 25 °C on a Bruker Avance DRX-400 spectrometer. ^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.16 MHz): internal standard solvent, external standard TMS; ^{31}P NMR (161.9 MHz): external standard 85 % H_3PO_4. IR spectra: KBr pellets were prepared in a nitrogen-filled glove box and the spectra were recorded on a Perkin-Elmer System 2000 FTIR spectrometer in the range 350–4000 cm^{-1}.

All solvents were purified by distillation, dried, saturated with argon and stored over potassium mirrors.

Elemental analyses were performed on a Vario EL (Heraeus) or on a Leco CHNS-932 microanalyser.

The melting points were determined in sealed capillaries under argon and are uncorrected.

$PdCl_2$(PMe_2Ph)$_2$],[12] [$PdCl_2$(PPh_3)$_2$],[14] [$NiCl_2$(PPh_3)$_2$],[14] [$NiCl_2$(bipy)],[15] [$PtCl_2$(PMe_2Ph)$_2$],[16] Na[*cyclo*-(P_5*t*Bu_4)] (**1**)[8] and [Ni{*cyclo*-(P_5*t*Bu_3)}(PEt_3)$_2$] (**2**)[8] were prepared as reported previously.

Data collection and structural refinement of 5–9: The data for **5**, **6** and **9** were collected on a Siemens SMART CCD diffractometer ($\lambda(Mo_{K\alpha}) = 0.71073$ Å) using φ scan mode, and those of **7** and **8** on a CCD Oxford Xcalibur S ($\lambda(Mo_{K\alpha}) = 0.71073$ Å) using ω and φ scan mode. Semi-empirical absorption corrections for **5**, **6** and **9** were performed with SADABS;[26a] semi-empirical absorption corrections from equivalents were carried out for the structures of **7** and **8**.[26a] All the structures were solved by direct methods.[27] Structure refinement was carried out with SHELXL-97.[28] All non-hydrogen atoms were refined anisotropically, and H atoms were located by difference maps and refined isotropically. Table 3 lists crystallographic details. The thermal ellipsoids of the molecular structures in Figures 3–8 are shown at the 50 % probability level.

Table 3. Crystal data and structure refinement for **5**–**9**.

	5	**6**	**7**	**8**	**9**
formula	$C_{32}H_{72}P_{10}Pd$	$C_{48}H_{57}P_7Pd$	$C_{32}H_{72}P_{10}Ni$	$C_{32}H_{72}P_{10}Ni$	$C_{24}H_{47}ClP_6Pt$
crystal size [mm^2]	0.10 × 0.10 × 0.05	0.10 × 0.02 × 0.02	0.10 × 0.08 × 0.05	0.40 × 0.20 × 0.03	0.30 × 0.20 × 0.20
colour	red	yellow	brown	brown	yellow
formula weight	873.00	957.13	825.31	825.31	751.98
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$I2a$	$P2_1/c$
a [pm]	902.9(1)	1010.6(4)	903.2(1)	1732.3(5)	1816.1(2)
b [pm]	1125.4(1)	1404.9(5)	1122.4(2)	1440.9(5)	1101.6(1)
c [pm]	1287.1(1)	1918.6(7)	1268.6(2)	3678.2(5)	1760.9(2)
α [°]	68.51(1)	69.34(1)	68.02(2)	90	90
β [°]	89.13(1)	77.44(1)	89.43(1)	100.91(1)	110.67(2)
γ [°]	68.78(1)	72.81(1)	69.50(1)	90	90
V [nm^3]	1.124(1)	2.416(1)	1.10(1)	9.02(1)	3.296(1)
Z	1	2	1	8	4
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	223(2)	203(2)	130(2)	130(2)	223(2)
ρ_{calcd} [Mg m^{-3}]	1.290	1.316	1.239	1.216	1.515
reflns. collected/2θ_{max} [°]	7328/58.98	10637/46.50	19451/58.26	50065/52.74	21229/57.62
unique reflections	5256	6892	5910	9208	7924
reflns. obs. [$I > 2\sigma(I)$]	2719	4789	3924	6234	5168
no. of parameters/rest	208/0	514/0	208/0	412/0	303/0
μ (mm^{-1})	0.789	0.647	0.821	0.806	4.641
$R1$ [$I > 2\sigma(I)$]	0.0438	0.0924	0.0527	0.0301	0.0342
$wR2$ (all data)	0.1126	0.2129	0.1347	0.0639	0.0868
GOF on F^2	0.824	1.194	0.987	0.909	0.904
residual density [eÅ^{-3}]	0.516/−0.394	0.576/−0.580	1.965/−0.337	0.382/−0.379	1.900/−1.292

CCDC-639625 (**5**), CCDC-639627 (**6**), CCDC-639628 (**7**), CCDC-639629 (**8**) and CCDC-639626 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[Pd{*cyclo*-(P$_5t$Bu$_3$)}(PMe$_2$Ph)$_2$] (3): At room temperature a suspension of [PdCl$_2$(PMe$_2$Ph)$_2$] (0.81 g, 1.79 mmol) in THF (20 mL) was added slowly to a solution of **1** (1.45 g, 3.57 mmol) in THF (20 mL). The colour changed from yellow to dark red. After 2 h the solvent was evaporated and the residue dissolved in *n*-pentane (10 mL), filtered (to remove NaCl) and the solvent evaporated. The resulting red residue is soluble in THF, toluene, diethyl ether, *n*-pentane and *n*-hexane. The ^{31}P NMR spectrum showed the presence of [Pd{*cyclo*-(P$_5t$Bu$_3$)}(PMe$_2$Ph)$_2$] (**3**) and *cyclo*-(P$_5t$Bu$_4$H).[13] Repeated crystallisation from *n*-pentane gave also a very small amount of wine-red rod-like crystals of [Pd{*cyclo*-(P$_5t$Bu$_4$)}$_2$] (**5**) at −27 °C. Yield of **3**: 0.29 g (23 %); m.p. 169–173 °C; ^{1}H NMR (C$_6$D$_6$): $\delta = 1.05$ (d, 6H, ^2J(P,H) = 8.0 Hz, PMe$_2$), 1.24 (d, 6H, ^2J(P,H) = 7.9 Hz, PMe$_2$), 1.27–1.58 (br, 27H, *t*Bu), 6.77 (m, 4H, *o*-H in Ph), 7.01 (m, 2H, *p*-H in Ph), 7.10 ppm (m, 4H, *m*-H in Ph); ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta = 16.2$ (d, ^1J(P,C) = 26.7 Hz, PMe$_2$), 17.0 (d, ^1J(P,C) = 29.0 Hz, PMe$_2$), 25.7–31.4 (br, *t*Bu), 131.8 (s, 4-C in Ph), 132.9 (s, 3,5-C in Ph), 134.0 (s, 2,6-C in Ph), 134.9 ppm (br, 1-C in Ph); ^{31}P{^{1}H} NMR (C$_6$D$_6$): see Table 1; IR (KBr): $\tilde{\nu} = 2970$ (s), 2934 (s), 2915 (s), 2882 (s), 2850 (s), 2755 (w), 1468 (m), 1455 (s), 1420 (m), 1354 (m), 1292 (m), 1169 (s), 1126 (m), 1101 (m), 1050 (s), 997 (m), 804 (s), 763 (s), 696 (w), 568 (m), 411 (m) cm^{-1}; FAB-MS, matrix: 3-nitrobenzyl alcohol (3-NBA); *m*/*z* (%): 709.4 (12.9) [M^++H], 708.4 (9.3) [M^+], 648.4 (0.3) [M^+−4Me], 631.3 (0.3) [M^+−Ph], 594.3 (4.1) [M^+−2*t*Bu], 571.3 (1.6) [M^+−4Me−Ph], 554.3 (0.3) [M^+−2Ph], 327.2 (7.7) [M^+−Pd−2(PMe$_2$Ph)] = [P$_5t$Bu$_3^+$]*, 292.2 (6.6) [M^+−P−2(Me$_2$Ph)−3*t*Bu] = [PdP$_6^+$], 261.2 (2.9) [M^+−2-(PMe$_2$Ph)−3*t*Bu] = [PdP$_5^+$], 230.2 (2.8) [M^+−P−2(PMe$_2$Ph)−3*t*Bu] = [PdP$_4^+$], 212.2 (3.6) [M^+−Pd−2(PMe$_2$Ph)−2*t*Bu] = [P$_5t$Bu$^+$]; (*P$_5t$Bu$_3$: theor.: 327.1); elemental analysis calcd (%) for C$_{28}$H$_{49}$P$_7$Pd, M = 708.92 g mol^{-1}: C 47.44, H 6.97; found: C 46.87, H 6.88.

[NiCl{*cyclo*-(P$_5t$Bu$_4$)}(PPh$_3$)] (4): At room temperature a suspension of [NiCl$_2$(PPh$_3$)$_2$] (0.72 g, 1.1 mmol) in *n*-pentane (10 mL) was added slowly to a solution of **1** (0.9 g, 2.2 mmol) in *n*-pentane (20 mL). The colour changed from yellow to blue. After 2 h the mixture was filtered and the blue residue washed several times with *n*-pentane. The *n*-pentane fractions were combined, concentrated to 10 mL and cooled to −27 °C. Red-brown crystals of **4** were obtained which were, however, unsuitable for X-ray diffraction studies. Yield: 0.58 g (64 %); m.p. 174–177 °C; ^{1}H NMR (C$_7$D$_8$): $\delta = 1.20$–1.99 (br, 36H, *t*Bu), 7.23–7.31 (br, 9H, *p*-H and *o*-H in Ph), 8.13 ppm (m, 6H, *m*-H in Ph); ^{13}C{^{1}H} NMR (C$_7$D$_8$): $\delta = 27.67$–32.66 (several s, *t*Bu), 132.92 (s, 4-C in Ph), 133.04 (s, 3,5-C in Ph), 134.11 (s, 2,6-C in Ph), 134.68 ppm (br, 1-C in Ph); ^{31}P{^{1}H} NMR (C$_7$D$_8$): see Table 1; IR (KBr): $\tilde{\nu} = 2964$ (s), 2934 (s), 2888 (s), 2853 (s), 1468 (s), 1456 (s), 1386 (m), 1357 (s), 1262 (s), 1167 (s), 1098 (s), 1020 (s), 867 (m), 804 (s), 696 (w), 466 (w) cm^{-1}; FAB-MS, matrix: 3-NBA; *m*/*z* (%): 740.0 (2.1) [M^++H], 739.1 (1.9) [M^+], 738.1 (2.6) [M^+−H], 704.1 (2.1) [M^+−Cl], 508.1 (2.0) [M^+−3Ph] = [NiClP$_6t$Bu$_4^+$], 477.0 (2.8) [M^+−PPh$_3$], 473.0 (2.5) [M^+−Cl−3Ph] = [NiP$_6t$Bu$_4^+$], 383.1 (10.2) [M^+−Ni−Cl−PPh$_3$] = [P$_5t$Bu$_4^+$]*, 327.1 (22.8) [M^+−(Ni−Cl−PPh$_3$−*t*Bu] = [P$_5t$Bu$_3^+$]*, 280.0 (13.0) [M^+−3Ph−4*t*Bu] = [NiClP$_6^+$], 262.0 (55.0) [M^+−Ni−Cl−P$_5t$Bu$_4$] = [PPh$_3^+$], 212.9 (9.1) [M^+−Cl−PPh$_3$−4*t*Bu] = [NiP$_5^+$]; (*P$_5t$Bu$_4$: theor.: 383.2; P$_5t$Bu$_3$: theor.: 327.1).

[Pd{*cyclo*-(P$_5t$Bu$_4$)}$_2$] (5): At room temperature a suspension of [PdCl$_2$-(PPh$_3$)$_2$] (0.36 g, 0.51 mmol) in petroleum ether (20 mL) was added slowly to a solution of **1** (0.42 g, 1.03 mmol) in petroleum ether (20 mL). The colour changed from yellow to wine red. After 2 h the mixture was filtered and the red residue washed several times with petroleum ether. The petroleum ether fractions were combined, concentrated to 5 mL and cooled to −27 °C. Wine-red rod-like crystals of [Pd{*cyclo*-(P$_5t$Bu$_4$)}$_2$] (**5**) were obtained. A ^{31}P NMR spectrum of the reaction mixture showed the formation of Pd{*cyclo*-(P$_5t$Bu$_4$)}$_2$] (**5**), {*cyclo*-(P$_5t$Bu$_4$)}$_2$[10] (24 %), *cyclo*-(P$_4t$Bu$_3$)P*t*Bu}$_2$[10] (17 %) *cyclo*-(P$_5t$Bu$_4$H)[13] (6 %) and a very small amount of [Pd{*cyclo*-(P$_5t$Bu$_3$)}(PPh$_3$)$_2$] (**6**). Compound **6** was obtained as crystals, always as a mixture with **5**, which was isolated by filtration. Yield: 0.22 g (50 %); m.p. 193–196 °C; ^{1}H NMR (C$_6$D$_6$): $\delta = 1.30$–1.66 ppm (br, *t*Bu); ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta = 29.9$–35.4 ppm (br, *t*Bu); ^{31}P{^{1}H} NMR ([D$_8$]THF): see Table 1; IR (KBr): $\tilde{\nu} = 2949$ (s), 2893 (s), 2855 (s), 1609 (m), 1452 (s), 1386 (m), 1358 (s), 1262 (s), 1167 (s), 1095 (s), 1016 (s), 803 (s), 792 (m), 466 (w) cm^{-1}; FAB-MS, matrix: 3-NBA; *m*/*z* (%): 874.0 (2.6) [M^++H], 873.0 (7.5) [M^+]*, 863.9 (1.3) [M^+−9H], 815.9 (1.0) [M^+−*t*Bu], 758.9 (2.4) [M^+−2*t*Bu], 702.0 (0.6) [M^+−3*t*Bu], 645.0 (0.6) [M^+−4*t*Bu], 530.3 (0.7) [M^+−6*t*Bu], 520.9 (2.3) [M^+ −4P−4*t*Bu], 385.1 (2.8) [M^+−P−8*t*Bu] = [PdP$_9^+$], 383.3 (23.2) [M^+

−Pd−5P−4*t*Bu] = $[\mathrm{P}_5t\mathrm{Bu}_4^+]^*$, 327.0 (25.8) [$M^+$−Pd−5P−5*t*Bu] = $[\mathrm{P}_5t\mathrm{Bu}_3^+]^*$, 292.0 (2.5) [$M^+$−4P−8*t*Bu] = $[\mathrm{PdP}_6^+]$, 261.0 (2.1) [M^+ −5P−8*t*Bu] = $[\mathrm{PdP}_5^+]$, 230.9 (2.6) [M^+−6P−8*t*Bu] = $[\mathrm{PdP}_4^+]$, 212.0 (1.9) [M^+−Pd−5P−7*t*Bu]; (*molecular ion peak: obs.: 873.0, theor.: 873.2; $\mathrm{P}_5t\mathrm{Bu}_4$: theor.: 383.2; $\mathrm{P}_5t\mathrm{Bu}_3$: theor.: 327.1); elemental analysis calcd (%) for $\mathrm{C_{32}H_{72}P_{10}Pd}$, $M = 873.00\,\mathrm{g\,mol^{-1}}$: C 44.02, H 8.79; found: C 44.03, H 8.08.

[Ni{*cyclo*-($\mathrm{P}_5t\mathrm{Bu}_4$)}$_2$] (7): At −78 °C a solution of **1** (1.20 g, 2.95 mmol) in THF (20 mL) was added dropwise to a suspension of $[\mathrm{NiCl_2(bipy)}]$ (0.42 g, 1.47 mmol) in THF (20 mL). The colour changed from green to dark brown. After 16 h the solvent was evaporated, and the brown residue was extracted twice with diethyl ether (20 mL). The diethyl ether fractions were combined, concentrated in vacuum to 10 mL and cooled to −27 °C. Dark brown plate-like crystals of [Ni{*cyclo*-($\mathrm{P}_5t\mathrm{Bu}_4$)}$_2$] (**7**) were obtained. A ^{31}P NMR spectrum of the reaction mixture showed the formation of [Ni{*cyclo*-($\mathrm{P}_5t\mathrm{Bu}_4$)}$_2$] (**7**) as the main product of the reaction as well as *cyclo*-($\mathrm{P}_5t\mathrm{Bu}_4\mathrm{H}$)[13] (11 %). Yield: 0.45 g (37 %); m.p. 189–191 °C; ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = 1.34$–1.70 ppm (br, *t*Bu); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 27.9$–34.3 ppm (br s, *t*Bu); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): see Table 1; IR (KBr): $\tilde{\nu} = 2947$ (s), 2889 (s), 2855 (s), 1601 (m), 1456 (s), 1386 (m), 1358 (s), 1260 (s), 1169 (s), 1095 (s), 1016 (s), 806 (s), 793 (m), 459 (w) cm^{-1}; FAB-MS, matrix: 3-NBA; *m*/*z* (%): 825.1 (86.0) [M^+]*, 824.0 (2.2) [M^+−H], 767.0 (100.0) [M^+−*t*Bu], 711.0 (29.8) [M^+−2*t*Bu], 652.9 (20.0) [M^+−3*t*Bu], 383.0 (26.5) [M^+−Ni−5P−4*t*Bu] = $[\mathrm{P}_5t\mathrm{Bu}_4^+]^*$, 274.7 (23.3) [$M^+$−3P−8*t*Bu] = $[\mathrm{NiP}_7^+]$, 243.9 (9.6) [M^+−4P−8*t*Bu] = $[\mathrm{NiP}_6^+]$, 212.8 (32.0) [M^+−5P−8*t*Bu] = $[\mathrm{NiP}_5^+]$, (*molecular ion peak: obs.: 825.0, theor.: 825.1; $\mathrm{P}_5t\mathrm{Bu}_4$: theor.: 383.2); elemental analysis calcd (%) for $\mathrm{C_{32}H_{72}P_{10}Ni}$, $M = 825.31\,\mathrm{g\,mol^{-1}}$: C 46.57, H 8.79: found: C 45.93, H 9.01.

[Ni{*cyclo*-($\mathrm{P}_5t\mathrm{Bu}_4$)P*t*Bu}{*cyclo*-($\mathrm{P}_4t\mathrm{Bu}_3$)}] (8): A solution of **7** (0.30 g, 0.36 mmol) in toluene (30 mL) was warmed to 50 °C for 20 min, and the mixture was then cooled to room temperature. The crystals obtained from this solution were isolated by filtration. They consisted of a mixture of **7** and **8** in an approximate ratio of 9:1. Yield: 0.12 g (40 %). In the filtrate the same ratio of **7**:**8** was observed by ^{31}P{^{1}H} NMR. ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = 1.87$–2.02 ppm (br s, *t*Bu in **7** and **8**); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 34.9$–36.9 ppm (br s, *t*Bu in **7** and **8**); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): see Table 1; the FAB-MS (matrix, 3-NBA) and IR spectra were identical to those of pure **7**.

[PtCl{*cyclo*-($\mathrm{P}_4t\mathrm{Bu}_3$)P*t*Bu}($\mathrm{PMe_2Ph}$)] (9): At room temperature a suspension of $[\mathrm{PtCl_2(PMe_2Ph)_2}]$ (0.11 g, 0.2 mmol) in THF (20 mL) was added slowly to a solution of **1** (0.16 g, 0.4 mmol) in THF (20 mL). The solvent was evaporated and the yellow residue dissolved in petroleum ether (20 mL) and filtered (to remove NaCl). The solution was cooled to −27 °C yielding yellow rods of [PtCl{*cyclo*-($\mathrm{P}_4t\mathrm{Bu}_3$)P*t*Bu}($\mathrm{PMe_2Ph}$)] (**9**). Yield: 0.10 g (68 %); m.p. 189–190 °C; ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = 1.18$ (d, ^3J(P,H) = 13.2 Hz, 27 H, *t*Bu), 1.23 (d, ^3J(P,H) = 11.2 Hz, 9 H, *t*Bu), 1.53 (d, ^2J(P,H) = 18.0 Hz, 3 H, $\mathrm{PMe_2}$), 1.80 (d, ^2J(P,H) = 14.4 Hz, 3 H, $\mathrm{PMe_2}$), 6.99 (m, 2 H, *o*-H in Ph), 7.08 (m, 1 H, *p*-H in Ph), 7.71 ppm (m, 2 H, *m*-H in Ph); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 15.9$ (d, $\mathrm{PMe_2}$, ^1J(P,C) = 26.1 Hz), 17.1 (d, $\mathrm{PMe_2}$, ^1J(P,C) = 24.9 Hz) 25.2–30.9 (br s, *t*Bu), 130.9 (s, 4-C in Ph), 132.0 (br, 3,5-C in Ph), 133.8 (br, 2,6-C in Ph), 134.9 ppm (br, 1-C in Ph); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): see Table 1; IR (KBr): $\tilde{\nu} = 2971$ (s), 2944 (s), 2890 (s), 2849 (s), 1470 (s), 1455 (s), 1386 (m), 1355 (s), 1261 (s), 1167 (s), 1102 (s), 1024 (s), 869 (w), 807 (m), 699 (w), 462 (w) cm^{-1}; FAB-MS, matrix: 3-NBA; *m*/*z* (%): 753.0 (9.9) [M^++H], 752.1 (10.5) [M^+], 751.1 (9.1) [M^+−H], 695.1 (70.3) [M^+−*t*Bu], 544.9 (2.9) [M^+−3P−2*t*Bu], 514.9 (5.7) [M^+−3P−2*t*Bu−2Me], 487.8 (3.0) [M^+−4*t*Bu−Cl], 425.9 (17.2) [M^+ −2P−4*t*Bu−Cl], 410.9 (3.5) [M^+−4*t*Bu−Ph−Cl], 395.9 (5.6) [M^+ −4*t*Bu−Me−Ph−Cl], 381.0 (4.3) [M^+−4*t*Bu−2Me−Ph−Cl], 349.9 (2.2) [M^+−$\mathrm{PMe_2Ph}$−4*t*Bu−Cl] = $[\mathrm{PtP}_5^+]$, 155.0 (7.6) [M^+−Pt−$\mathrm{PMe_2Ph}$−4*t*Bu−Cl] = $[\mathrm{P}_5^+]$, 124.0 (2.1) [M^+−Pt−P−$\mathrm{PMe_2Ph}$−4*t*Bu−Cl] = $[\mathrm{P}_4^+]$, 138.0 (9.4) [M^+−Pt−5P−4*t*Bu−Cl] = $[\mathrm{PMe_2Ph^+}]$, 107.1 (5.3) [M^+−Pt−5P−2Me−4*t*Bu−Cl] = $[\mathrm{PPh^+}]$; elemental analysis calcd (%) for $\mathrm{C_{24}H_{47}P_6ClPt}$, $M = 752.00\,\mathrm{g\,mol^{-1}}$: C 38.33, H 6.30; found: C 37.60, H 6.11.

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[1] M. Baudler, K. Glinka, *Chem. Rev.* **1993**, *93*, 1623–1667.
[2] H. Köhler, A. Michaelis, *Ber. Dtsch. Chem. Ges.* **1877**, *10*, 807–814.
[3] M. Baudler, Ch. Gruner, G. Fürstenberg, B. Kloth, F. Saykowski, U. Özer, *Z. Anorg. Allg. Chem.* **1978**, *446*, 169–176.
[4] M. Baudler, B. Makowka, *Z. Anorg. Allg. Chem.* **1985**, *528*, 7–21.
[5] A. Schmidpeter, G. Burget, *Phosphorus Sulfur Relat. Elem.* **1985**, *22*, 323–336.
[6] G. Fritz, K. Stoll, *Z. Anorg. Allg. Chem.* **1986**, *538*, 78–112.
[7] G. Fritz, R. Biastoch, K. Stoll, T. Vaahs, D. Hanke, H. W. Schneider, *Phosphorus Sulfur Relat. Elem.* **1987**, *30*, 385–388.
[8] A. Schisler, U. Huniar, P. Lönnecke, R. Ahlrichs, E. Hey-Hawkins, *Angew. Chem.* **2001**, *113*, 4345–4348; *Angew. Chem. Int. Ed.* **2001**, *40*, 4217–4219.
[9] A. Schisler, P. Lönnecke, E. Hey-Hawkins, *Inorg. Chem.* **2005**, *44*, 461–464.
[10] A. Schisler, P. Lönnecke, Th. Gelbrich, E. Hey-Hawkins, *Dalton Trans.* **2004**, 2895–2898.
[11] K. A. Jensen, *Z. Anorg. Allg. Chem.* **1936**, *229*, 265–284.
[12] H. Köpf, R. Voigtländer, *Chem. Ber.* **1981**, *114*, 2731–2743.
[13] a) W. Hölderich, G. Fritz, *Z. Anorg. Allg. Chem.* **1979**, *457*, 127–142; b) M. Baudler, *Angew. Chem.* **1987**, *99*, 429–451; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 419–441.
[14] A. Winzer, E. Born, *Z. Chem.* **1970**, *10*, 438–439.
[15] F. L. Wimmer, S. Wimmer, P. Castain, *Inorg. Synth.* **1991**, *29*, 185–190.
[16] R. D. Gillard, M. F. Pilbrow, *J. Chem. Soc. Dalton Trans.* **1974**, 2320–2325.
[17] A negative sign was generally used for the coupling constants ^1J(P–P) and the remaining signs and coupling constants were calculated with the program SpinWorks (K. Marat, SpinWorks, version 20000510, University of Manitoba).
[18] M. Schmidt, Dissertation, **1996**, TU Kaiserslautern.
[19] O. J. Scherer, T. Brück, G. Wolmershäuser, *Chem. Ber.* **1989**, *122*, 2049–2054.
[20] H. Günter, *NMR-Spektroskopie*, Georg Thieme Verlag, Stuttgart, **1973**, p. 73.
[21] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der Organischen Chemie*, 3rd ed., Georg Thieme Verlag, Stuttgart, **1987**, pp. 74–75.
[22] S. Berger, S. Braun, H.-O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen*, 1st ed., Georg Thieme Verlag, Stuttgart, **1993**, pp. 70, 123, 165.
[23] P. S. Pregosin, R. W. Kunz, *NMR Basic Principles and Progress: ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*, Springer Verlag, Berlin, **1979**.
[24] J. G. Verkade, *Coord. Chem. Rev.* **1972**, *9*, 1–106.
[25] D. Fenske, K. Merzweiler, *Angew. Chem.* **1984**, *96*, 600–602; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 635–637.
[26] a) G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction, Göttingen, **1998**; b) SCALE3 ABSPACK, Empirical absorption correction, CrysAlis–software package, Oxford Diffraction Ltd., **2006**.
[27] G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, **1997**.
[28] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, **1997**.

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