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P−P Bond Cleavage of Tetraphenyltetraphosphane-1,4-diide Facilitated by Nickel(0)

Santiago Gómez-Ruiz,[a] Stefan Zahn,[b] Barbara Kirchner,[b] Winfried Böhlmann,[c] and Evamarie Hey-Hawkins*[a]

Abstract: One equivalent of $[Na_2(thf)_5(P_4Ph_4)]$ (**1**) reacts with one equivalent of $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) to give the unexpected ionic compound $[Na(Et_2O)_3][Na_3(Et_2O)_2Ni_3(\mu\text{-}P_2Ph_2)_2(P_2Ph_2)_3]$ (**2**), whereas the reaction of $[Ni(cod)_2]$ with the less reactive $[K_2(pmdeta)_2(P_4Ph_4)]$ (**3**) leads to the formation of $[K(pmdeta)]_2[Ni(P_4Ph_4)(P_2Ph_2)]$ (**4**) (PMDETA = $NMe(CH_2CH_2NMe_2)_2$), in which K−Ni interactions are observed. The calculations for **4** confirm the structural parameters obtained by X-ray diffraction studies. A shared electron number (SEN) analysis was applied to investigate the K⋅⋅⋅Ni interactions. These studies indicate a SEN value of a typical three-center, two-electron bond for K1-Ni-K2 indicating a covalent contribution in the interaction between nickel and potassium.

Keywords: alkali metals · diphosphene ligands · metal–metal contacts · nickel · P ligands

Introduction

Alkali metal oligophosphanediides $M_2(P_nR_n)$ ($n = 2$–4),[1] which display unexpected and unpredictable reactivity, have great potential for the synthesis of phosphorus-rich main group and transition-metal complexes.[2,3c] Only recently have the structural principles governing this class of compounds been unraveled.[3–5] The intriguing chemistry of tetraphenyltetraphosphane-1,4-diide $(P_4Ph_4)^{2-}$ has been recently developed, and different patterns in transmetalation reactions were observed. We could show that, in spite of its highly reducing nature,[4c] the $(P_4Ph_4)^{2-}$ dianion remains intact in the transmetalation reaction with the valence-electron-rich late transition-metal halide[6] $[CuCl(PCyp_3)_2]$ (Cyp = *cyclo*-C_5H_9) yielding $[Cu_4(P_4Ph_4)_2(PCyp_3)_3]$,[2] whereas in the reaction with $[Cp^*TaCl_4]$ tantalum was apparently reduced by the dianion, followed by rearrangement and oxidative addition to give the tantalum(V) phosphinidene complex $[Cp^*Ta(Ph)(P_6Ph_5)]$.[7] Recently, we reported P−P bond cleavage of the $(P_4R_4)^{2-}$ dianion by nickel(II) complexes in an intramolecular redox reaction leading to nickel(0) diaryl diphosphene complexes.[3e] Herein we describe P−P bond cleavage of tetraphenyltetraphosphane-1,4-diide by nickel(0), which is highly surprising, since nickel(0) and nickel(II) complexes are excellent catalysts for olefin oligomerization reactions and formation of C−C bonds[8] from olefins, which are isolobal to diphosphenes.

Results and Discussion

$[Na_2(thf)_5(P_4Ph_4)]$ (**1**) reacts with one equivalent of $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) to give the ionic compound $[Na(Et_2O)_3][Na_3(Et_2O)_2Ni_3(\mu\text{-}P_2Ph_2)_2(P_2Ph_2)_3]$ (**2**; Scheme 1).

Compound **2** consists of a monoanionic core in which bridging of three nickel(0) atoms by two diphenyldiphosphanediide ligands results in a norbornane-like Ni_3P_4 metallabicyclic framework (Figure 1; Table 1), which is similar to a re-

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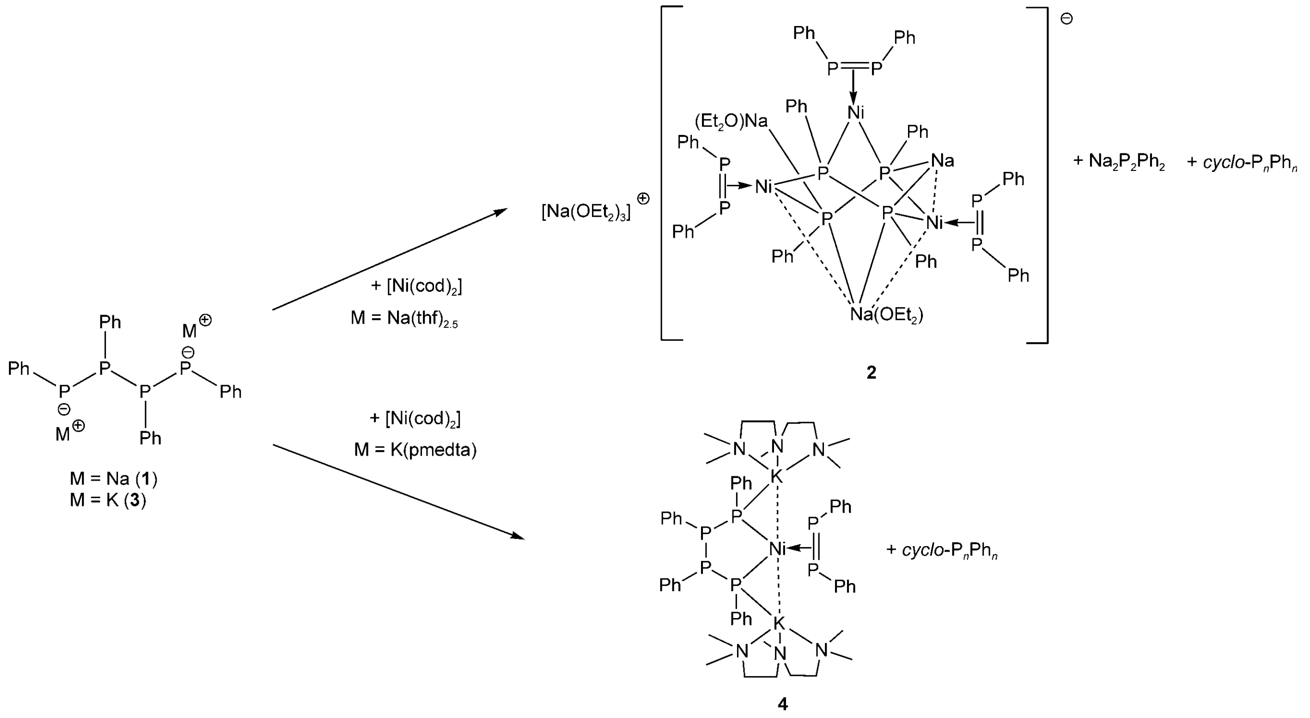
[a] Dr. S. Gómez-Ruiz, Prof. Dr. E. Hey-Hawkins
Institut für Anorganische Chemie der Universität Leipzig
Johannisallee 29, 04103 Leipzig (Germany)
Fax: (+49) 341-973-9319
E-mail: hey@rz.uni-leipzig.de

[b] Dipl.-Chem. S. Zahn, Prof. Dr. B. Kirchner
Wilhelm-Ostwald Institut für Physikalische und
Theoretische Chemie der Universität Leipzig
Linnéstrasse 2, 04103 Leipzig (Germany)

[c] Dr. W. Böhlmann
Institut für Experimentalphysik II der Universität Leipzig
Linnéstrasse 5, 04103 Leipzig (Germany)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200801089. $^{31}P\{^1H\}$ NMR, CP MAS $^{31}P\{^1H\}$ NMR spectra and ESI-MS spectrum of $[Na(Et_2O)_3][Na_3(Et_2O)_2Ni_3(\mu\text{-}P_2Ph_2)_2(P_2Ph_2)_3]$ (**2**), ^1H NMR, $^{13}C\{^1H\}$ NMR, $^{31}P\{^1H\}$ NMR $^{31}P\{^1H\}$–$^{31}P\{^1H\}$-COSY NMR spectra and ESI-MS spectrum of $[K(pmedta)]_2[Ni(P_4Ph_4)(P_2Ph_2)]$ (**4**), comparison of experimental and calculated structure of **4**, speculative mechanism of formation of **2**, full details of the calculation of **4** and SEN calculations.



Scheme 1.

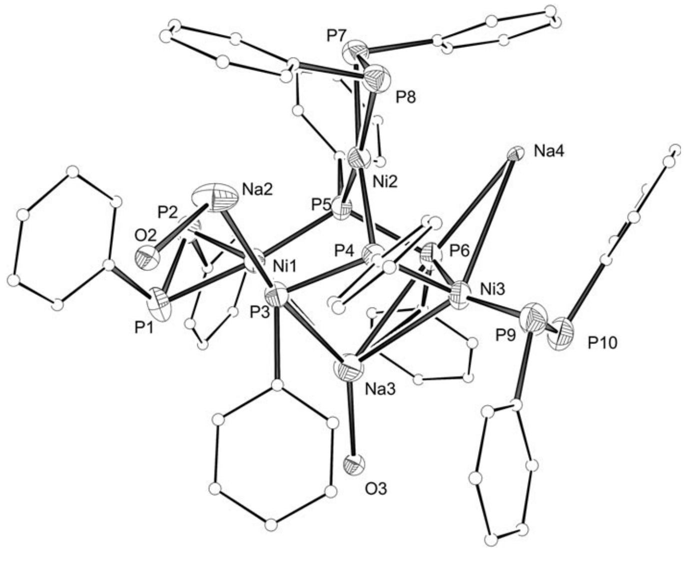


Figure 1. Solid-state molecular structure of the anion in **2** (without carbon atoms of the coordinated diethyl ether ligands and hydrogen atoms).

Table 1. Selected bond lengths [pm] and angles [°] for **2** and **4.**

Bond lengths [pm]	**2**	**4**	Bond lengths [pm]	**2**	**4**
Ni1−P1	225.0(3)	219.7(2)	P1−P2	213.4(4)	221.0(2)
Ni1−P2	221.0(3)		P2−P3		220.7(2)
Ni1−P3	219.9(3)		P3−P4	218.5(3)	218.9(2)
Ni1−P4		218.7(2)	P5−P6	219.2(3)	211.2(2)
Ni2−P4	220.9(2)		P7−P8	213.5(3)	
Ni3−P4	219.5(2)		P9−P10	211.5(3)	
Ni1−P5	219.4(2)	223.1(2)	Na1−P2	290.5(5)	
Ni2−P5	221.5(2)		Na2−P3	299.6(4)	
Ni1−P6		224.1(2)	Na3−P3	298.6(4)	
Ni3−P6	221.5(3)		Na3−P6	298.7(4)	
Ni2−P7	223.1(3)		Na4−P6	300.1(4)	
Ni2−P8	222.5(3)		K1−P4		354.5(2)
Ni3−P9	222.2(3)		K2−P1		362.0(3)
Ni3−P10	226.1(3)		Ni1−Na3	302.6(3)	
			Ni2−Na4	340.0(3)	
			Ni3−Na3	316.2(4)	
			Ni3−Na4	326.8(3)	
			Ni1−K1		318.5(2)
			Ni1−K2		310.7(2)
Bond angles [°]			Bond angles [°]		
C1-P1-P2	102.5(4)	97.5(2)	P1-P2-P3		92.7(1)
C7-P2-P1	103.0(3)	107.3(2)	P2-P3-P4		93.6(1)
C13-P3-P4	108.0(3)	105.2(2)	Ni1-Na3-Ni3	95.5(1)	
C19-P4-P3	103.0(3)	99.0(2)	Ni2-Na4-Ni3	63.0(1)	
C25-P5-P6	105.1(3)	101.1(2)	Na3-Ni3-Na4	126.4(1)	
C31-P6-P5	106.8(3)	100.4(2)	K1-Ni1-K2		163.4(1)
C37-P7-P8	99.5(3)				
C43-P8-P7	101.8(3)				
C49-P9-P10	104.9(4)				
C55-P10-P9	99.5(3)				

cently reported norbornane-like NiP_6 framework.[3d] The angle between the mean planes of the metallabicycle formed by Ni1-P5-P4-P3 and Ni3-P4-P5-P6 is about 55.9°. Ni1, P3, P6, and Ni3 are nearly coplanar, with a deviation from the mean plane of about 2.7 pm for each atom.

Each nickel atom is additionally coordinated in an η^2 manner by a diphenyldiphosphene ligand with the phenyl groups in *trans* conformation. The $P{-}P_{\text{diphosphanediide}}$ bond lengths (218.5(3) and 219.2(3) pm) are indicative of single bonds,[9] whereas the P–P$_{\text{diphosphene}}$ bond lengths (211.5(3)–213.5(3) pm) are typical for coordinated diaryl diphosphene ligands[10] and longer than expected for free diphosphenes.[11] The Ni–P$_{\text{diphosphene}}$ (221.0(3)–226.1(3) pm)[6b] and Ni–P$_{\text{diphosphanediide}}$ (219.4(2)–221.5(3) pm) bond lengths are shorter than in nickel phosphanido[6b] and polyphosphane complexes.[12]

Three of the four negative charges of the two diphenyldiphosphanediide ligands are counterbalanced by three sodium cations (Na2, Na3, and Na4), which interact with the phosphorus atoms of the diphenyldiphosphanediide ligands (Na2–P3 299.6(4), Na3–P3 298.6(4), Na3–P6 298.7(4), and Na4–P6 300.1(4) pm) and presumably with the nickel atoms (Na3–Ni1 302.6(3), Na3–Ni3 316.2(4), Na4–Ni3 326.8(3) pm). The Na–P distances are comparable to those previously reported in sodium phosphanide compounds.[5a,c] Na3 has an unusual five-coordinate geometry with Ni1, Ni3, P3, P6, and a diethyl ether molecule as ligands, whereas Na4 is bonded to P6 and has weakly contacts with Ni3 (Na4–Ni3 326.8(3) pm). An additional sodium ion (Na1) with three coordinated diethyl ether molecules acts as the cationic part of this ionic structure, and this atom additionally interacts with P2 (Na1–P2 290.5(5) pm). Contacts between Ni and alkali metals are extremely rare;[13] Ni···Na interactions (279.3 and 303.7 pm)[14] have been described by Brauer and co-workers.[15] All the nickel atoms have a distorted square-planar geometry[16] if the contacts with the sodium atoms are not considered.

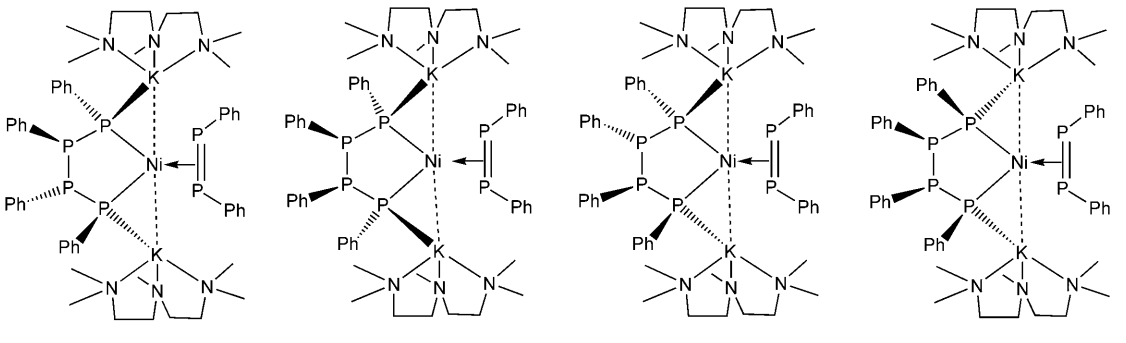
The ^{31}P{^{1}H} NMR spectrum in [D$_8$]THF exhibits very broad signals at about $\delta = 11, -9, -15, -29$, and -52 ppm at room and low temperatures (−80 °C). The solid-state ^{31}P{^{1}H} CP MAS NMR spectrum also showed broad signals at $\delta = 11, -13, -19, -24$, and -54 ppm, which suggest that the solid-state structure of **2** is retained in solution. Accordingly, **2** shows broad signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra for all of the magnetically inequivalent phenyl groups.

The possible mechanism of this reaction includes reduction of the $P_4Ph_4^{2-}$ ion to give two $P_2Ph_2^{2-}$ ions, which bridge the nickel atoms, and oxidation of $P_4Ph_4^{2-}$ to give two diphenyldiphosphene ligands. Apparently the stoichiometry of the reaction is 3:3; ten phosphorus atoms and three nickel atoms are present in the structure of **2**, and $Na_2P_2Ph_2$ is formed as a by-product.[17] Analysis of the insoluble residue by ^{31}P{^{1}H} NMR spectroscopy showed a small quantity of **2** as well as a mixture of oligophosphanes and oligophosphanides. Assuming that nickel(0) facilitates the reduction and nickel(II) the oxidation, as observed previously,[3e] the reaction seems to be catalyzed by nickel(0). However, when the reaction was carried out with catalytic amounts (3 %) of [Ni(cod)$_2$], only signals of *cyclo*-P_nPh_n and $P_4Ph_4^{2-}$ and no evidence for the formation of the $P_2Ph_2^{2-}$ ion were observed in the ^{31}P{^{1}H} NMR spectrum.

To obtain further insight into the mechanism of the formation of **2**, the less reactive [K$_2$(pmdeta)$_2$(P$_4$Ph$_4$)] (**3**) was treated with [Ni(cod)$_2$] (ratio 1:1 or 2:1). Fast formation of [K(pmdeta)]$_2$[Ni(P$_4$Ph$_4$)(P$_2$Ph$_2$)] (**4**) and *cyclo*-P_nPh_n was observed by ^{31}P{^{1}H} NMR spectroscopy, and this suggests that this is also a redox reaction. Compound **4** can be considered to be the potassium analogue of the possible intermediate in the formation of **2**, in which K–P and K–Ni interactions stabilize the NiP$_4$ framework (see Supporting Information). The ^{31}P{^{1}H} NMR spectrum of **4** consists of a set of three signals for an AA′BB′XX′ spin system: a triplet at $\delta = -7.5$ ppm corresponding to the phosphorus atoms of the diphosphene ligand and two multiplets at $\delta \approx 7.6$ and -3.8 ppm, corresponding to the $P_4Ph_4^{2-}$ ligand. A second set of signals with a similar coupling pattern at higher field in the spectrum presumably corresponds to one of the other possible isomers (Scheme 2).

In **4** (Figure 2), the phenyl groups of the P$_4$ chain have the expected all-*trans* conformation. Ni1 and P1–P4 form a puckered five-membered ring (δ conformation shown in Figure 2). The nickel atom has a distorted octahedral coordination environment with the diphosphene ligand (P5 and P6) and the terminal phosphorus atoms of the $P_4Ph_4^{2-}$ ion (P1 and P4) in the equatorial positions, and the potassium atoms (K1 and K2) in the axial positions (K1-Ni1-K2 163.4(1)°). The Ni–P$_{\text{diphosphene}}$ (223.1(2) and 224.1(2) pm) and P–P$_{\text{diphosphene}}$ bond lengths (211.2(2) pm) are comparable to those observed in related nickel diphosphene complexes.[10]

The Ni–P$_{\text{tetraphosphanediide}}$ bonds (Ni–P1 219.7(2) and Ni–P4 218.7(2) pm) are about 3 pm longer than those reported for nickel polyphosphane complexes,[12] and shorter than those observed in nickel phosphanido compounds.[6b] The P–P



trans-trans-trans *trans-cis-trans* *cis-trans-cis* *cis-cis-cis*

Scheme 2. Possible different isomers of **4**.

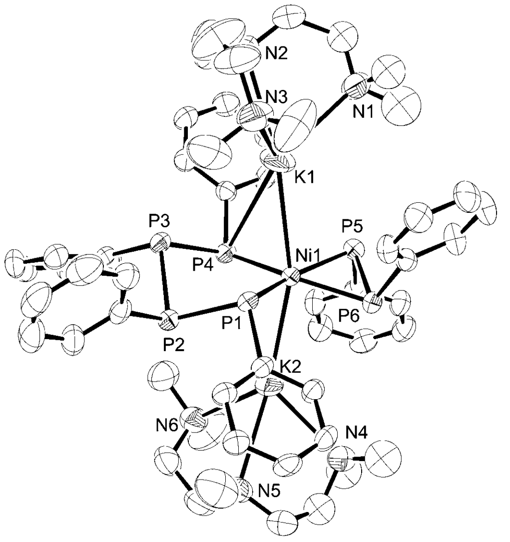


Figure 2. Solid-state molecular structure of **4** (without hydrogen atoms).

bonds in the $P_4Ph_4^{2-}$ ion (218.9(2)–221.0(2) pm) are in agreement with P–P single bonds.[9] The fact that the K–P distances between the potassium cations and the P_4 chain (354.5(2) and 362.0(3) pm) are significantly longer (about 20 pm) than those reported for **3** suggests a weaker interaction due to coordination of the P_4 dianion to nickel. In addition, short K···Ni contacts (318.5(2) pm for K1 and 310.7(2) pm for K2) are observed, which to our knowledge are the shortest distances reported for a Ni–K interaction in a complex.[18]

The structure of **4** was investigated with the ORCA[19] and TURBOMOLE[20] program suites. The calculations for **4** confirm the structural parameters obtained by X-ray diffraction studies. A shared electron number (SEN) analysis was applied to investigate the K···Ni interaction (see Supporting Information). The SEN can be correlated with the covalent interaction between the investigated atoms. The two-center SEN values $\sigma_{\text{Ni-K1}}$ (0.24) and $\sigma_{\text{Ni-K2}}$ (0.22) show a covalent contribution to the interaction between potassium and nickel. Additionally, the three-center SEN value $\sigma_{\text{K1-Ni-K2}}$ of 0.14 is large enough to indicate a three-center bond. The SEN value of a typical three-center, two-electron bond such as that in B_2H_6 is 0.64. Thus, covalent interaction of K and Ni due to a three-center, two-electron bonding orbital might play a role in this complex. Furthermore, natural bond orbital (NBO) analysis was applied to determine the occupation of this possible three-center, two-electron bonding orbital. The K1-Ni-K2 bonding orbital is occupied by 0.54 electrons, which is larger than the number of electrons in the corresponding antibonding orbitals (0.16 and 0.15). This again indicates a covalent contribution in the interaction between nickel and potassium. The polarization coefficient for Ni is $c_{\text{Ni}} = 0.85$, while $c_{\text{K1}} = 0.38$ and $c_{\text{K2}} = 0.37$. Therefore, the largest contribution to the K1-Ni-K2 bonding orbital corresponds to the 4 s atomic orbital of nickel (72.0 %). However, the potassium atoms also have significant participation in the three-center bonding orbital (K1 14.2, K2 13.8 %).

Conclusion

In summary, the $P_4Ph_4^{2-}$ anion reacts with $[Ni(cod)_2]$ in a redox reaction giving $[Na(Et_2O)_3][Na_3(Et_2O)_2Ni_3(\mu\text{-}P_2Ph_2)_2(P_2Ph_2)_3]$ (**2**) starting from the sodium salt or $[K(pmedta)]_2[Ni(P_4Ph_4)(P_2Ph_2)]$ (**4**) starting from the less reactive potassium salt. In **2** and **4**, Ni–Na and Ni–K contacts, respectively, are observed, and the Ni–K distance of about 310 pm is the shortest reported up to now.

Preliminary investigations of the reactivity of the tetraorgano tetraphosphanediides towards other metal(0) complexes reveal that, depending on the starting materials, redox chemistry does or does not play a role, and different novel phosphorus-rich complexes are obtained.

Experimental Section

General remarks: All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. The NMR spectra were recorded on a Bruker AVANCE-DRX-400 spectrometer. ^1H NMR (400.13 MHz), $^{13}C\{^1H\}$ NMR (100.16 MHz): internal standard solvent, external standard TMS; ^{31}P NMR (161.9 MHz): external standard 85 % H_3PO_4. The CP MAS $^{31}P\{^1H\}$ NMR spectrum was recorded on a Bruker MSL 500 spectrometer at a resonance frequency of 202.458 MHz. The sealed sample was rotated in a 4 mm zirconia rotor at a rotation frequency of 12 kHz. The ^{31}P CP (cross polarization) MAS (magic angle spinning) condition was a conventional CP sequence using $NH_4H_2PO_4$ as external Hartmann–Hahn matching standard with a recycle delay of 10 s, a pulse length of 6.3 μs, a mixing time of 6 ms, and 5650 scans for a sufficient signal to noise ratio. The spectrum was referenced against 85 % H_3PO_4 (0 ppm) as external standard. Similar conditions are described for a series of transition metal complexes containing phosphane ligands.[21] Besides the CP measurement a single pulsed spectrum was recorded by using a pulse length of 5.9 μs, a recycle delay of 12 s, a rotation frequency of 12 kHz, and 9380 scans. Regarding the influence of the nickel the signal to noise ratio was rather small. Therefore, peaks with low intensities could not be identified in the spectrum; ESI MS were recorded with an FT-ICR MS Bruker-Daltonics (APEX II, 7 Tesla, MASPEC II), and solutions of about 1 mg mL^{-1} of the compounds in a mixture of dry THF/CH_3CN (1:1) were injected; IR spectra: KBr pellets were prepared in a nitrogen-filled glove box and the spectra were recorded with an FTIR spectrometer Perkin-Elmer System 2000 in the range 350–4000 cm^{-1}. All solvents were purified by distillation, dried, saturated with argon, and stored over potassium mirror. $Na_2(P_4Ph_4)$ and $K_2(P_4Ph_4)$ were synthesized according to the literature procedure.[5b,e]

Data collection and structural refinement of 2 and 4: The data of **2** and **4** were collected on a CCD Oxford Xcalibur S ($\lambda(\text{Mo}_{K\alpha}) = 0.71073$ Å) using ω and φ scan modes. Semi-empirical absorption corrections were carried out with SCALE3 ABSPACK[22] and the structures were solved with direct methods by using SHELXS-97.[23] Structure refinement was carried out with SHELXL-97.[24] For **2**, some sodium and carbon atoms were refined with the FREE instruction. Some carbon atoms of the diethyl ether molecules which are bound to the sodium atoms are disordered; some diethyl ether molecules bound to sodium were refined over split positions with constrained geometry and fixed atomic displacement parameters (DFIX and EADP instructions). The thermal displacement parameters of some atoms of these molecules were refined isotropically. All other Ni, Na, P, O, and C atoms were refined anisotropically. For **4**, some carbon atoms of the PMDETA molecules that are bound to the potassium atoms are disordered. Some other carbon atoms of those PMDETA molecules were refined with the FREE instruction. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of **2** and **4** were refined at idealized positions.

Table 2. Crystallographic data for **2** and **4**.

	2	**4**
formula	$C_{80}H_{103}Na_4Ni_3O_5P_{10}$	$C_{54}H_{76}K_2N_6NiP_6$
M	1722.41	1131.94
T[K]	130(2)	180(2)
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	$Pbca$
a [pm]	1450.12(6)	1099.8(5)
b [pm]	4050.4(2)	2285.4(5)
c [pm]	1541.05(6)	4747.3(5)
α [°]	90	90
β [°]	111.490(5)	90
γ [°]	90	90
V [nm^3]	8.4222(6)	11.93(1)
Z	4	8
crystal size [mm^3]	$0.15\times0.05\times0.02$	$0.40\times0.10\times0.05$
ρ_{calcd}[Mg m^{-3}]	1.358	1.260
$F(000)$	3604	4784
absorption coefficient [mm^{-1}]	0.922	0.665
hkl range	$-14\leq h\leq 16$ $-45\leq k\leq 45$ $-17\leq l\leq 17$	$-13\leq h\leq 13$ $-27\leq k\leq 27$ $-55\leq l\leq 57$
$2\theta_{max}$ [°]	46.52	51.36
reflns collected/unique	57424/12073	186563/11324
R(int)	0.1465	0.0875
data/restraints/parameters	12073/40/905	11324/0/621
goodness of fit on F^2	0.996	1.262
R_1/wR_2 [$I>2\sigma(I)$]	0.0754/0.1332	0.0912/0.1554
R_1/wR_2 (all data)	0.1625/0.1680	0.1142/0.1628
largest diff. peak/hole [eÅ^{-3}]	0.764/−0.568	0.930/−0.485

CCDC-684571 (**2**), CCDC-684572 (**4**) 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. Table 2 lists crystallographic data of complexes **2** and **4**.

Synthesis of $[Na(Et_2O)_3][Na_3(Et_2O)_2Ni_3(\mu\text{-}P_2Ph_2)_2(P_2Ph_2)_3]$ (2): At −78 °C, a solution of **1** (1.65 g, 1.96 mmol) in THF (50 mL) was carefully added dropwise to a solution of [Ni(cod)$_2$] (0.54 g, 1.96 mmol) in THF (50 mL). A dark red solution formed which was allowed to warm to room temperature slowly over several hours and stirred overnight. The solvent was then removed under vacuum, and the resulting dark red oil was extracted twice with Et_2O (50 mL). The dark red Et_2O solution was filtered and the solvent was reduced to about 10 mL. A dark red crystalline solid formed at −28 °C overnight. Yield: 0.64 g (56 %); m.p. 313–314 °C (black oil); ^{1}H NMR (400.13 MHz, [D$_8$]THF, 25 °C, TMS): $\delta=$ 1.11 (t, ^3J(H,H) = 8.0 Hz, 30 H, CH_3 in Et_2O), 3.37 (q, ^3J(H,H) = 8.0 Hz, 20 H, CH_2 in Et_2O), 6.22–7.90 ppm (br, 50 H, Ph); ^{13}C{^{1}H} NMR (100.16 MHz, [D$_8$]THF, 25 °C, TMS): $\delta=$ 14.6 (s, CH_3 in Et_2O), 65.1 (s, CH_2 in Et_2O), 122.6–137.9 (several signals, Ph), 150.0–150.3 ppm (several signals, Ph); ^{31}P{^{1}H} NMR (161.97 MHz, [D$_8$]THF, 25 °C, TMS): $\delta=11$, −9, −15, −29, −52 ppm; IR (KBr): $\tilde{\nu}=3050$ (m), 2963 (s), 2821 (s), 2774 (s), 2278 (w), 1946 (w), 1875 (w), 1804 (w), 1573 (s), 1468 (s), 1428 (m), 1356 (w), 1300 (m), 1293 (m), 1261 (s), 1097 (s), 1024 (s), 932 (w), 862 (w), 803 (s), 740 (s), 697 (s), 569 (w), 479 (m) cm^{-1}; ESI MS: solution in CH_3CN:THF (1:1); m/z: 1340.92 $[M-5\,Et_2O-Ph+THF]^+$, calculated m/z for this fragment: 1340.91; elemental analysis calcd (%) for Et_2O-free $C_{60}H_{50}Na_4P_{10}Ni_3$ ($M=1348.82$ g mol^{-1}): C 53.43, H 3.74; found: C 53.01, H 4.04.

Synthesis of $[K(pmedta)]_2[Ni(P_4Ph_4)(P_2Ph_2)]$ (4): Compound **4** was prepared in a similar manner to **2** using **3** (0.57 g, 0.66 mmol) and [Ni(cod)$_2$] (0.18 g, 0.66 mmol). Yield: 0.24 g (32 %); m.p. 114–117 °C (dark red oil); ^{1}H NMR (400.13 MHz, [D$_8$]THF, 25 °C, TMS): $\delta=2.14$ (s, 24 H, N-$(CH_3)_2$), 2.19 (s, 6 H, N(CH_3)), 2.30 (m, 8 H, CH_2), 2.41 (m, 8 H, CH_2), 6.67–7.19 (br, 20 H, Ph), 7.61–7.92 ppm (br, 10 H, Ph); ^{13}C{^{1}H} NMR (100.16 MHz, [D$_8$]THF, 25 °C, TMS): $\delta=$ 42.3 (s, N(CH_3)), 45.2 (s, N-$(CH_3)_2$), 56.4 (s, CH_2), 57.9 (s, CH_2), 121.4–122.9 (several signals, Ph), 125.9–126.8 (several signals, Ph), 132.0–134.0 ppm (several signals, Ph); ^{31}P{^{1}H} NMR (161.97 MHz, [D$_8$]THF, 25 °C, TMS): $\delta=$ 7.6 (m, appear as a qm, P-Ni of the P_4 chain), −3.8 (m, appear as a dm, P2 and P3 of the P_4 chain), −7.5 ppm (m, appear as a t, P–Ni of the diphosphene). Owing to the presence of more than one isomer in solution, the signals reported are those corresponding to the major isomer, presumably all-*trans* (Scheme 2). The coupling constants could not be obtained by simulation of the spectrum without ambiguity due to the presence of signals corresponding to the other isomers; IR (KBr): $\tilde{\nu}=3046$ (s), 2970 (m), 2873 (w), 2272 (w), 1951 (w), 1879 (w), 1815 (w), 1572 (s), 1471 (s), 1427 (s), 1384 (w), 1300 (w), 1261 (m), 1175 (w), 1152 (w), 1095 (m), 1064 (m), 1023 (s), 866 (w), 803 (m), 740 (s), 698 (s) 480 (m) cm^{-1}; ESI MS: solution in CH_3CN:THF (1:1); m/z: 958.14, $[M-\text{PMDETA}+H]^+$; 784.95, $[M-2\,\text{PMDETA}+H]^+$; elemental analysis calcd (%) for $C_{54}H_{76}K_2N_6P_6Ni$ ($M=$ 1131.94 g mol^{-1}): C 57.30, H 6.77, N 7.42; found: C 56.78, H 6.82, N 7.42.

Calculations: The programs provided by the ORCA-suite[19] were applied for geometry optimization. The final structure for wave function analysis was obtained by employing the BP86-D[25] density functional where the resolution of identity approximation can be employed. The SVP basis set was applied for structure optimization and the convergency criterion of the iteration cycle was increased to 10^{-7} Hartree.

The Turbomole-suite[20] was employed for the shared electron number (SEN) analysis. The wave function was obtained employing the BP86[25a,b] functional with the SVP basis set. Again the resolution of identity approximation was applied. Please note that the dispersion correction proposed by S. Grimme does not affect the wave function.[25c] Therefore, the BP86 and BP86-D functional have the same electronic wave function which was investigated. The Gaussian03 program[26] was employed for the natural bond orbital (NBO) analysis[27] with the SVP basis set on H, C, N and the larger TZVP basis set on K, Ni, and P. The NBO analysis was carried out employing the BP86 functional without the resolution of identity approximation. Several interactions of nickel and potassium were found but no NBO between Ni and K was assigned without user specified NBOs. Employing the default settings no three-center, two-electron NBOs are considered. Therefore, a three-center, two-electron NBO was assigned to potassium nickel potassium to determine the covalent interaction.

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