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Synthesis and reactivity of nickel-stabilised $\mu^2:\eta^2,\eta^2\text{-P}_2$, As_2 and PAs units.

Gabriele Hierlmeier,^[a] Alexander Hinz,^[b] Robert Wolf,^{*[a]} Jose M. Goicoechea^{*[b]}

Abstract: The reactivity of two paramagnetic nickel(I) compounds, $\text{CpNi}(\text{NHC})$ (where Cp = cyclopentadienyl; NHC = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes) or 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr)), towards $[\text{Na}(\text{dioxane})_x][\text{PnCO}]$ ($\text{Pn} = \text{P}, \text{As}$) is described. These reactions afford symmetric bimetallic compounds $(\mu^2:\eta^2,\eta^2\text{-Pn}_2)\{\text{Ni}(\text{NHC})(\text{CO})\}_2$. Several novel intermediates *en route* to such species are identified and characterised, including a compound containing the PCO^- anion in an unprecedented $\mu^2:\eta^2,\eta^2$ -binding mode. Ultimately, on treatment of the $(\mu^2:\eta^2,\eta^2\text{-Pn}_2)\{\text{Ni}(\text{NHC})(\text{CO})\}_2$ compounds with carbon monoxide the Pn_2 units can be released, affording P_4 in the case of the phosphorus-containing species, and elemental arsenic in the case of $(\mu^2:\eta^2,\eta^2\text{-As}_2)\{\text{Ni}(\text{IMes})(\text{CO})\}_2$.

Over the last three years, the 2-phosphaethynolate anion, PCO^- , has emerged as a versatile reagent for the synthesis of a variety of novel phosphorus compounds. This remarkable species was first isolated as $[\text{Li}(\text{DME})_2][\text{PCO}]$ (where DME = dimethoxyethane), however due to difficulties associated with the manipulation of this particular salt, the synthetic utility of PCO^- lay dormant for two decades.^[1] In 2011 and 2012, novel syntheses of sodium salts of the anion were published,^[2,3] followed by a further report on the synthesis of a $[\text{K}(\text{18-crown-6})]^+$ salt a year later.^[4] However it was not until 2014, that a reliable and scalable synthesis of the anion was reported.^[5] In the ensuing years, the 2-phosphaethynolate anion has been employed for the synthesis of novel phosphines and organophosphorus compounds,^[6,7] as a pseudo-halide in the coordination sphere of main group, transition metal and actinide compounds,^[8–10] and in a number of processes where the anion is shown to decarbonylate, acting as a formal source of a monoanionic phosphide ion (P^-).^[11] The recently synthesised arsenic-containing analogue, AsCO^- , has also been shown to readily lose carbon monoxide.^[12] Arguably this latter reactivity mode is the most interesting of those available to PnCO^- ($\text{Pn} = \text{P}, \text{As}$) and one that will form the focus of this report.

Salt-metathesis reactions of $[\text{Na}(\text{dioxane})_x][\text{PCO}]$ (where $x = 1\text{--}5$) with a variety of main group and transition metal halides afford phosphaketene compounds where PCO^- bonds to the

element in question via the phosphorus atom ($\text{E}=\text{P}=\text{C}=\text{O}$).^[13] These species thermally and/or photolytically decarbonylate to afford putative phosphinidene intermediates,^[14] however such species typically dimerise to compounds which largely fall into one of two main categories: 1) diphosphacyclobutadiene analogues (**A** in Figure 1), or 2) diphosphene-bridged compounds (**B**, **C** and **D** in Figure 1). Diarsacyclobutadiene type compounds analogous to **A** have also recently been reported using AsCO^- as a reagent.^[15]

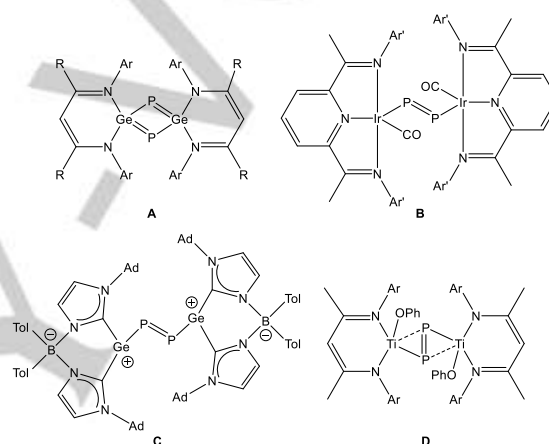


Figure 1. Selected examples of dimeric compounds resulting from the decarbonylation of phosphaketene precursors. $\text{Ar} = 2,6$ -diisopropylphenyl; $\text{R} = \text{H}, \text{Me}, \text{tBu}$; $\text{Ar}' = 2,6$ -dimethylphenyl; $\text{Ad} = 1$ -adamantyl; $\text{Tol} = p$ -tolyl; $\text{Ph} = \text{phenyl}$. $\text{P}=\text{P}$ interatomic distances: **A**: 3.606 Å (mean value for two crystallographically independent molecules); **B**: 2.021(1) Å; **C**: 2.045(1) Å; **D**: 2.1113(2) Å.

The further reactivity of the E_2Pn_2 cores of the resulting molecules remains largely unexplored despite the fact that, particularly in the diphosphene bridged compounds, they may be of relevance for the synthesis of novel pnictogen-containing molecules. Also, given that such species are formed through dimerisations, it is also possible to envision the synthesis of compounds with a phospharsene (PAs) core through the dimerization of a phosphinidene with an arsinidene. In this report we describe our attempts to explore such possibilities. We investigate the reactivity of two nickel(I) compounds, $\text{CpNi}(\text{NHC})$ (where Cp = cyclopentadienyl; NHC = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes) or 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr)),^[16] towards $[\text{Na}(\text{dioxane})_x][\text{PnCO}]$ ($\text{Pn} = \text{P}, \text{As}$) salts, which ultimately give rise to compounds with butterfly-like cores $(\mu^2:\eta^2,\eta^2\text{-Pn}_2)\{\text{Ni}(\text{NHC})(\text{CO})\}_2$. While both of the aforementioned reagents ultimately yield similar reaction products, we were able to isolate different intermediates depending on the N-heterocyclic carbene (NHC) associated with the nickel(I) centre.

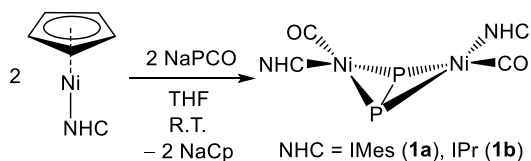
Reactions of $\text{CpNi}(\text{NHC})$ with one equivalent of $[\text{Na}(\text{dioxane})_{1,8}][\text{PCO}]$ in THF afford the compounds $(\mu^2:\eta^2,\eta^2\text{-Pn}_2)\{\text{Ni}(\text{NHC})(\text{CO})\}_2$.

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Supporting information (including experimental and analytical data) for this article is given via a link at the end of the document.

$P_2\{Ni(NHC)(CO)\}_2$ (NHC = IMes (**1a**) and IPr (**1b**)), with NaCp generated as a side product (Scheme 1).



Scheme 1. Synthesis of **1a** and **1b** by reaction of CpNi(NHC) (NHC = IMes, IPr) with one equivalent of $[Na(dioxane)_{1.8}][PCO]$.

The single crystal X-ray structure of **1a** (Figure 2) reveals a butterfly core that is unlike other E_2P_2 systems synthesised through decarbonylation reactions involving PCO^- , but closely related to well established compounds typically accessed by dehalosilylation of silylphosphanes or the activation of white phosphorus.^[17] Examples include a handful of isoelectronic and isostructural group 10 compounds.^[18] The P–P bond length in **1a** (2.076(2) Å) is close to the value expected for a P=P double bond (2.04 Å),^[19] and similar to the values reported for $(\mu^2:\eta^2,\eta^2-P_2)\{Ni(depe)\}_2$ (depe = bis(diethylphosphino)ethane; 2.121(6) Å) and $(\mu^2:\eta^2,\eta^2-P_2)\{Ni(IPr)_2\}_2$ (IPr = 1,3-bis(isopropyl)-imidazol-2-ylidene; 2.091(1) Å). The structure of **1b** is very similar with that of **1a** (see Supporting Information).

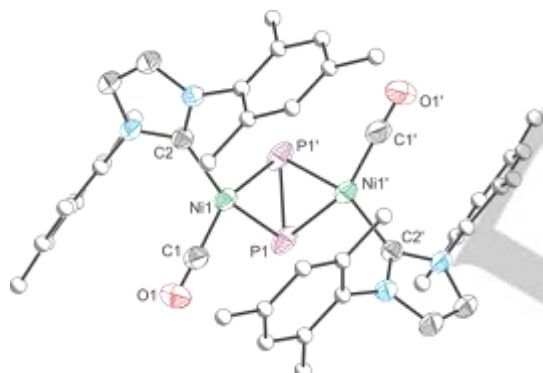
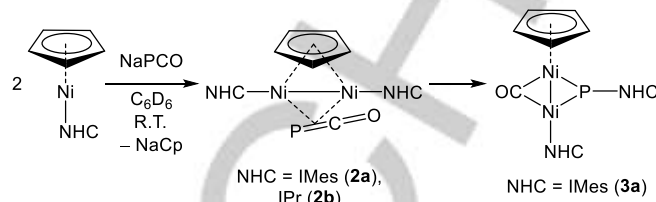


Figure 2. Molecular structure of **1a**-hexane. Anisotropic displacement ellipsoids pictured at 50% probability. Hydrogen atoms and solvent of crystallization omitted for clarity. Atoms of the Mes groups pictured as spheres of arbitrary radius. Selected bond lengths (Å) and angles (°): Ni1–C1, 1.752(3); Ni1–C2, 1.922(2); Ni1–P1, 2.241(1); Ni1–P1', 2.250(1); C1–O1, 1.140(4); P1–P1', 2.076(2); Ni1...Ni1' 2.988(7). C1–Ni1–C2, 107.17(11); C1–Ni1–P1, 98.16(9); C1–Ni1–P1', 152.96(9); C2–Ni1–P1, 152.88(7); C2–Ni1–P1', 98.73(7); P1–Ni1–P1', 55.07(3). Symmetry operation $': -x, 1-y, z$.

Singlet resonances are observed in the ^{31}P NMR spectrum at 120.0 and 130.3 ppm (in C_6D_6) for **1a** and **1b**, respectively. The 1H , and $^{13}C\{^1H\}$ NMR data are consistent with the molecular structures obtained by X-ray crystallography (see the Supporting Information). Infrared spectra reveal bands at 1952 and 1967 cm^{-1} , for **1a** and **1b**, respectively, arising from terminal CO ligands.

With the aim of identifying reaction intermediates, we reacted the CpNi(NHC) complexes (NHC = IMes and IPr) with 0.5 equivalents of $[Na(dioxane)_{1.8}][PCO]$. ^{31}P NMR spectra reveal resonances at –293.1 (**2a**) and –288.9 ppm (**2b**),

respectively, comparable those recorded for metallo-phosphaketene type compounds. In the case of CpNi(IMes), this species is short-lived (approximately 20 minutes), but for CpNi(IPr) this compound is sufficiently stable to be isolated and characterised.



Scheme 2. Synthesis of **2a/2b** and **3a** by reaction of CpNi(NHC) with 0.5 equivalents of $[Na(dioxane)_{1.8}][PCO]$.

Crystals of **2b**-hexane grown from hexane at –30 °C reveal a symmetrical bimetallic dimer $(\mu^2:\eta^5,\eta^5-Cp)[\mu^2:\eta^2,\eta^2-PCO]\{Ni(IPr)\}_2$ (**2b**; Figure 3). The PCO^- ion bridges the two nickel(I) centres in an unprecedented $\mu^2:\eta^2,\eta^2$ -binding mode. A related chloride-bridged dimer $(\mu^2:\eta^5,\eta^5-Cp)[\mu^2-Cl]\{Ni(IPr)\}_2$ was reported by Nova, Hazari and co-workers.^[16a] Due to positional disorder of the 2-phosphaethynolate and cyclopentadienide anion, the interpretation of bond metric data should be performed with caution, nonetheless, there is no ambiguity regarding the coordination mode of the PCO^- ion. The phosphorus and carbon atoms are equidistant from the two nickel(I) centres. The side on coordination of a PCO^- ion is rare, and has only been reported for a copper complex with a cyclic alkyl amino carbene.^[13a]

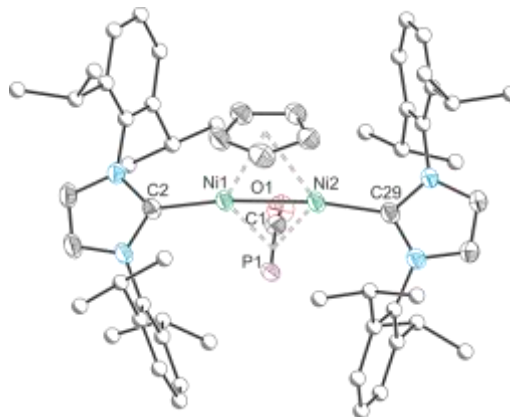


Figure 3. Molecular structure of **2b**-hexane (minor positionally disordered component omitted for clarity). Anisotropic displacement ellipsoids pictured at 50% probability. Hydrogen atoms and solvent of crystallization omitted for clarity. Atoms of the Dipp groups pictured as spheres of arbitrary radius. Selected bond lengths (Å) and angles (°): P1–C1, 1.80(2); C1–O1, 1.15(2); Ni1–P1, 2.187(5); Ni1–C1, 2.087(18); Ni2–P1, 2.186(4); Ni2–C1, 2.095(17); Ni1–C2, 1.9262(17); Ni1–Cpcent, 2.411(10); Ni1–Ni2, 2.3719(4); Ni2–C29, 1.9260(17); Ni2–Cpcent, 2.454(10); P1–C1–O1, 158.5(10); C2–Ni1–P1, 114.71(13); C2–Ni1–C1, 115.1(5); C2–Ni1–Ni2, 169.91(5); C29–Ni2–P1, 114.14(14); C29–Ni2–C1, 116.3(5); C29–Ni2–Ni1 170.26(5); Ni1–P1–Ni2, 65.70(13); Ni1–C1–Ni2, 69.1(5).

The reaction of 0.5 equivalents of $[Na(dioxane)_{1.8}][PCO]$ with CpNi(IMes) ultimately affords the carbene-phosphinidenyl-

bridged dimer, $(\mu^2\text{-CO})[\mu^2\text{-P(IMes)}]\text{Ni}_2(\text{IMes})\text{Cp}$ (**3a**). The clean formation of **3a** is evidenced by a singlet resonance at -16.5 ppm in the ^{31}P NMR spectrum, and the observation of two magnetically inequivalent IMes substituents in the ^1H NMR spectrum.

Single crystals of **3a**·0.5toluene obtained from toluene reveal a dimeric compound with a Ni–Ni bond length of $2.399(1)$ Å consistent with a single bond (Figure 4).^[19] One of the nickel atoms retains a cyclopentadienyl ligand (and has a formal valence electron count of 18), while the second is coordinated by an IMes ligand (and has a valence electron count of 16). Both centres are bridged in a μ^2 -fashion by a carbonyl (originating from the PCO^- reagent) and a formally anionic phosphinidenyl ligand, $[\text{P(IMes)}]^-$. Metal compounds with $[\text{P(NHC)}]^-$ type ligands are rare and have only recently become synthetically available.^[20] The $[\text{P(IMes)}]^-$ ligand is largely equidistant from both of the nickel centres ($2.269(1)$ and $2.186(1)$ Å), with the shortest distance being to the least electronically saturated nickel centre. The same is also true of the Ni–CO distances: $1.909(3)$ and $1.793(3)$ Å.

$(\mu^2:\eta^5, \eta^5\text{-Cp})[\mu^2:\eta^2, \eta^2\text{-PCO}]\{\text{Ni(IMes)}\}_2$ (**2a**) is likely an intermediate in the formation of **3a** (both compounds are constitutional isomers). **3a** would be formed by decarbonylation and carbene migration from a nickel(I) centre to the resulting phosphinidyne. We believe that the short-lived intermediate observed at -293.1 ppm in the ^{31}P NMR spectrum of crude reaction mixtures which ultimately afford **3a** is **2a**. Compounds **2b** and **3a** both react further with one equivalent of $[\text{Na(dioxane)}]_{1.8}[\text{PCO}]$ to afford **1b** and **1a**, respectively.

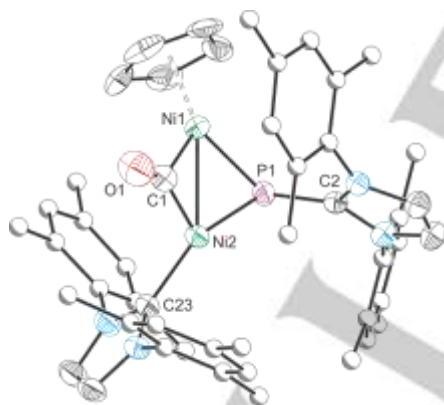


Figure 4. Molecular structure of **3a**·0.5toluene. Anisotropic displacement ellipsoids pictured at 50% probability. Hydrogen atoms and solvent of crystallization omitted for clarity. Atoms of the Mes groups pictured as spheres of arbitrary radius. Selected bond lengths (Å) and angles (°): Ni1–Ni2, $2.399(1)$; Ni1–Cpcent, $1.779(4)$; Ni1–C1, $1.909(3)$; Ni1–P1, $2.269(1)$; C1–O1, $1.179(4)$; P1–C2, $1.797(3)$; C1–Ni2, $1.793(3)$; P1–Ni2, $2.186(1)$; Ni2–C23, $1.891(2)$; Ni1–C1–Ni2, $80.74(13)$; Ni1–P1–Ni2, $65.15(2)$; Ni1–Ni2–C23, $145.02(5)$; Ni1–P1–C2, $114.76(10)$; C1–Ni2–C23, $104.67(10)$; C2–P1–Ni2, $103.83(9)$; P1–Ni2–C23, $144.80(6)$.

Reactions of CpNi(NHC) and $[\text{Na(dioxane)}]_{3.0}[\text{AsCO}]$ in a 1:1 ratio yielded $(\mu^2:\eta^2, \eta^2\text{-As}_2)\{\text{Ni(NHC)(CO)}\}_2$ (NHC = IMes (**4a**) and IPr (**4b**)). Crystals of **4a**·hexane obtained from concentrated hexane solutions are isomorphous with the phosphorus analogue **1a**·hexane. The As–As bond ($2.301(2)$ Å) is 0.225 Å

longer than the P–P bond in **1a**, in line with the increased covalent radius of arsenic ($r_{\text{As}} - r_{\text{P}} = 0.12$ Å).^[19a] Related compounds with a $(\mu^2:\eta^2, \eta^2\text{-As}_2)\text{E}_2$ core are relatively well known,^[21] however there is only one isoelectronic group 10 metal complex, $(\mu^2:\eta^2, \eta^2\text{-As}_2)\{\text{Pt(PPh}_3)_2\}_2$ [As–As $2.274 (\pm 0.001)$ Å].^[22] Compound **4b** could be isolated using a similar procedure, although extensive crystal twinning precluded a satisfactory structure determination.

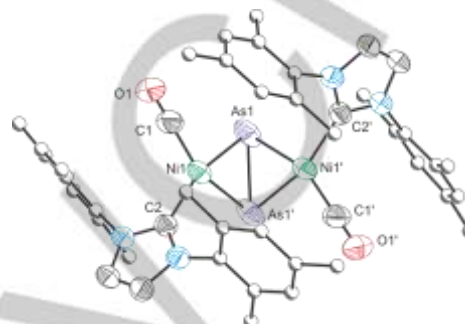


Figure 5. Molecular structure of **4a**·hexane. Anisotropic displacement ellipsoids pictured at 50% probability. Hydrogen atoms and solvent of crystallization omitted for clarity. Atoms of the Mes groups pictured as spheres of arbitrary radius. Selected bond lengths (Å) and angles (°): Ni1–C1, $1.760(10)$; Ni1–C2, $1.934(7)$; Ni1–As1, $2.3405(13)$; Ni1–As1', $2.3450(16)$; C1–O1, $1.127(12)$; As1–As1', $2.3006(18)$; Ni1...Ni1' $3.055(2)$; C1–Ni1–C2, $107.3(4)$; C1–Ni1–As1, $95.9(3)$; C1–Ni1–As1', $154.5(3)$; C2–Ni1–As1, $154.5(2)$; C2–Ni1–As1', $97.1(2)$; As1–Ni1–As1', $58.81(5)$. Symmetry operation $': 2-x, 1-y, z$.

^1H NMR spectroscopy suggests that reactions of CpNi(IMes) with 0.5 equivalents of $[\text{Na(dioxane)}]_{3.0}[\text{AsCO}]$ proceed to the carbene-arsinidenyl-bridged dimer, $(\mu^2\text{-CO})[\mu^2\text{-As(IMes)}]\text{Ni}_2(\text{IMes})\text{Cp}$ (**5a**). Addition of a molar equivalent of $[\text{Na(dioxane)}]_{3.0}[\text{AsCO}]$ to **5a** readily affords **4a**. Single-crystal XRD on **5a**·0.5hexane grown from toluene/hexane revealed a formally anionic arsinidenyl ligand $[\text{As(IMes)}]^-$ which bridges two nickel(I) centres. To our knowledge, to date there are no structurally authenticated NHC-arsinidenyl compounds reported.

In an attempt to access $\mu^2:\eta^2, \eta^2\text{-PAs}$ bridged compounds, we reacted the phosphaketenyl-bridged compound, **2b**, and the phosphinidenyl-bridged compound, **3a**, with one equivalent of $[\text{Na(dioxane)}]_{3.0}[\text{AsCO}]$. Equivalent reactions with $[\text{Na(dioxane)}]_{1.8}[\text{PCO}]$ readily give rise to the $\mu^2:\eta^2, \eta^2\text{-P}_2$ bridged compounds **1a** and **1b**. Similarly, the arsinidenyl-bridged dimer, **5a**, was reacted with $[\text{Na(dioxane)}]_{1.8}[\text{PCO}]$ in an attempt to form $(\mu^2:\eta^2, \eta^2\text{-PAs})\{\text{Ni(IMes)(CO)}\}_2$. Each of these reactions gave novel compounds, including the targeted complexes $(\mu^2:\eta^2, \eta^2\text{-PAs})\{\text{Ni(IMes)(CO)}\}_2$ (**6a**; ^{31}P NMR: 175.3 ppm) and $(\mu^2:\eta^2, \eta^2\text{-PAs})\{\text{Ni(IPr)(CO)}\}_2$ (**6b**; ^{31}P NMR: 187.9 ppm), however these species cannot be accessed quantitatively as the formation of the $\mu^2:\eta^2, \eta^2\text{-P}_2$ and $\mu^2:\eta^2, \eta^2\text{-As}_2$ bridged compounds cannot be avoided. Nonetheless, these preliminary findings, and subsequent reactivity studies, strongly suggest that the formation of novel compounds with a $\mu^2:\eta^2, \eta^2\text{-PAs}$ bridge, may be possible by modifying reaction conditions, and/or in the coordination sphere of other metals.

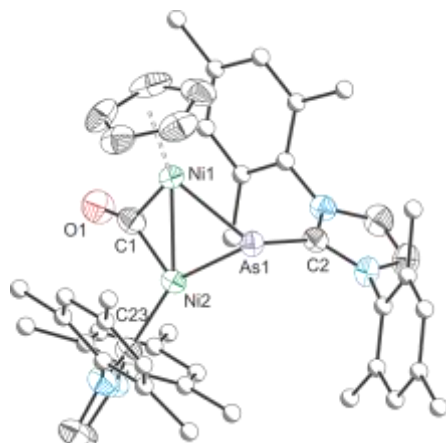
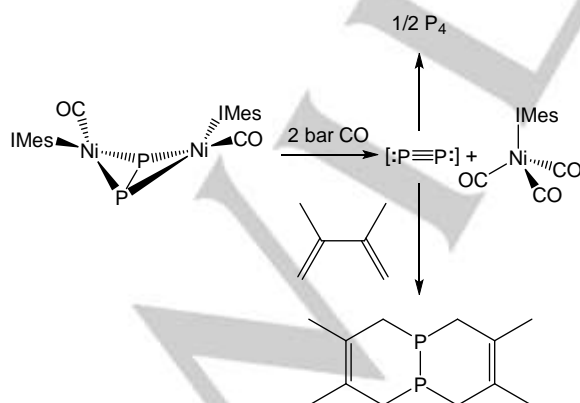


Figure 6. Molecular structure of **5a**·0.5hexane. Anisotropic displacement ellipsoids pictured at 50% probability. Hydrogen atoms and solvent of crystallization omitted for clarity. Atoms of the Mes groups pictured as spheres of arbitrary radius. Selected bond lengths (Å) and angles (°): Ni1–Ni2, 2.424(1); Ni1–Cpcent, 1.774(4); Ni1–C1, 1.898(3); Ni1–As1, 2.389(1); C1–O1, 1.188(4); As1–C2, 1.955(3); C1–Ni2, 1.782(4); As1–Ni2, 2.282(1); Ni2–C23, 1.877(3); Ni1–C1–Ni2, 82.33(13); Ni1–As1–Ni2, 62.467(19); Ni1–Ni2–C23, 146.43(10); Ni1–As1–C2, 112.15(8); C1–Ni2–C23, 105.95(14); C2–As1–Ni2, 102.66(8); As1–Ni2–C23, 144.29(9).

Treatment of solutions of **1a** and **4a** with carbon monoxide (2 bar) affords $\text{Ni}(\text{IMes})(\text{CO})_3$ as corroborated by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR, and infrared spectroscopy.^[23] The ^{31}P NMR spectrum of a solution of **1a** pressurised with CO reveals the formation of P_4 after just seven hours (^{31}P NMR = -521.1 ppm in C_6D_6). Similarly, trapping reactions employing 2,3-dimethyl-1,3-butadiene (DMB) yield the desired Diels–Alder cycloaddition product 3,4,8,9-tetramethyl-1,6-diphosphabicyclo(4.4.0)deca-3,8-diene (TMDPDD) (observed in the ^{31}P NMR spectrum at -54.2 ppm, Scheme 3). This strategy has been previously employed by Cummins to trap transient P_2 molecules.^[24] Reactions involving **4a** and CO, by contrast, result in the formation of grey arsenic as determined by EDX spectroscopy (not As_4). Trapping reactions with DMB show evidence for formation of 3,4,8,9-tetramethyl-1,6-diarsabicyclo(4.4.0)deca-3,8-diene (see Supporting Information).



Scheme 3. Reactivity of **1a** towards CO both in the absence and presence of 3-dimethyl-1,3-butadiene.

While trapping reactions using DMB cleanly afford TMDPDD and $\text{Ni}(\text{IMes})(\text{CO})_3$ as the sole reaction products, treatment of the products under a dynamic vacuum and redissolution gives rise to a number of species in the ^{31}P NMR spectrum. We believe that this is due to the decarbonylation of $\text{Ni}(\text{IMes})(\text{CO})_3$ under a dynamic vacuum, which results in complexation of TMDPDD by nickel(0). When treated with further CO, such mixtures readily revert back to TMDPDD and $\text{Ni}(\text{IMes})(\text{CO})_3$. Through fractional crystallisation from the partially decarbonylated mixtures, we have identified several compounds crystallographically, including a TMDPDD-bridged dimeric compound, $(\mu^2\text{-}\eta^1, \eta^1\text{-TMDPDD})\{\text{Ni}(\text{IMes})(\text{CO})_2\}_2$ (**7**) and a trimetallic compound bridged by three TMDPDD ligands and a 4,5-dimethyl-3,6-dihydro-1,2-diphosphinine species (**8**), a formal cycloaddition product of P_2 with one equivalent of DMB (see Supporting Information for structures). The uncontrolled nature of the synthesis of these compounds, coupled with the concomitant low yields, precluded their full characterisation.

^{31}P NMR spectroscopy evidenced the formation of P_4 (-521.3 ppm) and AsP_3 (-485.2 ppm) when reaction mixtures containing **1b** and the heteroatomic bridged compound **6b** were treated with CO. AsP_3 was first reported by Cummins and co-workers, and has a characteristic singlet resonance in its ^{31}P NMR spectrum, which allows for its characterisation.^[25] These carbonylation reactions strongly suggest that $(\mu^2\text{-}\eta^2, \eta^2\text{-PAs})\{\text{Ni}(\text{IPr})(\text{CO})\}_2$ is present in the reaction mixture, and that AsP_3 results from the recombination of P_2 and PAs or their nickel-coordinated synthetic equivalents.

To conclude, we prepared compounds of the type $(\mu^2\text{-}\eta^2, \eta^2\text{-Pn}_2)\{\text{Ni}(\text{NHC})(\text{CO})\}_2$ ($\text{Pn} = \text{P}$, $\text{NHC} = \text{IMes}$ (**1a**) or IPr (**1b**); $\text{Pn} = \text{As}$, $\text{NHC} = \text{IMes}$ (**4a**) or IPr (**4b**)) by salt metathesis of $[\text{Na}(\text{dioxane})_x][\text{PnCO}]$ ($\text{Pn} = \text{P}$, As) with N-heterocyclic carbene cyclopentadienyl nickel(I) complexes. Several intermediates *en route* to these novel compounds were identified and characterised, including an unusual bimetallic compound in which the PCO^- ion bridges two metal centres in an unprecedented $\mu^2\text{-}\eta^2, \eta^2\text{-binding}$ mode (**2b**), and the first structurally authenticated example of an arsinidenyl-bridged compound (**5a**). Reactions of the novel butterfly compounds with CO reveal that these species may be used as Pn_2 sources. Further reactivity studies in this field are currently on-going.

Acknowledgements

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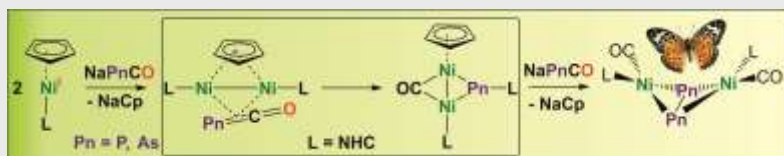
Keywords: 2-phosphaethynolate • 2-arsaethynolate • phosphorus • arsenic • nickel(I) compounds

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Layout 2:

COMMUNICATION



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Synthesis and reactivity of nickel-stabilised $\mu^2:\eta^2, \eta^2$ -P₂, As₂ and PAs units

The reactivity of two paramagnetic nickel(I) compounds, CpNi(NHC) (where Cp = cyclopentadienyl; NHC = N-heterocyclic carbene), towards [Na(dioxane)_x][PnCO] (Pn = P, As) is described.