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A General Synthetic Route to NHC-Phosphinidenes: NHC-mediated Dehydrogenation of Primary Phosphines

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Dedicated to Prof. Dr. Peter Klüfers on the Occasion of his 70th birthday

ABSTRACT: The dehydrocoupling of primary phosphines with N-heterocyclic carbenes (NHCs) to yield NHC-phosphinidenes is reported. The reaction of two equivalents of the NHCs Me₂Im (1,3-dimethylimidazolin-2-ylidene), Me₄Im (1,3,4,5-tetramethylimidazolin-2-ylidene), iPr₂Im (1,3-di-iso-propylimidazolin-2-ylidene) and Mes₂Im (2,4,6-trimethylphenylimidazolin-2-ylidene) with PhPH₂ and MesPH₂ led to the NHC stabilized phosphinidenes (NHC)PAr: (iPr₂Im)PPh (1), (Mes₂Im)PPh (2), (Me₄Im)PPh (3), (Mes₂Im)PMes (4), (Me₂Im)PMes (5), (Me₄Im)PMes (6) and iPr₂Im=PMes (7). The reaction of tBuPH₂ with two equivalents of the NHCs afforded the corresponding NHC stabilized parent phosphinidenes (NHC)PH: (iPr₂Im)PH (8), (Mes₂Im)PH (9) and (Me₄Im)PH (10). Reaction of 1 with oxygen and sulfur led to isolation of iPr₂Im=P(O)₂Ph (11) and iPr₂Im=P(S)₂Ph (12), whereas the reaction with elemental selenium and tellurium gave (NHC)PPh cleavage with formation of (iPr₂Im)Peh}W(CO)₅] (15), [Co(CO)₂(NO){(iPr₂Im)PPh}] (16) and [(η^{5} -C₅Me₅)Co(η^{2} -C₂H₄){(iPr₂Im)PPh] (17) have been prepared starting from 1 and a

suitable transition metal complex precursor. The complexes **16** and **17** decompose in solution upon heating to ca. 80°C to yield the NHC complexes $[Co(iPr_2Im)(CO)_2(NO)]$ and $[(\eta^5-C_5Me_5)Co(iPr_2Im)(\eta^2-C_2H_4)]$ with formation of cyclo-oligophosphines. The reaction of **1** with $[Ni(COD)_2]$ afforded the diphosphene complex $[Ni(iPr_2Im)_2(trans-PhP=PPh)]$ **18**.

Introduction

Phosphinidenes^[1] represent a group of highly reactive, low-valent, six electron species, which can be made manageable by terminal coordination on either transition metal complexes or *Lewis*-bases.^[2,3] In the early 1980s 7-phosphinonorbornadienes were found to be promising starting materials for the preparation of phosphinidenes in solution, yet their isolation turned out to be difficult. Coordination to $[M(CO)_5]$ (M = group VI metal) complexes made 7-phosphinobornadienes isolable and moreover led to the discovery of the electrophilic terminal transition metal phosphinidene complex [(OC)₅W=PPh] by Matthey et al. These complexes with the general formula [(OC)₅M=PPh] are not isolable, but can be generated *in situ* for further reactions.^[2a, 4] All literature known metal carbonyl phosphinidene-complexes of the general formula room $[(OC)_n M(PR)]$ are unstable at temperature except of $[(Dipp_2Im^{H/Me})C(Ph)]P]Fe(CO)_4$ (Dipp = 2,6-di-*iso*-propylphenyl) published recently by Ghadwal and coworkers.^[4c] First examples of nucleophilic transition metal phosphinidene complexes, the bent metallocene complexes $[(\eta^5-C_5H_5)_2M=PMes^*]$ (Mes^{*} = 2,4,6-^tBuC₆H₂; M = Mo, W) were presented by Lappert *et al.* in 1987.^[5] These 18-electron phosphinidene complexes were synthesized using salt metathesis of lithium metallocene hydrides [{ $(\eta^5-C_5H_5)_2$ MHLi}] with dichlorophosphine Mes*PCl₂ under elimination of LiCl. Salt metathesis is the most common route to synthesize nucleophilic phosphinidene complexes, which resulted in variations of bent metallocene phosphinidene complexes including early-transition-metal complexes $[(\eta^5-C_5H_5)_2M(Me_3P)(=PMes^*)];$ (M = Zr, Hf),^[6, 7] as well as the uranium complex $[[(\eta^5 C_5Me_5)_2U(Me_3PO)(=PMes^*)]$.^[8] Lammertsma *et al.* demonstrated that this synthetic route is also feasible for late transition metals, e.g., by treating the dichloro complexes $[((\eta^{5}-C_{5}H_{5})Ir(L)CI_{2})]$ $(L = PPh_3,$ *i*Pr₂Im^{Me}) with LiPHMes* give to [(ŋ⁵- C_5H_5)Ir(L)(=PMes^{*})].^[9]

The stabilization of metal-free phosphinidenes was introduced with an early example by Schmidpeter *et al.* in 1980 with a report on the isolation of cyanophosphinidene-

substituted heterocycles.^[10] Arduengo *et al.* reported in 1997 the synthesis and isolation of the NHC pnictinidene adducts Mes₂Im=PnR (Mes₂Im = 1,3-dimesitylimidazolin-2-ylidene; Pn = P, As; R = C₆H₆, CF₃, C₅F₅) and related compounds such as (Me₄Im)PPh (NHC = *N*-heterocyclic carbene, Me₄Im = 1,3,4,5-tetramethyl-imidazolin-2-ylidene), and provided thus the first example that NHCs are suitable molecules for the stabilization of reactive phosphinidenes.^[11] Since then, synthesis and application of NHC-phosphinidenes gained more and more importance.^[3]

Several synthetic routes have been developed for the preparation of NHC phosphinidene adducts since then (Scheme 1).^[3] The aforementioned first 'bottleable' NHC-phosphinidenes such as (Me₄Im)PPh were obtained by reaction of Me₄Im and pentaphenyl-*cyclo*-pentaphosphine (PPh)₅.^[11] Several NHC-phosphinidenes such as (Mes₂Im)PPh or (Mes₂Im)PCF₃, have been synthesized from (PPh)₅ or similar compounds such as (PCF₃)₄ following this methodology (Scheme 1).^[3, 11] However the scope of this procedure is strongly dependent on the availability of the cyclo-phosphine used. The synthesis of NHC-phosphinidenes is also feasible via the reaction of two equivalents of free carbene with dichlorophosphines, which in selected cases leads to the NHC-phosphinidene and [NHC-CI]⁺Cl^{-.[11a]} Instead of using NHC as the chlorine acceptor, Bertrand et al. presented a reductive pathway, i.e. the reaction of the NHC with dichlorophosphines and subsequent two electron reduction with potassium graphite or magnesium powder, which leads to the desired NHC-phosphinidenes (Scheme 1).^[12] The formation of NHC-phosphinidenes is also known from a variety of other NHC and phosphinidene precursors aside from the commonly applied routes starting from chloro-,^[11a, 12] and *cyclo*-polyphosphines.^[11] For example, (Me₄Im)P(Rind) was synthesized from the reaction of diphosphenes (Rind)P=P(Rind) (Rind = 1,1,3,3,5,5,7,7-octa-R-substituted s-hydrindacen-4-yl; R = Et, Me) and two equivalents of the free carbene Me₄Im.^[13] The reaction of P(SiMe₃)₃ with N.N'-1,3-bis(2,6diisopropylphenyl)-2,2-difluoroimidazoline led to (Dipp₂Im)P(SiMe₃) and subsequently to (Dipp₂Im)PH upon addition of methanol.^[14] Another efficient route to NHCphosphinidenes was established by Grützmacher and Gudat et al. by using the phosphaethynolate anion OCP- as phosphorus transfer reagent in the reaction with Narylated imidazolium salts.^[15] Na(OCP) is also a useful reagent for the preparation of tetrel-substituted phosphaketenes (e.g. Ph₃E(PCO), E = Sn, Ge), which afforded NHCphosphinidene adducts upon coordination to NHCs and subsequent thermolysis.^[16] An interesting example of an intramolecular carbene-stabilized phosphinidene was provided by Hahn *et al.*, which was synthesized from the reaction of the phosphaalkyne *i*Pr₂NCP with Me₄Im. The bicyclic azaphospholene product of this reaction is formed by unusual C-H activation at the nitrogen substituent of the NHC.^[17] Similar to polyphosphines, other polyphosphorus compounds such as Na₃P₇ or (Me₃Si)₃P₇ also provide access to NHC-phosphinidenes of NHCs of varying steric demand by reaction with dihydroimidazolium chlorides, as reported by Grützmacher and Gudat *et al.*^[15] Moreover Hey-Hawkins and co-workers demonstrated that Na₂(THF)₄P₄Mes₄ is a suitable precursor for (Me₂Im)PMes, if reacted with Me₂Im or [Me₂Im-H]⁺I⁻.^[18]



Scheme 1. Major synthetic routes to NHC-phosphinidenes.

We recently explored the reactivity of NHCs and related molecules with group 13 to 15 main group element hydrides^[19] and other main group element compounds.^[20] We demonstrated that the reaction of *i*Pr₂Im (1,3-diisopropylimidazolin-2-ylidene) with substrates such as hydrostannanes^[19d] or primary and secondary phosphines^[19b] leads to dehydrogenative element element coupling. P-P coupling was exemplified by the

stoichiometric reaction of *i*Pr₂Im with secondary phosphines, e.g. Ph₂PH, which afforded the dihydroaminal iPr_2ImH_2 and the P-P coupled product Ph₄P₂ in 89% yield. A similar reaction protocol with primary phosphines $ArPH_2$ (Ar = Ph, pTol) leads to the P-P coupled rings P₄Ph₄, P₅Ph₅ and P₆Ph₆. In contrast, using primary phosphines in sub-stoichiometric amounts, i.e. a 1:2 ratio regarding to *i*Pr₂Im, yields the dihydroaminal *i*Pr₂ImH₂ and the NHC-phosphinidene (*i*Pr₂Im)PAr (Ar = Ph, pTol) quantitatively as judged from NMR spectroscopy. In this reaction, the ambiphilic character of the NHC is exploited i) as an activator of the primary phosphine P-H bond and ii) as a hydrogen acceptor. Thus, we considered the NHC mediated dehydrogenation of phosphines as a very interesting approach for the selective synthesis of NHC-phosphinidenes (Scheme 1, bottom) and we report herein on primary phosphine dehydrocoupling using different NHCs as a general and convenient synthetic approach to prepare NHC-phosphinidenes in moderate to high isolated yields (up to 71%). Furthermore, we also report a novel synthesis to different parent NHCphosphinidenes (NHC)PH and preliminary investigations concerning the reactivity of (*i*Pr₂Im)PPh towards chalcogenides and selected transitions metals complexes.

Results and Discussion

Our previous work demonstrated that the reaction of the primary aryl-substituted phosphines PhPH₂ and *p*-TolPH₂ with *i*Pr₂Im in a stoichiometric ratio NHC:phosphine = 2:1 led selectively to the formation of the NHC-phosphinidene adduct (*i*Pr₂Im)PPh (**1**) and (*i*Pr₂Im)PTol in good isolated yield. One equivalent of the NHC serves as a hydrogen acceptor leading to the dihydroaminal *i*Pr₂ImH₂ and the other equivalent is needed to stabilize the phosphinidene generated. ^[19b] As this approach represents a convenient way to access NHC-phosphinidenes we were interested to explore this preparative route in more detail. Thus, we reacted two equivalents of different NHCs with PhPH₂ to probe their ability to act as hydrogen-acceptor as well as different primary phosphines, i.e. PhPH₂, MesPH₂ and *t*BuPH₂ with different NHCs to probe different phosphines (Scheme 2).



Scheme 2. Dehydrogenative synthesis of NHC-phosphinidenes (NHC)PAr (1–7, top) and (NHC)PH (8-10, bottom).

Thus, we applied the same reaction protocol on the primary phosphines PhPH₂, MesPH₂ and *t*BuPH₂ in combination with *i*Pr₂Im, Mes₂Im, Me₂Im and the backbone methylated NHC, Me₄Im. The reaction of two equivalents Mes₂Im and Me₄Im with one equivalent phenyl phosphine in xylene or toluene at 135°C and 110°C, respectively, was monitored via ³¹P NMR spectroscopy. During the reactions new species were detected in the ³¹P NMR spectra, the corresponding ³¹P resonances were significantly downfield shifted in comparison to phenyl phosphine (c.f. -124.2 ppm). The signals at -23.7 ppm ((Mes₂lm)PPh (2)) and -52.9 ppm ((Me₄lm)PPh (3)) were assigned accordingly to the corresponding NHC-phosphinidenes and are in good agreement with those reported earlier by Arduengo et al. and by Layfield and coworkers (Table 1).^[11, 21] For the reaction of Mes₂Im with PhPH₂ no NMR signals for corresponding P-P coupling products were observed. After the reaction reached quantitative conversion without any side products formed, as judged from ³¹P NMR spectroscopy, the solvent was evaporated, and the residue suspended in *n*-hexane. Subsequent filtration and washing with portions of *n*-hexane to remove the residual dihydroaminal NHCH₂ led to the isolation of (Mes₂Im)PPh (2) as a bright yellow solid in good yield (61%). The reaction of two equivalents Me₄Im with PhPH₂, however,

afforded aside from the product (Me₄Im)PPh (**3**) *cyclo*-oligophosphines P₄Ph₄, P₅Ph₅ and P₆Ph₆ as major side products, even in presence of an excess of NHC (i.e. 2.1 equivalents). Thus, (Me₄Im)PPh (**3**) was also formed using this procedure, but only in low yields of approximately 14 % judged from the integration of the ³¹P NMR signals of the isolated yellow solid, which contained a mixture of (Me₄Im)PPh (**3**) and different oligophosphines. We did not try to separate the *cyclo*-oligophospines from (Me₄Im)PPh (**3**).

As the primary aryl phosphines seem to be suitable sources for the dehydrogenative route to NHC-phosphinidenes, we also investigated the reaction of mesityl phosphine MesPH₂ towards NHCs. MesPH₂ was reacted in a 1:2 ratio with the four different NHCs at higher temperatures. After the phosphine was completely consumed (judged on ³¹P NMR spectroscopy) and subsequent work up, the literature known NHCphosphinidenes (Mes₂Im)PMes (4), (Me₂Im)PMes (5) and (Me₄Im)PMes (6) were isolated in moderate to fair yields (4: 33%, 5: 53%, 6: 47%). Layfield and coworkers reported an iron- and cobalt-catalyzed synthesis for the NHC-phosphinidenes (Mes₂Im)PMes (4) and (Me₄Im)PMes (6).^[21] Layfield et al. also reacted Mes₂Im directly with MesPH₂ to exclude formation of the NHC-phosphinidene without any catalyst under otherwise catalytic conditions. Upon heating Mes_2Im and $Dipp_2Im$ with $MesPH_2$ at 80°C in deutereobenzene for several days, these authors observe no reaction, whereas ¹H and ³¹P NMR spectra of the combination Me₄Im/MesPH₂ showed that MesPH₂, MesP(H)Me, and IMe₄·PMes are present in an approximate ratio of 7:1:1 and the mixture is thus dominated by starting materials.^[21] However, using more elevated temperatures up to 110°C or higher, dehydrocoupling is feasible even without the need for a catalyst with formation of (Mes₂Im)PMes (**4**), (Me₂Im)PMes (**5**), (Me₄Im)PMes (**6**) and $(iPr_2Im)PMes$ (7).^[19a] For (Me₄Im)PMes (6), the direct reaction of two equivalents of Me₄Im with one equivalent of MesPH₂ results in the complete consumption of starting materials after 10 days at 110°C. This simple, yet efficient synthetic route represents an alternative, even though long reaction times are required. It is remarkable that these simple reactions are in some cases (*i.e.* for Me₄Im=PMes 6) high in yield compared to the catalyzed analogues.^[21] Due to limited rotations around the C-P bond some signals in the ¹H NMR spectrum of (Me₄Im)PMes (6) are significantly broadened at room temperature, which was also observed by Layfield et al.^[21] Hence, temperature dependent NMR spectra in THF-d₈ were recorded which show splitting into sharp signals at 248 K (see Figure S11 in the SI). This is in good agreement to the data reported before.^[21] In a similar fashion, the hitherto unknown (*i*Pr₂Im)PMes (**7**) was synthesized and isolated as a sticky oil. The formation of (*i*Pr₂Im)PMes (**7**) was unambiguously verified by ¹H, ¹³C{¹H} and ³¹P NMR spectroscopy. (*i*Pr₂Im)PMes (**7**)shows a single resonance at -81.0 ppm in the ³¹P NMR spectrum, similar to other (NHC)PMes species such as (Mes₂Im)PMes (**4**) (-50.0 ppm), (Me₂Im)PMes (**5**) (-73.5 ppm) and (Me₄Im)PMes (**6**) (-74.8 ppm) (see Table 1). However, the NMR spectra of the isolated yellow oil show small amounts of different, unassigned side products, which could not be separated. A doublet resonance for the NHC carbene carbon atom of (*i*Pr₂Im)PMes (**7**) in the ¹³C{¹H} NMR spectrum at a chemical shift of 168.4 ppm with a ¹J_{CP} coupling constant of 105.0 Hz to the adjacent phosphorus atom verifies the formation of the NHC-phosphinidene. Compared to the free NHC, this resonance is noticeably shifted to higher field and is also in perfect agreement to the ¹³C{¹H} NMR spectroscopic data for the carbene carbon atom of (*i*Pr₂Im)PPh (**1**) at 168.2 ppm (Table 1).

Table 1	. Important ³¹ I	P and ¹³	³ C{ ¹ H}	chemical	shifts	(P=C _{NHC})	and	$^{1}J_{CP}$	coupling	constants	recorded	in
C ₆ D ₆ and	d isolated yiel	ds of co	ompoun	ds 1-7 .								

Compound	δ _{NCN} ¹³ C{ ¹ H} [ppm]	δ ³¹ Ρ [ppm]	¹ J _{CP} [Hz]	yield [%]
(<i>i</i> Pr ₂ Im)PPh (1)	168.2	-59.9	104	88
(Mes₂Im)PPh (2)	169.8	-23.7	103	61
(Me₄lm)PPh (3)	168.9	-52.9	97	14
(Mes ₂ Im)PMes (4)	170.3	-59.0	103	33
(Me ₂ Im)PMes (5)	170.4	-73.5	101	53
(Me₄Im)PMes (6)	169.5	-74.8	100	47
(<i>i</i> Pr ₂ Im)PMes (7)	168.4	-79.5	105	-

In addition to the characterization by NMR spectroscopy and high-resolution mass spectrometry, the NHC-phosphinidene (Me₄Im)PMes (**6**) was also structurally characterized. Single-crystals of **6** suitable for X-ray diffraction were obtained by storing a saturated solution of this compound in *n*-pentane at room temperature for several days (see Figure 1).

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Figure 1. Molecular structure of (Me₄Im)PMes (**6**) in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and angles (°) for **6**: P1–C1 1.791(2), C1–N1 1.363(3), C1–N2 1.358(3), P1–C2 1.842(2), C2–C3 1.425(3), C2–C4 1.409(3); C2–P1–C1 102.3(1), N1–C1–N2 104.8(2); N–C–P–C 67.4(2).

(Me₄Im)PMes (**6**) crystallizes in the space group Cc with one molecule in the asymmetric unit. The P-C distance of 1.791(2) Å is similar to those of P–C_{Carbene} bonds observed in the molecular structures of other NHC-phosphinidenes (Me₄Im)PR reported earlier, which lie in a range of 1.77 to 1.79 Å for a variety of substituents at the P atom with different steric bulk ((Me₄Im)PH 1.7721(14) Å, (Me₄Im)PPh 1.794(3) Å, (Me₄Im)P(Dmp) 1.786(4) Å).^[3a] The angle C1–P1–C2 of 102.3(1)° for (Me₄Im)PMes (**6**) matches the C–P–C angle of (Me₄Im)PPh (102.34(14)°),^[3a] whereas the torsion angle N–C–P–C of **6** of 67.4(2)° is widened compared to (Me₄Im)PPh (51.0(3)°) and (Me₄Im)P(Dmp) (55.5(4)°).^[3a]

In comparison to aryl phosphinidenes, there are far less examples for alkyl substituted NHC-phosphinidenes and unsubstituted, i.e. parent NHC-phosphinidenes. One example for a CF₃ substituted species was presented by Arduengo *et al.*,^[11a] while NHC adducts of the parent phosphinidene (:PH) include examples of NHCs with different steric properties as well as saturated and unsaturated NHC backbones. The first synthesis of such a compound was reported by Driess *et al.* in 2013. These authors obtained (Dipp₂Im)PH (II) (Scheme 3) by treating phospasilene I with the carbene Dipp₂Im, which results in a room temperature transfer of the PH moiety.^[22] The synthesis of (Dipp₂Im)PH (II) is also feasible starting from the [HCI] salt of the carbene (III) and react it with phosphaethynolate, Na(OCP), or TMS₃P₇ as "P" transfer reagent as described by Grützmacher *et al.*^[23] Another synthetic route presented by Tamm *et al.* uses *N*,*N'*-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazoline (IV) and P(SiMe₃)₃ which forms the (NHC)PSiMe₃ adduct. Subsequent treatment of (NHC)PSiMe₃ with methanol furnishes II in good yield (Scheme 3).^[14]



Scheme 3. Synthetic routes to NHC-phosphinidenes (NHC)PH.

Grützmacher and Gudat and coworkers reported an alternative synthesis for NHC=PH compounds mainly of sterically less demanding NHCs in 2016. Whereas the reaction of the imidazolium salts **V** with P₄ and KOtBu only led to unselective product formation and polyphosphorous side products, the reaction of **V** with Na₃P₇ in THF afforded the NHC-phosphinidenes (**VI**) selectively.^[24] For the synthesis of (*s*Dipp₂Im)PH (**IX**) (*s*Dipp₂Im = 1,3-Bis-(2,6-di-*iso*-propylphenyl)-imidazolidin-2-ylidene) either PH₃ or {[Na(OtBu)]_{2.5}[Na(PH₂)]} can be used as phosphinidene source, and treatment with the [HCI]-salt (**VII**) and dehydrocoupling of the intermediate **VIII** with quinone afforded the desired compound. Dehydrogenation to the phosphinidene-carbene adduct **VIII** was achieved using an *ortho*-quinone as hydrogen acceptor.^[25] Recently von Hänisch *et al.* reported a synthesis for (*s*Mes₂Im)PH (**XI**) (*s*Mes₂Im = 1,3-Dimesityl-imidazolidin-2-ylidene) applying a slightly modified reaction protocol based on the synthesis for (Dipp₂Im)PH (**II**) developed by Grützmacher (Scheme 3).^[23, 26]

Treating $tBuPH_2$ with two equivalents of iPr_2Im in xylene at 125°C for 5 days resulted in complete consumption of the primary phosphine. After workup, a pale-yellow solid was isolated and ³¹P and ³¹P{¹H} spectroscopy revealed a resonance at -149.9 ppm with a ¹J_{PH} coupling constant of 166 Hz, which is consistent with the existence of a phosphorous bound hydrogen atom. These data obtained match perfectly with the data reported earlier by Grützmacher and Gudat and coworkers for (iPr_2Im)PH (**8**) (Table 2).^[24] Thus, the reaction did not afford the expected *tert*-butyl substituted NHC-phosphinidene, but the parent NHC phosphinidene (iPr_2Im)PH (**8**) was isolated in 28% yield instead. To gain a better insight into the course of the transformation we repeated the reaction in a temperature range between -78°C and 0°C, but only starting material in form of *t*BuPH₂ was detected by means of ³¹P NMR spectroscopy. However, a ³¹P NMR resonance of (iPr_2Im)PH (**8**) was already observed when heating the 2:1 mixture of *i*Pr₂Im and *t*BuPH₂ to 50°C, and an intermediate *tert*-butyl substituted phosphinidene species was never isolated or observed for this reaction spectroscopically.

Also (Mes₂Im)PH (**9**) and (Me₄Im)PH (**10**) can be synthesized from the reaction of *t*BuPH₂ and two equivalents NHC (Mes₂Im: 135°C in xylene, Me₄Im: 110°C in toluene). The primary phosphine 'BuPH₂ was completely consumed after five days and the NHC-phosphinindenes (Mes₂Im)PH (**9**) ($\delta^{31}P = -147.2 \text{ ppm}$) and (Me₄Im)PH (**10**) ($\delta^{31}P = -149.9 \text{ ppm}$) were isolated as off-white and colorless solids in yields of 71% and 51 %, respectively (Table 2). Formation of the H substituted species was also supported by the observation of the corresponding P–H vibrations in the IR spectra of the compounds **8-10** (**8**: 2302 cm⁻¹, **9**: 2269 cm⁻¹, **10**: 2293 cm⁻¹, Table 2). Compared to other established synthetic routes for (Mes₂Im)PH (**9**) and (Me₄Im)PH (**10**), these reactions are remarkably high yielding using a standard primary phosphine,^[24] but also limited in the NHC used. As an example, we have found that the reaction of Me₂Im with *t*BuPH₂ in a 2:1 ratio in toluene at 115°C leads to (Me₂Im)PH (**11**) only in traces even after 10 days and the mixture is dominated by starting material (according to ³¹P NMR spectroscopy).

Compound	δ _{ΝCN} ¹³ C{ ¹ H} [ppm]	δ ³¹ Ρ [ppm]	δ _{PH} ¹ H [ppm]	¹ Ј _{РН} [Hz]	¹ J _{CP} [Hz]	<i>⊽_{РН}</i> [ст⁻¹]	yield [%]
(<i>i</i> Pr ₂ Im)PH (8)	173.7	-149.9	2.64	166	93	2302	28
(Mes₂Im)PH (9)	176.3	-147.2	2.07	164	85	2269	71
(Me₄lm)PH (10)	174.6	-149.9	2.49	165	88	2293	51

Table 2. Important ³¹P, ¹H and ¹³C{¹H} chemical shifts ($P=C_{NHC}$) and coupling constants recorded in C₆D₆, IR data and isolated yields of compounds **8-10**.



Figure 2. Molecular structure of (*i*Pr₂Im)PH (**8**) in the solid state. Hydrogen atoms are omitted for clarity with exception of H1. Atomic displacement ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and angles (°) for **8**: P1–H1 1.3504(4), P1–C1 1.7788(4), C1–N1 1.3636(3), C1–N2 1.3613(3); H1–P1–C1 92.886(9), N1–C1–N2 105.278(16); H1–P1–C1–N1) 2.612.

Single crystals of (*i*Pr₂Im)PH (**8**) suitable for X-Ray diffraction analysis were obtained by storing a saturated solution of the compound in *n*-hexane at room temperature (see Figure 2). NHC-phosphinidene **8** crystallizes in the space group P2₁2₁2₁ with one molecule in the asymmetric unit. The P-C distance of 1.7788(4) Å observed for **8** is similar to that of the Me₄Im analogue (Me₄Im)PH (1.7721(14) Å) reported previously.^[3a] The angle C–P–H of 92.886(9)° and the torsion angle H–P–C–N of 2.612° reveal an almost ideal eclipsed conformation between the phosphinidene moiety and the NHC ligand.



Scheme 4. Reactions of NHC-phosphinidene 1 with chalcogenids.

The dehydrocoupling route presented here allows the synthesis and isolation of $(iPr_2Im)PPh$ (**1**) on a multigram (here: 4 g) scale with an excellent yield of 88%. With this NHC-phosphinidene at hand we were interested in first reactivity studies. To probe

oxygen sensitivity, we initially reacted the NHC-phosphinidene (*i*Pr₂Im)PPh (**1**) with dry oxygen (0.5 bar) in toluene. Directly after addition of oxygen, the reaction mixture changes its color from orange to colorless with formation of a colorless precipitate. After workup, compound *i*Pr₂Im–P(O)₂Ph (**11**) was isolated as a colorless solid in 55% yield. NMR spectroscopic investigations revealed a significant downfield shift of the ³¹P NMR resonance at -0.8 ppm in CD₃CN compared to the NHC-phosphinidene **1**, similar as observed for the NHC adducts of phenyldioxophosphorane presented previously by Tamm *et al.* (Me₄Im-P(O)₂Ph: -1.0 ppm, Mes₂Im-P(O)₂Ph: -23.0 ppm, Dipp₂Im-P(O)₂Ph: -18.9 ppm).^[27] Further, the doublet resonance for the NHC carbene carbon atom is noticeably shifted in the ¹³C{¹H} NMR spectrum, i.e. *i*Pr₂Im–P(O)₂Ph (**11**) gives rise to a signal at 147.9 ppm (¹J_{CP} = 94.5 Hz), whereas the resonance for (*i*Pr₂Im)PPh (**1**) is located at 168.2 ppm (¹J_{CP} = 104 Hz).

Similarly, the reaction between equimolar amounts of (*i*Pr₂Im)PPh (**1**) and elemental sulfur (S₈) in THF afforded the NHC adduct of phenyldithiophosphorane *i*Pr₂Im–P(S)₂Ph (**12**), which gives rise to a ³¹P NMR resonance at 54.1 ppm in CDCl₃. This compound is well soluble and sufficiently stable in acetonitrile and chloroform which allows full characterization by NMR spectroscopy. A doublet for the NHC carbene carbon atom was detected in the ¹³C{¹H} NMR spectrum at 147.2 ppm with a coupling constant ¹J_{PC} of 40.4 Hz, which is much smaller than ¹J_{PC} coupling observed for *i*Pr₂Im–P(O)₂Ph (**11**) (¹J_{PC(NHC)} = 94.5 Hz). Similarly, the ¹J_{PC} coupling constant of the ¹³C{¹H} NMR resonance at 142.3 ppm for the phenyl C_{*ipso*} attached to phosphorous of 91.0 Hz is much smaller compared to **11** (¹J_{PC(Ph)} = 145.6 Hz). Furthermore, the compound *i*Pr₂Im–P(S)₂Ph (**12**) was also characterized by X-ray diffraction (see Figure 3).



Figure 3. Molecular structure of *i*Pr₂Im–P(S)₂Ph (**12**) in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and angles (°) for **12**: P1–C1 1.8732(14), P1–S1 1.9739(5), P1–S2 1.9626(5), P1–C2 1.8247(14); C1–P1–S1 107.17(5), C1–P1–S2 104.29(4); C1–P1–C2 99.33(6), S1–P1–S2 119.29(2), S2–P1–C2 112.45(4), S1–P1–C2 107.17(5).

*i*Pr₂Im–P(S)₂Ph (**12**) crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. The molecular structure of **12** reveals a distorted tetrahedral geometry at phosphorus with a large S–P–S angle of 119.29(2)°. The the P–C_{Carbene} bond length of 1.8732(14) Å is significantly longer than the P–C_{Phenyl} bond of 1.8247(14) Å and the C=P bond observed in NHC-phosphinidenes (*vide supra*). However, the bond lengths and angles obtained for **12** are in good agreement with the data reported by Tamm *et al.* for Me₄Im–P(S)₂Ph previously.^[27]

The reaction of **1** with elemental (grey) selenium and tellurium did not lead to the selenium and tellurium analogues of **11** and **12**, but yielded (NHC)PPh cleavage with formation of the isolated compounds (*i*Pr₂Im)Se (**13**) and (*i*Pr₂Im)Te (**14**) and different *cyclo*-oligophospines, according to NMR spectroscopy (³¹P-NMR: P₄Ph₄ -48.2, P₆Ph₆ -22.0, P₅Ph₅ -3.6 to -2.7 ppm). The NMR data of **13** are in good agreement to those reported by Ganter *et al.*,^[28] most characteristic is the ¹³C{¹H} NMR resonance of the NHC carbene carbon atom at 153.5 ppm and a singlet at -19.7 ppm in the ⁷⁷Se{¹H} NMR spectrum. Tamm and coworkers reported the isolation of Me₄Im substituted diselenophosphorane from the analogous reaction of (Me₄Im)PPh with grey selenium in THF at room temperature.^[27] The compound (*i*Pr₂Im)Te (**14**) shows a characteristic resonance at -184.6 ppm in the ¹²³Te{¹H} NMR spectrum which is in agreement with the ¹²³Te NMR spectrum reported for closely related *i*Pr₂Im^{Me}=Te at -167.8 ppm as reported by Kuhn and Henkel et al.^[29]



Figure 4. Molecular structure of (*i*Pr₂Im)Te (**14**) in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and angles (°) for **14**: C1–Te1 2.092(4), N1–C1 1.340(6), C1–N2 1.355(6).

 $(i\Pr_2 Im)Te$ (**14**) crystallizes in the triclinic space group P1 with two molecules in the asymmetric unit. The molecular structure shows as expected a Te atom bonded to the

NHC *i*Pr₂Im. The bond length C1–Te1 of 2.092(4) Å is identical within standard deviation to the closely related C-Te distance reported for (*i*Pr₂Im^{Me})Te.^[29b]

The developed synthetic protocol for NHC-phosphinidenes of the general formula (NHC)PR paired with the observation of (NHC)PPh cleavage by treatment of $(iPr_2Im)PPh$ (1) with elemental selenium and tellurium to yield $(iPr_2Im)Se$ (13) and $(iPr_2Im)Te$ (14) is particularly useful to determine the electronic properties of NHCs by ³¹P and ⁷⁷Se NMR spectroscopy as demonstrated by Bertrand and Ghadwal recently.^[12, 30]

Several transition metal complexes of NHC-phosphinidenes have been reported so far in the literature. Larocque and Lavoie provided an early example in 2014 and reported the reaction of a first-generation ruthenium benzylidene Grubbs complex with (Mes₂Im)PPh. Ligand exchange of one PPh₃ ligand occurred and led to the formation of a ruthenium NHC-phosphinidene complex, maintaining the NHC-phosphinidene.^[31] Tamm et al. reported the synthesis of NHC-phosphinidene coinage metal complexes from the reaction of the NHC-phosphinidene (Dipp₂Im)PPh with MCI (M = Cu, Ag, Au)^[32] and a series of tungsten and molybdenum pentacarbonyl complexes of NHCphosphinidenes.^[33] Different complexes [{(Dipp₂Im)PR}M(CO)₅] (R = H, Ph, Mes, M = Mo, W) of NHC-phosphinidenes of the sterically demanding Dipp₂Im have been synthesized and it has been demonstrated that NHC phospinidenes are good donor ligands. For example, the CO band for the CO stretch in the IR spectrum of [{(Dipp₂Im)PPh}Rh(CO)₂CI] at 2006 cm⁻¹ lies much lower compared to those of other important ligand classes in complexes [(L)Rh(CO)₂Cl], e.g. phosphines (PPh₃: 2052 cm⁻¹) or NHCs (Mes₂Im: 2038 cm⁻¹, Dipp₂Im: 2037 cm⁻¹).^[33] These results encouraged us to study the ligation properties of the sterically less demanding NHC-phosphinidene (*i*Pr₂Im)PPh (**1**) with respect to selected transition metal complexes (Scheme 5). The tetrahydrofuran adduct [W(CO)₅(thf)], which was in situ generated by photolysis of $[W(CO)_6]$ in THF, was reacted with (*i*Pr₂Im)PPh (**1**) and yielded $[\{(iPr_2Im)PPh\}W(CO)_5]$ 15 in quantitative yield according to ³¹P NMR spectroscopy. This complex was isolated as a yellow solid in 54% yield. The ³¹P NMR resonance of the NHC-phosphinidene tungsten complex was observed at -81.1 ppm, significantly shifted from -60.1 ppm for (*i*Pr₂Im)PPh (**1**), and coupling of the phosphorus nucleus with the tungsten center with a coupling constant of ${}^{1}J_{PW}$ = 112.3 Hz was observed. Tamm *et al.* reported a wide

range of ³¹P NMR chemical shifts for similar compounds, e.g. -57.7 ppm in THF-d₈ for $[{(Dipp_2Im)PPh}W(CO)_5]$ with a coupling constant of ¹*J*_{PW} = 120 Hz, close to our data.^[33]



Scheme 5. Reaction of (*i*Pr₂Im)PPh (1) with selected transition metal complexes.

We recently reported the reaction of $[Co(CO)_3(NO)]^{[34]}$ with different NHCs, which leads to replacement of carbonyl ligands and to formation of either $[Co(NHC)(CO)_2(NO)]$ or $[Co(NHC)_2(CO)(NO)]$ in overall good yields.^[35] The use of the sterically demanding NHCs Dipp₂Im, Mes₂Im and the cyclic (alkyl)(amino)carbene ^{Me}cAAC selectively led to complexes of the type $[Co(NHC)(CO)_2(NO)]$, even if an excess of NHC was provided. Similarly, NHC phosphine complexes $[Co('Pr_2Im)(PR_3)(CO)(NO)]$ (PR₃ = PMe₃, PEt₃, PH/Pr₂) and $[Co(NHC)(PMe_3)(CO)(NO)]$ (NHC = Me₄Im, Me/PrIm, MetBuIm, *i*Pr₂Im^{Me}) are available from the reaction of $[Co(NHC)(CO)_2(NO)]$ and phosphines.^[35b] Therefore, $[Co(CO)_3(NO)]$ might be a suitable precursor for either a cobalt NHC-phosphinidene complex $[Co\{(NHC)PR\}(CO)_2(NO)]$ or a NHC-stabilized cobalt phosphinidene complex [Co(NHC)(PR)(CO)(NO)] or $[Co(NHC)(PR)(CO)_2]$.^[35] However, the reaction of $(iPr_2Im)PPh$ (1)with $[Co(CO)_3NO]$ resulted with CO release in the formation of the red complex $[Co\{(iPr_2Im)PPh\}(CO)_2(NO)]$ (16) in 42% yield. Complex 16 reveals significantly shifted ¹H NMR data as compared to the analogous NHC complex $[Co(CO)_2(NO)(iPr_2Im)]$ (XII),^[35] i.e. a doublet at 0.82 ppm (XII: 0.92 ppm) for the methyl protons and a doublet of septets at 5.02 ppm (XII: 4.60 ppm) for the methine protons of the *i*Pr substituent as well as a broad doublet at 6.07 ppm (XII: 6.40 ppm) for the NHC-backbone protons. The resonances of the NHC carbene carbon atom in the ¹³C{¹H} NMR spectrum of **16** at 163.7 ppm (**XII**: 219.8 ppm) reveals a ${}^{1}J_{CP}$ coupling constant to the phosphorus atom of 91.2 Hz, which is in accordance with an intact NHC-phosphinidene unit and thus confirms the formation of the NHC-phosphinidene ligated complex **16**. The large guadrupole moment of ⁵⁹Co affects the NHC carbene carbon and the carbonyl carbon resonance in the ¹³C{¹H} NMR spectrum, the latter was not observed, but also the ³¹P NMR resonance, which appears as a broadened signal at -45.5 ppm. This resonance is also in good agreement with other reported NHC-phosphinidene carbonyl complexes, which show ³¹P resonances typically in the range between -25 to -164 ppm.^[33] In addition, an intense NO (1694 cm⁻¹) and two CO (1925 cm⁻¹ and 1992 cm⁻¹) stretching modes were observed in the IR spectrum of **16**, which indicate a high electron density at the cobalt atom. However, heating of 16 in solution led to decomposition of this complex with formation of [Co(*i*Pr₂Im)(CO)₂(NO)] and cyclo-oligophosphines and not to the formation of an NHC-stabilized cobalt phosphinidene complex, as might expected.

Various group 8 and 9 half sandwich phosphinidene complexes of the type $[(n^{6} C_6R_6$)M(L)(=PAr)] (M= Ru, Os; L= PR₃, NHC)^[37] or [(n⁵-C₅R₅)M(L)(=PAr)] (Co^[38a], Rh^[38a], Ir^[9a, 2b]; L= PR₃, NHC) as well as related NHC-phosphinidene metal complexes known.^[38] Therefore, we envisioned the synthesis of NHC-stabilized are phosphinidene complexes $[(n^5-C_5R_5)Co(NHC)(=PAr)]$ starting from $(iPr_2Im)PPh$ (1) and $[(C_5R_5)C_0]$ -synthons such as $[(C_5R_5)C_0(\eta^2-C_2H_4)_2]$. We have reported previously different complexes with the $[(\eta^5-C_5R_5)Co(NHC)]$ complex moiety on several occasions.^[36] The reaction of $[(C_5Me_5)Co(\eta^2-C_2H_4)_2]$ with (*i*Pr₂Im)PPh (**1**) afforded the NHC-phosphinidene cobalt complex $[(n^5-C_5Me_5)Co\{(iPr_2Im)PPh\}(n^2-C_2H_4)]$ (17) (Scheme 5). Complexes **17** and $[(\eta^5-C_5Me_5)Co(iPr_2Im)(\eta^2-C_2H_4)]$ (**XIII**) reported previousely^[36a] can be easily distinguished by NMR spectroscopy. The ¹H NMR spectrum of **17**, for example, reveals a resonance at 1.93 ppm (XIII: 1.78 ppm) characteristic for C₅Me₅ protons and the *iso*-propyl methine protons give rise to a broadened doublet of septets at 4.57 ppm (XIII: one septet at 6.20 ppm). The NHC carbene carbon atom resonance at 163.7 ppm (XIII: 193.8 ppm) in the ¹³C{¹H} NMR spectrum shows ${}^{1}J_{CP}$ coupling of 98.7 Hz, and ${}^{31}P$ NMR resonance at +25.8 ppm is shifted compared to the NMR resonance of **1** at -60.1 ppm.

Similar as observed for **16**, complex **17** decomposes upon heating in solution. At room temperature, both NHC-phosphinidene complexes are stable in solution for a prolonged period of time. However, after gradually heating both complexes up to 80°C the NHC complex $[(\eta^5-C_5Me_5)Co(iPr_2Im)(\eta^2-C_2H_4)]$ was formed together with *cyclo*oligophosphines.

To support these experimental observations, additional quantum-mechanical DFT calculations on the BP86/def2-TZVP level of theory were performed. According to these calculations the decomposition of $[Co{(iPr_2Im)PPh}(CO)_2(NO)]$ **16** to yield $[Co(iPr_2Im)(CO)_2(NO)]$ and *cyclo*-P₅Ph₅ is exergonic by ΔG^{298} = -37.46 kJ·mol, whereas the formation of $[Co(iPr_2Im)(PPh)(CO)(NO)]$ (and CO) is endergonic by ΔG^{298} = +129.43 kJ·mol (Figure 5). Thus, the calculations clearly predict [PPh] cleavage from **16** and oligophosphine formation, a transfer to the cobalt atom with substitution of a CO ligand seems not to be feasible.



Figure 5. Free reaction enthalpies (ΔG^{298} , at 298 K) calculated at the def2-TZVP/BP86-level of theory for the formation of [Co(*i*Pr₂Im)(CO)₂(NO)] **II** and *cyclo*-P₅Ph₅ (top) or [Co(*i*Pr₂Im)(PPh)(CO)(NO)] (bottom) starting from [Co(CO)₂(NO){(*i*Pr₂Im)PPh}] (**16**).

Over the past years we investigated the chemistry of different NHC-stabilized nickel complexes in stochiometric and catalytic reactions in some detail.^[39] As NHC-phosphinidenes have not been used as ligands in any nickel complex so far, we became interested to use (*i*Pr₂Im)PPh (**1**) in nickel chemistry. Wolf and Goicoechea reported the reaction of the paramagnetic nickel(I) NHC complex [(η -C₅H₅)Ni(Mes₂Im)]

with [Na(dioxane)_{1.8}][PCO] which led to the isolation of carbene-phosphinidenylbridged dimer (μ^2 -CO)[μ^2 -P(Mes₂Im)]Ni₂(Mes₂Im)Cp.^[40]

The reaction of (*i*Pr₂Im)PPh (1) with the nickel(0) precursor [Ni(COD)₂] in a 2:1 molar ratio in toluene at room temperature led to isolation of a diphosphene complex [Ni(*i*Pr₂Im)₂(*trans*-PhP=PPh)] (18) (Scheme 5), which was characterized using NMR spectroscopy, elemental analysis, and high-resolution mass spectroscopy. In contrast to the transition metal complexes of **1** with tungsten and cobalt reported here, no η^{1} coordination of $(iPr_2Im)PPh$ (1) was observed but direct coordination of iPr_2Im to the nickel center with coupling of the phoshinidene units occurred instead. Thus, complex **18** is formed by formal NHC-phosphinidene cleavage and phosphinidene coupling in the coordination sphere of nickel with coordination of the NHC and the diphosphene to the nickel atom. However, independent on the stoichiometry and temperature we were using, we could not detect any intermediate for this reaction. For 18, a single resonance in the ${}^{31}P$ NMR spectrum was detected at -40.9 ppm in C₆D₆ and -42.9 ppm in toluened₈, which lies in a similar region as observed for the palladium and platinum derivatives [Pd(dppe)(trans-PhP=PPh)] ($\delta = -34$ ppm) and [Pt(dppe)(trans-PhP=PPh)] ($\delta = -24$ ppm) previousely.^[41] The resonance of the NHC carbene carbon atoms in the ¹³C{¹H} NMR spectrum of **18** appear as a triplet at 193.9 ppm, in the typical range for this kind of NHC nickel complexes,^[39] with a ${}^{2}J_{CP}$ coupling constant of 8.3 Hz, which is much smaller than the ${}^{1}J_{CP}$ coupling constant typically observed for NHC-phosphinidene complexes (typically ca. 90 Hz, vide supra). The ¹H NMR resonances of the NHC ligands in **18** are broadened at room temperature, consistent with a hindered rotation of the ArP=PAr ligand around the Ni-(PP)_{centroid} vector and/or of the NHC ligands around the Ni-C bonds. Cooling to -50 °C resolved the spectra into four iPr methyl and two *i*Pr methine resonances, as typically found for a pseudo-C_{2v} type structure in solution. At 90°C, two *i*Pr methyl resonances and a single *i*Pr methine signal were observed, which were still broadened (see Figure S66 of the SI).

Conclusion

The dehydrocoupling of primary phosphines with NHCs to yield NHC-phosphinidenes was investigated and we demonstrate here that dehydrocoupling of primary phosphine using NHCs is a general and convenient synthetic approach to prepare NHCphosphinidenes in moderate to high isolated yields. The reaction of primary phosphines $ArPH_2$ (Ar = Ph, *p*Tol, Mes) with NHCs led to addition of hydrogen to the NHC carbene carbon atom with formation of the dihydroaminal NHCH₂ and the NHCphosphinidene (NHC)PAr. The NHC phosphinidenes (*i*Pr₂Im)PPh (1), (Mes₂Im)PPh (2), (Me₄Im)PPh (3), (Mes₂Im)PMes (4), (Me₂Im)PMes (5), (Me₄Im)PMes (6) and (*i*Pr₂Im)PMes (7) have been synthesized using this approach. If *t*BuPH₂ is used as the phosphine source, the parent NHC-phosphinidenes (NHC)PH were obtained, as exemplified by the preparation of $(i Pr_2 Im)PH$ (8), $(Mes_2 Im)PH$ (9) and $(Me_4 Im)PH$ (10). The NHC-phosphinidene (*i*Pr₂Im)PPh (**1**) is oxygen-sensitive, as the reaction of **1** with oxygen led to the isolation of $iPr_2Im-P(O)_2Ph$ (11). The reaction with elemental sulphur afforded *i*Pr₂Im–P(S)₂Ph (**12**). Treatment of **1** with elemental selenium and tellurium did not lead to the selenium and tellurium analogues of **11** and **12**, but to (NHC)PPh cleavage with formation of (*i*Pr₂Im)Se (13) and (*i*Pr₂Im)Te (14) and different cyclooligophospines. Furthermore, several transition metal complexes of the NHCphosphinidene 1 were synthesized. In situ prepared [W(CO)₅(thf)] reacts with 1 quantitatively to yield $[{(iPr_2Im)PPh}W(CO)_5]$ (15), the reaction of 1 with $[Co(CO)_3NO]$ results with CO release in the formation of $[Co{(iPr_2Im)PPh}(CO)_2(NO)]$ (16) and the reaction of $[(C_5Me_5)Co(\eta^2-C_2H_4)_2]$ with **1** afforded $[(\eta^5-C_5Me_5)Co\{iPr_2Im\}PPh\}(\eta^2 C_2H_4$] (17). Both cobalt complexes, [Co{(*i*Pr₂Im)PPh}(CO)₂(NO)] (16) and [(η^5 - $C_5Me_5)Co{iPr_2Im}PPh{(\eta^2-C_2H_4)]}$ (17) are stable in the solid state and in solution at room temperature, but decompose to the NHC complexes [Co(*i*Pr₂Im)(CO)₂(NO)] and $[(\eta^5-C_5Me_5)Co(iPr_2Im)(\eta^2-C_2H_4)]$, respectively, and *cyclo*-oligophosphines upon heating to 80°C in solution. A different behavior was observed for the reaction of (*i*Pr₂Im)PPh (1) with the common nickel(0) precursor [Ni(COD)₂], which afforded the diphosphene complex [Ni(*i*Pr₂Im)₂(*trans*-PhP=PPh)] (**18**). This complex was formed by formal NHC-phosphinidene cleavage, NHC coordination to nickel and phosphinidene coupling in the coordination sphere of the nickel atom.

Experimental Section

General considerations

All reactions and subsequent manipulations involving organometallic reagents were performed under argon atmosphere by using standard Schlenk techniques or in a Glovebox (Innovative Technology Inc. and MBraun Uni Lab) as reported previously.^[39] All reactions were carried out in oven-dried glassware. Toluene, *n*-hexane and THF were obtained from a solvent purification station (Innovative Technology) by previous purification through alumina columns. The deuterated benzene solvent was purchased

from Sigma-Aldrich and dried thoroughly over molecular sieves. The carbene ligands iPr_2Im , Me₂Im, Me₄Im^[42] and IMes^[43] were prepared according to published procedures. Elemental analyses were performed in the microanalytical laboratory of the University of Würzburg with an Elementar vario micro cube. Infrared spectra were recorded on a Bruker alpha spectrometer as solids by using an ATR unit. NMR spectra were recorded at 298 K using Bruker Avance 400 (¹H, 400.1 MHz; ¹³C, 100.6 MHz, ³¹P, 162.0 MHz) and Bruker Avance 500 (¹H, 500.1 MHz; ¹³C, 125.8 MHz, ³¹P, 202.5 MHz) spectrometers. ¹H NMR chemical shifts are listed in parts per million (ppm) and reported relative to TMS and were referenced via residual proton resonances of the deuterated solvent (C₆D₅H: 7.16 ppm (C₆D₆); C₇D₇H: 2.08, 6.97, 7.01, 7.09 ppm (tol-d₈); C₄D₇HO: 1.72, 3.58 ppm (thf-d₈); C₂D₂HN: 1.94 (CD₃CN); CHCl₃: 7.26 (CDCl₃)) whereas ¹³C{¹H} NMR spectra are reported relative to TMS using the natural-abundance carbon resonances (C₆D₆: 128.06 ppm; tol-d₈: 20.43, 125.13, 127.96, 128.87, 137.48 ppm; thf-d₈: 25.31, 67.21; CD₃CN: 1.92, 118.26; CDCl₃: 77.16).^[44]

Synthesis of (*i*Pr₂Im)PPh (1): Phenyl phosphine (2.00 g, 18.2 mmol) was added at room temperature to a solution of *i*Pr₂Im (5.80 g, 36.3 mmol) in 20 mL of toluene and the clear solution was heated to 105 °C for 3 h. All volatiles were removed in vacuo and a light orange residue was suspended in 20 mL of *n*-hexane. After filtration, the yellow solid was washed with *n*-hexane (3 x 10 mL) and dried *in vacuo* to afford 4.15 g (15.9 mmol; 88 %) of a yellow solid. ¹H NMR (400.1 MHz, C₆D₆, 298 K): δ = 0.90 (d, 12 H, ${}^{3}J_{HH}$ = 6.7 Hz, *i*Pr-CH₃), 5.06 (dsept, 2 H, ${}^{3}J_{HH}$ = 6.7 Hz, ${}^{4}J_{PH}$ = 4.0 Hz, *i*Pr-CH), 6.19 (s, 2 H, CHCH), 6.91, 7.07, 7.64 (m, 5 H, aryl-H). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, **298 K):** δ = 21.8 (s, *i*Pr-CH₃), 49.9 (d, ³J_{CP} = 10 Hz, *i*Pr-CH), 115.4 (d, ¹J_{CC} = 3 Hz, CHCH), 122.2, 128.1 (aryl-CH), 132.1 (d, ${}^{2}J_{CP}$ = 19 Hz, aryl-CH_{ortho}), 150.3 (d, ${}^{1}J_{CP}$ = 50 Hz, aryl-CH_{ipso}), 168.2 (d, ¹J_{CP} = 104 Hz, NCN). ³¹P NMR (162.0 MHz, C₆D₆, 298 **K**): δ = -59.9 (s, P). C₁₅H₂₁N₂P (260.32 g/mol): calcd.: 69.21, H 8.13, N 10.76; found: C 69.80, H 7.91, N 10.60 **HRMS LIFDI** (m/z): calculated for C₁₅H₂₁N₂P [M⁺]: 260.1437; found: 260.1429. **IR** (ATR[cm⁻¹]): 458 (m), 493 (m), 583 (w), 658 (w), 676 (s), 693 (vs, δ_{CH}), 738 (vs, δ_{CHoop}), 878 (w), 1021 (w, δ_{PAroop}), 1070 (m), 1198 (s), 1300 (m), 1370 (m, δ_{CH}), 1406 (m, δ_{CH}), 1466 (m, δ_{CH}), 1574 (m, ν_{CC}), 2010 (νw), 2183 (νw), 2970 (νw, vcн), 3050 (vw, vcн).

Synthesis of (Mes₂Im)PPh (2): Phenyl phosphine (150 mg, 1.36 mmol) was added at room temperature to a solution of Mes₂Im (871 mg, 2.86 mmol) in 12 mL of xylene and the clear solution was heated to 135 °C for 3 d. All volatiles were removed *in vacuo*

and the pale-yellow residue was suspended in 11 mL of *n*-hexane. After filtration, the yellow solid was washed with 8 mL of *n*-hexane and dried in vacuo to afford 340 mg (824 µmol; 61 %) of a yellow solid. ¹H NMR (400.1 MHz, C₆D₆, 298 K): δ = 2.03 (s, 6 H, mesityl-CH_{3para}), 2.24 (s, 12 H, mesityl-CH_{3ortho}), 5.83 (s, 2 H, CHCH), 6.57 (s, 4 H, mesityl-CH_{meta}), 6.68, 6.75 (m, 3 H, aryl-H), 7.45 (m, 2 H, aryl-H). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 18.5 (d, ⁵J_{CP} = 2.88 Hz, mesityl-CH_{3ortho}), 21.0 (s, mesityl- CH_{3para}), 118.6 (d, ${}^{3}J_{CP}$ = 3.5 Hz, CHCH), 124.8 (s, Ph- C_{para}), 126.5 (d, ${}^{3}J_{CP}$ = 3.8 Hz, Ph- C_{meta}), 129.4 (s, Mes- C_{meta}), 134.4 (s, Mes- C_{ipso}), 135.9 (d, ${}^{4}J_{CP}$ = 1.9 Hz, Mes- C_{ortho}), 137.5 (d, ${}^{2}J_{CP}$ = 14.3 Hz, Ph- C_{ortho}), 138.4 (s, Mes- C_{para}), 139.4 (d, ${}^{1}J_{CP}$ = 42.0 Hz, Ph- C_{ipso}), 169.8 (d, ¹ J_{CP} = 102.5 Hz, NCN). ³¹**P NMR** (162.0 MHz, C₆D₆, 298 K): δ = -23.7 (s, P). C₂₇H₂₉N₂P (412.52 g/mol): calcd.: 78.61, H 7.09, N 6.79; found: C 78.11, H 7.05, N 6.59. **HRMS LIFDI** (m/z): calculated for C₂₇H₂₉N₂P [M⁺]: 412.2063; found: 412.2051. IR (ATR[cm⁻¹]): 405 (w), 466 (m), 485 (m), 517 (w), 566 (m), 577 (s), 668 (m, v_{PC}), 699 (vs, δ_{CHoop}), 738 (m, δ_{CHoop}), 850 (s, δ_{CHoop}), 921 (m, δ_{CHoop}), 1031 (w), 1038 (w), 1117 (vw, v_{PAr}), 1217 (m), 1264 (w), 1290 (m), 1327 (vs), 1394 (m, δ_{CH}), 1437 (m, δ_{CH}), 1482 (s, δ_{CH}), 1590 (m, ν_{CC}), 1604 (m, ν_{CC}), 1990 (νw), 2151 (νw), 2206 (w). 2907 (vw, v_{CH}), 2942 (vw, v_{CH}), 2999 (vw, v_{CH}), 3136 (w, v_{CH}).

Synthesis of (Me₄Im)PPh (3): Phenyl phosphine (50 mg, 454 µmol) was added at room temperature to a solution of Me₄Im (119 mg, 954 µmol) in 10 mL of toluene and the clear solution was heated to 110 °C for 7 d. All volatiles were removed in vacuo and the residue was suspended in 12 mL of *n*-pentane. After filtration, the yellow solid was washed with 8 mL of *n*-pentane and dried *in vacuo* to afford 88 mg (379 µmol; 14 %, P_nPh_n impurities) of a yellow solid. ¹**H NMR** (400.1 MHz, C₆D₆, 298 K): δ = 1.25 (s, 6 H, CH₃), 3.02 (s, 6 H, NCH₃), 6.95, 7.13 (m, 3 H, aryl-H), 7.63 (m, 2 H, aryl-H). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 8.4 (s, CH₃), 33.5 (d, ³J_{CP} = 10.4 Hz, NCH₃), 122.1 (s, aryl-CH), 122.4 (d, ${}^{1}J_{CC}$ = 3.2 Hz, C=C), 127.9 (d, J_{CP} = 5.6 Hz, aryl-CH), 132.5 (d, J_{CP} = 19.0 Hz, aryl-CH), 149.6 (d, J_{CP} = 48.7 Hz, aryl-CH), 168.9 (d, ${}^{1}J_{CP}$ = 97.3 Hz, NCN). ³¹P NMR (162.0 MHz, C₆D₆, 298 K): δ = -52.9 (s, P). HRMS LIFDI (m/z): calculated for CHNP [M⁺]: 232.1124; found: 232.1121. **IR** (ATR[cm⁻¹]): 413 (w), 448 (m), 481 (s), 546 (w), 621 (vw), 662 (m), 695 (vs, δ_{CH}), 734 (vs, v_{PC}), 856 (m), 990 (w), 1021 (m, ν_{CH}), 1064 (s), 1094 (m, ν_{PAr}), 1170 (m), 1209 (wδ_{CH}), 1364 (s, δ_{CH}), 1425 (m, δ_{CH}), 1470 (m, δ_{CH}), 1576 (s, ν_{CC}), 1651 (m, ν_{CC}), 1981 (w, ν_{CC}), 2008 (w, ν_{CC}), 2151 (m, vcc), 3048 (vw, vcн).

Synthesis of (Mes₂Im)PMes (4): Mesityl phosphine (50 mg, 329 µmol) was added at room temperature to a solution of Mes₂Im (210 mg, 690 µmol) in 10 mL of xylene and the clear solution was heated to 135 °C for 12 d. All volatiles were removed in vacuo and the residue was suspended in 10 mL of *n*-pentane. After filtration, the orange solid was washed with 8 mL of n-pentane and dried in vacuo to afford 50 mg (110 µmol; 33 %) of an orange solid. ¹**H NMR** (400.1 MHz, THF-d₈, 298 K): δ = 2.03 (s, 6 H, mesityl-CH_{3para}), 2.08 (s, 6 H, mesityl-CH_{3ortho}), 2.13 (s_{br}, 3 H, mesityl-CH_{3para}), 2.29 (s, 12 H, mesityl-CH_{3ortho}), 6.34 (s, 2 H, mesityl-CH_{meta}), 6.48 (s_{br}, 2 H, mesityl-CH_{meta}), 6.66 (s, 1 H, CHCH), 6.98 (s, 1 H, CHCH), 7.02 (s, 2 H, mesityl-CH_{meta}). ¹H NMR (500.1 MHz, THF-d₈, 248 K): δ = 2.04 (s, 3 H, mesityl-CH_{3para}), 2.10 (s, 6 H, mesityl-CH_{3ortho}), 2.13 (s, 3 H, mesityl-CH_{3para}), 2.28 (s, 12 H, mesityl-CH_{3ortho}), 2.32 (s, mesityl-CH_{3para}), 6.35 (s, 2 H, mesityl-CH_{meta}), 6.48 (s, 2 H, mesityl-CH_{meta}), 6.72 (s, 1 H, CHCH), 6.85 (s, 1 H, CHCH), 7.01 (s, 2 H, mesityl-CH_{meta}). ¹³C{¹H} NMR (100.6 MHz, THF-d₈, 298 K): δ = 17.7 (d, mesityl-CH_{3ortho.} ${}^{3}J_{CP}$ = 48.5 Hz), 18.9 (s, mesityl-CH_{3para}), 21.1 (s, mesityl-CH_{3para}), 25.7 (s, mesityl-CH_{3ortho}), 124.0 (s, CHCH), 127.7 (s, mesityl-CH_{meta}), 129.5 (s, CHCH), 129.9 (s, mesityl-CH_{meta}), 134.8 (s_{br}, mesityl- C_{para}), 136.1 (d, ¹ J_{CP} = 43.0 Hz, mesityl- C_{ipso}), 144.4 (d, J = 8.9 Hz, mesityl- C_{ortho}), 170.5 (d, ${}^{1}J_{CP} = 103.2$ Hz, NCN). ³¹**P NMR** (162.0 MHz, C₆D₆, 298 K): δ = -59.0 (s, *P*). ³¹**P NMR** (202.5 MHz, THF-d₈, 298 K): δ = -60.6 (s, P). ³¹P NMR (202.5 MHz, THF-d₈, 248 K): δ = -63.2 (s, P). C₃₀H₃₅N₂P (454.60 g/mol): calcd.: 79.26, H 7.76, N 6.16; found: C 76.84, H 8.27, N 6.57. **HRMS LIFDI** (m/z): calculated for C₃₀H₃₅N₂P [M⁺]: 454.2532; found: 454.2519. **IR** (ATR[cm⁻¹]): 481 (s), 577 (m), 654 (m, ν_{PC}), 703 (vs, δ_{CHoop}), 805 (m), 842 (s), 919 (m), 1078 (s, v_{PAr}), 1113 (s, v_{PAr}), 1213 (w), 1264 (m), 1288 (s), 1321 (vs), 1390 (m, δ_{CH}), 1482 (m, δ_{CH}), 1606 (vw, v_{CC}), 2004 (m), 2061 (w), 2126 (vw), 2222 (vw), 2911 (w), 3129 (w, vcн).

Synthesis of (Me₂Im)PMes (5): Mesityl phosphine (50 mg, 329 µmol) was added at room temperature to a solution of Me₂Im (66 mg, 690 µmol) in 10 mL of toluene and the clear solution was heated to 115 °C for 7 d. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-pentane. After filtration, the yellow solid was washed with 8 mL of *n*-pentane and dried *in vacuo* to afford 43 mg (175 µmol; 53 %) of a yellow solid. ¹H NMR (400.1 MHz, C₆D₆, 298 K): δ = 2.24 (s, 3 H, mesityl-CH_{3para}), 2.67 (d, 6 H, NCH₃), 2.67 (s, 6 H, mesityl-CH_{3ortho}), 5.57 (s, 2 H, CHCH), 6.95 (s, 2 H, mesityl-CH_{meta}). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 21.2 (s, mesityl-CH_{3para}), 25.0 (d, ³J_{CP} = 12.0 Hz, mesityl-CH_{3ortho}), 35.6 (d, ³J_{CP} = 10.6 Hz, NCH₃), 118.1 (d, ${}^{3}J_{CP}$ = 3.3 Hz, CHCH), 134.3 (s, Mes- C_{para}), 138.7 (d, ${}^{1}J_{CP}$ = 44.8 Hz, Mes- C_{ipso}), 143.3 (d, ${}^{2}J_{CP}$ = 10.0 Hz, Mes- C_{ortho}), 170.4 (d, ${}^{1}J_{CP}$ = 101.2 Hz, NCN). ${}^{31}P$ NMR (162.0 MHz, C₆D₆, 298 K): δ = -73.5 (s, *P*). C₁₄H₁₉N₂P (246.29 g/mol): calcd.: 68.27, H 7.78, N 11.37; found: C 62.37, H 7.57, N 14.05. HRMS LIFDI (m/z): calculated for C₁₄H₁₉N₂P [M⁺]: 246.12870; found: 246.1275. IR (ATR[cm⁻¹]): 460 (w), 475 (m), 503 (vs), 552 (m), 570 (vs), 634 (vs), 723 (s, δ_{CH}), 752 (m, δ_{CHoop}), 846 (m, δ_{CHoop}), 1048 (m), 1097 (s, v_{PAr}), 1147 (m), 1186 (w), 1233 (m), 1329 (m, δ_{CH}), 1382 (m, δ_{CH}), 1457 (m, v_{CC}), 1568 (w, v_{CC}), 1602 (w, v_{CC}), 1924 (vw), 1963 (vw), 2169 (w).

Synthesis of (Me₄Im)PMes (6): Mesityl phosphine (50 mg, 329 µmol) was added at room temperature to a solution of Me₄Im (86 mg, 690 µmol) in 10 mL of toluene and the clear solution was heated to 110 °C for 10 d. All volatiles were removed in vacuo and the residue was suspended in 10 mL of *n*-pentane. After filtration, the solid was washed with 8 mL of *n*-pentane and dried *in vacuo* to afford 42 mg (153 µmol; 47 %) of a pale yellow solid. ¹H NMR (400.1 MHz, C₆D₆, 298 K): δ = 1.25 (s, 6 H, CCH₃), 2.28 (s, 3 H, mesityl-CH_{3para}), 2.71 (s, 6 H, mesityl-CH_{3ortho}), 2.81 (d, 6 H, ${}^{2}J_{HN}$ = 0.8 Hz, NCH₃), 7.00 (m, 2 H, mesityl-CH_{meta}). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 8.4 (s, CH₃), 21.3 (s, mesityl-CH_{3para}), 25.1 (d, ${}^{3}J_{CP}$ = 12.5 Hz, mesityl-CH_{3ortho}), 32.3 (d, ${}^{3}J_{CP}$ = 11.6 Hz, NCH₃), 120.9 (d, ${}^{1}J_{CC}$ = 3.4 Hz, CHCH), 133.6 (s, mesityl-CH), 140.5 (d, J_{CP} = 47.8 Hz, mesityl-CH), 142.6 (d, J_{CP} = 10.2 Hz, mesityl-CH), 169.5 (d, ${}^{1}J_{CP}$ = 99.6 Hz, NCN). ³¹**P NMR** (162.0 MHz, C₆D₆, 298 K): δ = -74.8 (s, *P*). **IR** (ATR[cm⁻¹]): 403 (w), 450 (vs), 479 (vs), 517 (w), 564 (m), 617 (m), 636 (w, vpc), 699 (m, vch), 725 (m, v_{CH}), 829 (w, δ_{CHoop}), 850 (s, δ_{CHoop}), 1046 (s, v_{CH}), 1092 (vs, v_{PAr}), 1194 (vs), 1384 (m, δ_{CH}), 1449 (m, δ_{CH}), 1574 (s, v_{CC}), 1651 (w), 1994 (m), 2049 (m), 2141 (s, v_{CC}), 2194 (m, vcc), 2208 (m, vcc), 2518 (w), 2840 (w, vcн), 2875 (w, vcн), 3615 (w).

Synthesis of (*i*Pr₂Im)PMes (7): Mesityl phosphine (200 mg, 1.31 mmol) was added at room temperature to a solution of *i*Pr₂Im (420 mg, 2.76 mmol) in 10 mL of xylene and the clear solution was heated to 135 °C for 5 d. All volatiles were removed *in vacuo* and the sticky residue was washed with *n*-hexane (3 x 10 ml) and dried *in vacuo* to afford a sticky orange oil. ¹H NMR (400.1 MHz, C₆D₆, 298 K): δ = 0.90 (d, 12 H, ³*J*_{HH} = 6.7 Hz, *i*Pr-CH₃), 2.24 (s, 3 H, mesityl-CH_{3para}), 2.72 (s, 6 H, mesityl-CH_{3ortho}) 4.69 (dsept, 2 H, ³*J*_{HH} = 4.1 Hz, ⁴*J*_{PH} = 2.6 Hz, *i*Pr-CH), 6.12 (s, 2 H, CHCH), 6.97 (s, 2 H, mesityl-CH_{meta}). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): 21.2 (s, mesityl-CH_{3para}), 21.6 (s, *i*Pr-CH₃), 25.0 (d, ³*J*_{CP} = 12.2 Hz, mesityl-CH_{3ortho}), 49.0 (d, ³*J*_{CP} = 11.1 Hz, *i*Pr-CH), 114.3 (d, ¹*J*_{CC} = 3.6 Hz, CHCH), 128.5 (s, mesityl-CH_{meta}), 133.7 (s, mesityl-C_{para}), 140.4 (d, ${}^{1}J_{CP}$ = 48.4 Hz, mesityl- C_{ipso}), 142.6 (d, ${}^{2}J_{CP}$ = 10.4 Hz, mesityl- C_{meta}), 168.4 (d, ${}^{1}J_{CP}$ = 105.0 Hz, NCN). ³¹**P NMR** (162.0 MHz, C₆D₆, 298 K): δ = -79.5 (s, *P*).

Synthesis of (*iPr*₂Im)PH (8): tert-Butyl phosphine (169 mg, 1.88 mmol) was added at room temperature to a solution of *i*Pr₂Im (600 mg, 3.94 mmol) in 10 mL of xylene and the clear solution was heated to 125 °C for 5 d. All volatiles were removed in vacuo and the residue was suspended in 10 mL of *n*-hexane. After filtration, the solid was washed with 8 mL of n-hexane and dried in vacuo to afford 97 mg (530 µmol; 28 %) of a pale vellow solid. ¹H NMR (400.1 MHz, C₆D₆, 298 K): δ = 0.95 (d, 12 H, ³J_{HH} = 6.7 Hz, $iPr-CH_3$), 2.64 (d, 1 H, $^{1}J_{PH}$ = 166.1 Hz, PH), 4.49 (dsept, 2 H, $^{3}J_{HH}$ = 6.7 Hz, $^{4}J_{PH}$ = 2.7 Hz, iPr-CH), 6.09 (s, 2 H, CHCH). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 21.1 (s, $iPr-CH_3$), 48.8 (d, ${}^{3}J_{CP}$ = 7.9 Hz, iPr-CH), 113.1 (d, ${}^{3}J_{CP}$ = 3.0 Hz, CHCH), 173.7 (d, ${}^{1}J_{CP}$ = 92.9 Hz, NCN). ${}^{31}P{}^{1}H$ NMR (162.0 MHz, C₆D₆, 298 K): δ = -149.9 (s, *P*). ³¹**P** NMR (162.0 MHz, C₆D₆, 298 K): δ = -149.9 (d, ¹J_{PH} = 166.1 Hz, *P*H). C₉H₁₇N₂P (184.22 g/mol): calcd.: 58.68, H 9.30, N 15.21; found: C 58.67, H 9.30, N 15.02. HRMS **LIFDI** (m/z): calculated for C₉H₁₇N₂P [M⁺]: 184.1124; found: 184.1122. **IR** (ATR[cm⁻¹]): 460 (vs), 638 (s, v_{PC}), 670 (m, δ_{CHoop}), 736 (s, δ_{CHoop}), 884 (s, v_{PH}), 1066 (s), 1131 (m), 1174 (m), 1217 (s), 1329 (m, δ_{CH}), 1364 (s, δ_{CH}), 1408 (vs, δ_{CH}), 1464 (w), 1566 (w), 2179 (vw), 2302 (m, v_{PH}), 2968 (m, v_{CH}), 3070 (m, v_{CH}).

Synthesis of (Mes₂Im)PH (9): tert-Butyl phosphine (50 mg, 555 µmol) was added at room temperature to a solution of Mes₂Im (355 mg, 1.17 mmol) in 10 mL of xylene and the clear solution was heated to 135 °C for 5 d. All volatiles were removed in vacuo and the residue was suspended in 10 mL of *n*-hexane. After filtration, the off-white solid was washed with 8 mL of *n*-hexane and dried in vacuo to afford 132 mg (392 µmol; 71 %) of an off-white solid. ¹H NMR (400.1 MHz, C₆D₆, 298 K): δ = 2.07 (d, 1 H, ¹J_{PH} = 164 Hz, PH), 2.09 (s, 6 H, mesityl-CH_{3para}), 2.21 (s, 12 H, mesityl-CH_{3ortho}), 5.92 (s, 2 H, CHCH), 6.76 (s, 4 H, mesityl-CH_{meta}). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 18.2 (d, ${}^{5}J_{CP}$ = 1.9 Hz, mesityl-CH_{3ortho}), 21.1 (s, mesityl-CH_{3para}), 117.7 (d, mesityl-CH, J_{CP} = 2.9 Hz), 129.8 (s, mesityl-CH_{meta}), 134.7 (s, mesityl-CH), 136.5 (s, CHCH), 138.9 (s, mesityl-CH), 176.3 (d, NCN, ${}^{1}J_{CP}$ = 85.4 Hz). ${}^{31}P{}^{1}H$ NMR (162.0 MHz, C₆D₆, 298 K): δ = -147.2 (s, *P*). ³¹**P NMR** (162.0 MHz, C₆D₆, 298 K): δ = -147.2 (d, ¹J_{PH} = 164 Hz, *P*H). C₂₁H₂₅N₂P (336.42 g/mol): calcd.: 74.98, H 7.49, N 8.33; found: C 71.47, H 7.17, N 7.65. **HRMS LIFDI** (m/z): calculated for C₂₁H₂₅N₂P [M⁺]: 336.1750; found: 336.1738. **IR** (ATR[cm⁻¹]):477 (m), 501 (m), 572 (s), 603 (m), 666 (s, ν_{PC}), 697 (vs, δ_{CHoop}), 762 (m, δ_{CHoop}), 852 (vs), 872 (s), 929 (w, v_{PH}), 1033 (m), 1099 (m), 1143 (w), 1225 (vs), 1339 (vs, δ_{CH}), 1355 (vs, δ_{CH}), 1398 (m, δ_{CH}), 1437 (m, δ_{CH}), 1484 (s, δ_{CH}), 1588 (m, v_{CC}), 2269 (m, v_{PH}), 2913 (vw, v_{CH}), 2944 (vw, v_{CH}), 3021 (vw, v_{CH}), 3138 (vw).

Synthesis of (Me₄Im)PH (10): *tert*-Butylphosphine (50 mg, 555 µmol) was added at room temperature to a solution of Me₄Im (145 mg, 1.17 mmol) in 10 mL of toluene and was heated to 110 °C for 5 d. All volatiles were removed in vacuo and the residue was suspended in 10 mL of *n*-pentane. After filtration, the solid was washed with 8 mL of *n*-pentane and dried *in vacuo* to afford 44 mg (282 µmol; 51 %) of a colorless solid. ¹H **NMR** (400.1 MHz, C₆D₆, 298 K): δ = 1.26 (s, 6 H, CH₃), 2.49 (d, 1 H, ¹J_{PH} = 165 Hz, PH), 2.84 (s, 6 H, NCH₃). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 8.4 (s, CH₃), 31.6 (d, ${}^{3}J_{CP}$ = 7.8 Hz, NCH₃), 120.2 (d, ${}^{1}J_{CC}$ = 3.1 Hz, CHCH), 174.6 (d, ${}^{1}J_{PC}$ = 88.0 Hz, NCN). ³¹P{¹H} NMR (162.0 MHz, C₆D₆, 298 K): δ = -149.9 (s, P). ³¹P NMR (162.0 MHz, C₆D₆, 298 K): δ = -149.9 (d, ¹J_{PH} =165 Hz, *P*H). C₇H₁₃N₂P (156.17 g/mol): calcd.: 53.84, H 8.39, N 17.94; found: C 51.22, H 7.98, N 16.64. HRMS LIFDI (m/z): calculated for C₇H₁₃N₂P [M⁺]: 156.0811; found: 156.0809. **IR** (ATR[cm⁻¹]): 436 (s), 481 (m), 621 (w), 833 (w, δ_{CHoop}), 921 (m, δ_{PHoop}), 1064 (m, ν_{CH}), 1099 (s, ν_{CC}), 1164 (m), 1209 (m, δ_{CH}), 1260 (vw, δ_{CH}), 1345 (m, δ_{CH}), 1384 (vs, δ_{CH}), 1433 (m), 1457 (m), 1576 (m, v_{CC}), 1663 (w, v_{CC}), 2014 (vw), 2155 (vw, v_{CC}), 2208 (vw, v_{CC}), 2293 (m, v_{PH}), 3019 (vw, νсн).

Synthesis of *i***Pr**₂**Im**–**P(O)**₂**Ph (11):** A solution of (*i***Pr**₂**Im**)**PPh (1) (100 mg, 384 µmol,** 1.0 eq) in 5 mL toluene was thoroughly stirred under an atmosphere of 0.5 bar O₂ at room temperature for 1 h. The resulting solid was filtered off, washed with n-hexane (3x 5 mL) and dried in vacuo. Yield : 61.2 mg (209 µmol, 55%) of a colorless solid. ¹H **NMR (500.1 MHz, CD₃CN, 298 K):** $\delta = 1.31$ (d, 12 H, ³J_{HH} = 6.8 Hz, *i*Pr-CH₃), 6.28 (sept, 2 H, ³J_{HH} = 6.8 Hz, *i*Pr-CH), 7.43 (d, 2 H, ⁴J_{HP} = 1.2 Hz, CHCH), 7.38 – 7.43 (m, 3 H, aryl-H), 7.71 – 7.77 (m, 2 H, aryl-H) ppm. ¹³C{¹H} NMR (125.8 MHz, CD₃CN, **298 K):** δ = 23.3 (*i*Pr-CH₃), 51.5 (*i*Pr-CH), 120.3 (d, ³J_{CP} = 3.6 Hz, CHCH), 129.2 (d, ${}^{2}J_{CP}$ = 12.7 Hz, aryl-CH), 131.6 (d, ${}^{4}J_{CP}$ = 2.8 Hz, aryl-CH), 132,2 (d, ${}^{3}J_{CP}$ = 9.8 Hz, aryl-CH), 140.8 (d, ${}^{1}J_{CP}$ = 145.6 Hz, aryl-CP), 147.9 (d, ${}^{1}J_{CP}$ = 94.5 Hz, NCN) ppm. ³¹P{¹H} NMR (202.5 MHz, CD₃CN, 298 K): δ = -0.8 (s) ppm. ³¹P NMR (202.5 MHz, **CD₃CN**, **298 K**): δ = -0.8 (t, ³J_{PH} = 12.3 Hz, *P*) ppm. C₁₅H₂₁N₂PO₂ (292.32 g/mol): calcd.: 61.63, H 7.24, N 9.58; found: C 61.09, H 7.23, N 9.17. HRMS LIFDI (m/z): calculated for C₁₅H₂₁N₂PO₂: 292.3188; found [M+H⁺]: 293.1413. **IR** (ATR[cm⁻¹]): 436 (m), 447 (w), 494 (m), 555 (s), 579 (s), 614 (w), 630 (w), 673 (vs), 699 (s), 743 (w), 765 (w), 787 (vw), 881 (vw), 995 (vw), 1024 (vw), 1071 (vw), 1092 (w), 1136 (w), 1158

(vw), 1173 (vw), 1201 (m), 1305 (vw), 1373 (vw), 1399 (vw), 1419 (vw), 1436 (w), 1462 (vw), 1562 (vw), 2297 (vw), 2929 (vw), 2980 (vw), 3045 (vw), 3078 (vw), 3100 (vw), 3139 (vw), 3182 (vw).

Synthesis of *i*Pr₂Im-P(S)₂Ph (12): A solution of (*i*Pr₂Im)PPh (1) (100 mg, 384 µmol) and S₈ (14.0 mg, 436 µmol) in 5 mL THF was heated for 24 h at 65°C. The precipitate was filtered off and washed with THF (3x 5 mL) and n-hexane (1x 5 mL). The product was dried in vacuo to afford 41.2 mg (126 µmol, 33%) of a light yellow solid.¹H NMR (500.1 MHz, CDCI₃, 298 K): δ = 1.28 (d, 12 H, ³J_{HH} = 6.8 Hz, ^{*i*}Pr-CH₃), 6.08 (sept, 2 H, ${}^{3}J_{HH}$ = 6.6 Hz, ^{*i*}Pr-CH), 7.16 (d, 2 H, ${}^{4}J_{PH}$ = 1.1 Hz, CHCH), 7.41 – 7.48 (m, 3 H, aryl-H), 8.19- 8.27 (m, 2 H, aryl-H) ppm.¹³C{¹H} NMR (125.8 MHz, CDCl₃, 298 K): δ = 23.0 (s, *i*Pr-CH₃), 51.2 (d, ${}^{3}J_{CP}$ = 1,0 Hz, *i*Pr-CH), 118.5 (d, ${}^{3}J_{CP}$ = 1.2 Hz, CHCH), 128.4 (d, ${}^{2}J_{CP}$ = 13.6 Hz, aryl-CH), 131.0 (d, ${}^{4}J_{CP}$ = 3.4 Hz, aryl-CH), 131.1 (d, ${}^{3}J_{CP}$ = 12.0 Hz, aryl-CH), 142.3 (d, ${}^{1}J_{CP}$ = 91.0 Hz, aryl-CP), 146.9 (d, ${}^{1}J_{CP}$ = 38.9 Hz, NCN) ppm. ³¹P{¹H} NMR (202.5 MHz, CDCI₃, 298 K): $\delta = 53.9$ (s) ppm. ³¹P NMR (202.5 MHz, **CDCI₃**, **298** K): $\delta = 53.9$ (t, ³ $J_{PH} = 14.7$ Hz, P) ppm. C₁₅H₂₁N₂PS₂ (324.44 g/mol): calcd.: 55.53, H 6.52, N 8.63; found: C 55.25, H 6.72, N 8.55. HRMS LIFDI (m/z): calculated for C₁₅H₂₁N₂PS₂ [M⁺]: 324.0884; found: 324.0878. **IR** (ATR[cm⁻¹]): 410 (vw),432 (vw), 461 (w), 524 (vs), 548 (vs), 589 (vw), 669(vw), 702 (s), 722 (vw), 754 (w), 803 (w), 885 (m), 907 (vw), 940 (vw), 979 (vw), 1003 (vw), 1024 (vw), 1050 (m), 1067 (m), 1081 (w), 1132 (m), 1150 (vw), 1179 (w), 1213 (w), 1252 (s), 1350 (w), 1373 (vw), 1393 (vw), 1417 (vw), 1434 (vw).

Synthesis of (*i*Pr₂Im)Se (13): A suspension of (*i*Pr₂Im)PPh (1) (100 mg, 384 μmol) and black selenium (30.3 mg, 384 μmol) in 5 mL toluene was heated for 24 h at 85°C. The resulting Solution was filtered off and all volatiles were removed *in vacuo*. The remaining residue was suspended in 5 mL *n*-hexane. The suspension was filtered off, washed *n*-hexane (2x 5 mL) and dried *in vacuo* to afford 38.3 mg (165 μmol, 43%) of a colorless solid. ¹H NMR (500.1 MHz, CDCl₃, 298 K): δ = 1.39 (d, 12 H, ³*J*_{HH} = 6.9 Hz, *i*Pr-C*H*₃), 5.30 (sept, 2 H, ³*J*_{HH} = 6.8 Hz, *i*Pr-C*H*), 6.92 (s, 2 H, C*H*C*H*) ppm.¹³C{¹H} NMR (125.8 MHz, CDCl₃, 298 K): δ = 22.2 (s, *i*Pr-CH₃), 50.7 (s, *i*Pr-CH), 115.4 (s, CHCH), 153.5 (s, NCN) ppm. ⁷⁷Se{¹H} NMR (95.4 MHz, CDCl₃, 298 K): δ = -19.7 (s) ppm. C₉H₁₆N₂Se (231.21 g/mol): calcd.: 46.75, H 6.98, N 12.12; found: C 49.97, H 6.16, N 8.26. HRMS LIFDI (m/z): calculated for C₁₅H₂₁N₂Se [M ⁺]: 232.0479 found: 232.0474.

Synthesis of (*i*Pr₂Im)Te (14): A suspension of (*i*Pr₂Im)PPh (1) (100 mg, 384 µmol) and amorphous tellurium (75.0 mg, 588 µmol) in 5 mL toluene was heated for 24 h at 85°C. The resulting solution was filtered and all volatiles of the filtrate were removed *in vacuo*. The remaining residue was suspended in 5 mL hexane, filtered and washed with n-hexane (2x 5mL) and dried *in vacuo* to afford 27.4 mg (98.0 µmol, 26%) of an off-white solid. ¹H NMR (500.1 MHz, C₆D₆, 298 K): δ = 0.93 (d, 12 H, ³*J*_{HH} = 6.8 Hz, *i*Pr-C*H*₃), 5.45 (sept, 2 H, ³*J*_{HH} = 6.8 Hz, *i*Pr-C*H*), 6.26 (s, 2 H, C*H*C*H*) ppm. ¹³C{¹H} NMR (125.8 MHz, C₆D₆, 298 K): δ = 21.8 (s, *i*Pr-CH₃), 54.0 (s, *i*Pr-CH), 116.7 (s, CHCH), 131.5 (s, NCN) ppm. ¹²³Te{¹H} NMR (130.9 MHz, C₆D₆, 298 K): δ = -184.6 (s, *Te*) ppm. C₉H₁₆N₂Te (279.84 g/mol): calcd.: 38.63, H 5.76, N 10.01; found: C 40.62, H 6.16, N 8.26. HRMS LIFDI (m/z): calculated for C₁₅H₂₁N₂Te [M ⁺]: 282.0376; found: 282.03693.

Synthesis of [(W(CO)₅){(*i*Pr₂Im)PPh}] (15): W(CO)₆ (135 mg, 384 µmol) was suspended in THF (7 mL) and irradiated with UV light for 16 h. To this solution, (*i*Pr₂Im)PPh (**1**) (100 mg, 384 µmol) dissolved in THF (5 mL) was added. The reaction mixture stirred at room temperature overnight. All volatiles were removed in vacuo and the residue was suspended in 10 mL of *n*-pentane. After filtration, the solid was washed with *n*-pentane (2 x 6 mL) and dried *in vacuo* to afford 122 mg (208 µmol; 54 %) of a yellow solid. ¹**H NMR** (400.1 MHz, C₆D₆, 298 K): δ = 0.80 (d, 12 H, ³J_{HH} = 6.7 Hz, ^{*i*}Pr-CH₃), 4.98 (dsept, 2 H, Pr-CH), 6.00 (s, 2 H, CHCH), 7.02 (m, 3 H, aryl-H), 7.63 (m, 2 H, aryl-H). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 22.2 (s, ^{*i*}Pr-CH₃), 50.9 (d, ³J_{CP}) = 12.9 Hz, iPr-CH), 117.3 (d, ${}^{1}J_{CC}$ = 2.2 Hz, CHCH), 126.1 (d, ${}^{4}J_{CP}$ = 1.1 Hz, aryl- CH_{para}), 128.7 (d, ${}^{3}J_{CP}$ = 4.0 Hz, aryl- CH_{meta}), 135.3 (d, ${}^{2}J_{CP}$ = 15.6 Hz, aryl- CH_{ortho}), 141.0 (d, ${}^{1}J_{CP}$ = 26.3 Hz, aryl- C_{ipso}), 164.3 (d, ${}^{1}J_{CP}$ = 86.4 Hz, NCN), 200.5 (d, ${}^{2}J_{CP}$ = 4.1 Hz, CO). ³¹**P** NMR (162.0 MHz, C₆D₆, 298 K): δ = -80.9 (m, ¹J_{PW} = 112.3 Hz, P). C₂₀H₂₁N₂O₅PW (584.21 g/mol): calcd.: 41.12, H 3.62, N 4.80; found: C 40.97, H 3.16, N 4.02. **HRMS LIFDI** (m/z): calculated for $C_{20}H_{21}N_2O_5PW$ [M⁺]: 584.0692; found: 584.0685. **IR** (ATR[cm⁻¹]): 405 (m), 438 (m), 491 (m), 579 (s), 605 (m), 691 (m), 738 (s, v_{CH}), 801 (m, δ_{CHoop}), 1023 (w), 1131 (vw), 1194 (vw), 1207 (m), 1260 (w), 1319 (vw), 1370 (w), 1396 (w), 1431 (m), 1464 (w), 1561 (w), 1578 (w), 1810 (vs, vco), 1833 (vs, vco), 1855 (s, vco), 1880 (s), 1969 (s), 1996 (m), 2051 (w, vcc), 2968 (vw), 3140 (vw, v_{CH}), 3168 (vw, v_{CH}).

Synthesis of $[Co(CO)_2(NO){(iPr_2Im)PPh}]$ (16): A solution of $(iPr_2Im)PPh$ (1) (224 mg, 861 µmol) in 6 mL THF was added to a pre-cooled (-78°C) solution of

[Co(CO)₃(NO)] (149 mg, 861 µmol) in 6 mL THF. The mixture was allowed to warm up to room temperature and the solvent was removed under vacuum. The residue was suspended in *n*-pentane and filtered and the remaining solid was washed with *n*pentane (2x 5 mL) and dried in vacuo to afford 144 mg (357 µmol, 42%) of a red solid.¹H NMR (500.1 MHz, C₆D₆, 25 °C): δ = 0.81 (d, 12 H, ³J_{HH} = 6.7 Hz, *i*Pr-CH₃), 5.02 (d_{sept}, 2 H, ³J_{HH} = 6.7 Hz, ⁴J_{PH} = 1.35 Hz, *i*Pr-CH), 6.07 (d_{br}, 2 H, CHCH), 6.59 -6.99 (m, 1 H, *p*-CH_{Ar}), 7.04 – 7.07 (m, 2 H, *o*-CH_{Ar}), 7.46 – 7.67 (m, 2 H, *m*-CH_{Ar}) ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K): δ = 22.3 (*i*Pr-CH₃), 50.9 (d, ³J_{PC} = 12.4 Hz, *i*Pr-CH), 117.6 (d, ⁴J_{PC} = 2.24 Hz, CHCH), 125.5 (d, ⁴J_{PC} = 1.24 Hz, *p*-CH_{Ar}), 128.4 (o-CH_{Ar}), 133.9 (d, ${}^{3}J_{PC}$ = 15.4 Hz, *m*-CH_{Ar}), 144.1 (d, ${}^{1}J_{PC}$ = 31.9 Hz, q.-C_{Ar}), 163.7 (d, ${}^{1}J_{PC}$ = 91.2 Hz, NCN), the carbonyl carbon atom were not detected. ${}^{31}P$ NMR (202 **MHz, C₆D₆)** δ = -45.5 (br, *P*). C₁₇H₂₁CoN₃O₃P (405.3 g/mol): calcd.: 50.38, H 5.22, N 11.97; found: C 49.55, H 5.35, N 9.93. HRMS LIFDI (m/z): [M]+ for C₁₇H₂₁CoN₃O₃P calcd.: 405.0647, found: 405.0639. **IR (ATR):** $\tilde{\nu}$ [cm⁻¹] = 499 (vs), 581 (vs), 670 (m), 699 (vs), 744(vs), 801 (w), 833 (w), 1023 (m), 1066 (m), 1135 (m), 1176 (m), 1209 (s), 1374 (m), 1435 (m), 1464 (m), 1560 (m), 1576 (m), 1694 (vs, $v_{N=0, str.}$), 1925 (vs, $v_{C=1}$ O, str.(B1)), 1992 (vs, ν_{C≡O}, str.(A1)), 2873 (w, ν_{C-H}, str.), 2934 (w, ν_{C-H}, str.), 2981 (m, ν_{C-H}, str.), 3059 (w, v_{C-H, str.}), 3144 (w, v_{C-H, str.}), 3171 (w, v_{C-H, str.}).

Synthesis of $[(\eta^5-C_5Me_5)Co(C_2H_4){iPr_2Im}PPh]$ (17): $(iPr_2Im)PPh$ (1) (157 mg, 599 μ mol) was added to a solution of $[(\eta^5-C_5Me_5)Co(C_2H_4)_2]$ (150 mg, 599 μ mol) in 15 mL toluene at room temperature and the mixture was stirred for additional 16 h. Immediately the formation of gaseous C_2H_4 and a color change to red was observed. The solvent was removed and the residue was suspended in 5 mL *n*-pentane, filtered off and washed with *n*-pentan (2x 5 mL) and dried in vacuo to afford 98.3 mg (203.7 µmol, 34%) of a dark brown solid.¹H NMR (500.1 MHz, C₆D₆, 298 K): δ = 0.71 (d_{br}, 2 H, n^2 -C₂H₄), 0.95 (d, 12 H, ³J_{HH} = 6.59 Hz, *i*Pr-CH₃), 1.37 (d, 2 H, ³J_{HH} = 8.08 Hz, n^2 - C_2H_4), 1.93 (s, 15 H, η^5 - $C_5(CH_3)_5$), 4.57 (sept, 2 H, $^3J_{HH}$ = 5.80 Hz, *i*Pr-CH), 6.04 (d_{br}, 2 H, CHCH), 7.05 – 7.09 (m, 1 H, p-CH_{Ar}.), 7.19 – 7.23 (m, 2 H, m-CH_{Ar}.), 8.30 – 8.33 (m, 2 H, o-CH_{Ar}.) ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆, 25 °C): δ = 9.88 (d, ³J_{PC} = 5.07 Hz, η⁵-C₅(CH₃)₅), 22.5 (*i*Pr-CH₃), 28.2 (η²-C₂H₄), 49.1 (d, ²J_{PC} = 12.7 Hz, *i*Pr-CH), 87.9 $(d, {}^{2}J_{PC} = 3.02 \text{ Hz}, n^{5}-C_{5}\text{Me}_{5}), 116.3 (d, {}^{3}J_{PC} = 2.73 \text{ Hz}, CHCH), 125.5 (d, {}^{4}J_{PC} = 0.9 \text{ Hz}, 125.5 \text{ Hz}, 125$ *p*-CH_{Ar}.), 127.6 (d, ³*J*_{PC} = 3.24 Hz, *m*-CH_{Ar}.), 136.4 (d, ²*J*_{PC} = 14.6 Hz, *o*-CH_{Ar}.), 142.3 $(d, {}^{1}J_{PC} = 33.2 \text{ Hz}, q-C_{Ar}), 163.7 (d, {}^{1}J_{PC} = 98.5 \text{ Hz}, \text{ NCN}). {}^{31}P \text{ NMR} (202 \text{ MHz}, C_{6}D_{6})$ δ = 25.8 (br, P). C₂₇H₄₀CoN₂P (482.53 g/mol): calcd.: 67.21, H 8.36, N 5.81; found: C 66.55, H 8.31, N 5.36. **HRMS LIFDI** (m/z): [M]+ for C₂₇H₄₀CoN₂P calcd.: 482.2246, found: 482.2256.

Synthesis of $[Ni(iPr_2Im)_2(n^2-PhP=PPh)]$ (18): $[Ni(COD)_2]$ (80 mg, 291 µmol) and (*i*Pr₂Im)PPh (1) (151 mg, 580 µmol) were dissolved in 9 mL of toluene at room temperature. The reaction mixture was stirred at room temperature for 2 d and additionally for 1 d at 80°C. All volatiles were removed in vacuo and the residue was suspended in 10 mL of *n*-hexane. After filtration, the solid was washed with 7 mL of *n*hexane and dried *in vacuo* to afford 76 mg (131 µmol; 45 %) of a brown solid. ¹H NMR (400.1 MHz, Toluol-*d*₈, 298 K): δ = 0.49 (s_{br}, 6 H, ^{*i*}Pr-CH₃), 0.86 (s_{br}, 6 H, ^{*i*}Pr-CH₃), 1.02 (sbr, 6 H, Pr-CH₃), 1.57 (sbr, 6 H, Pr-CH₃), 4.68 (sbr, 2 H, Pr-CH), 5.64 (sbr, 2 H, Pr-CH), 6.40 (s_{br}, 4 H, CHCH), 6.85-6.93 (m, 4 H, aryl-CH), 7.59-7.64 (m, 4 H, aryl-CH). ¹**H NMR** (500.1 MHz, Toluol- d_8 , 248 K): δ = 0.47 (d, 6 H, *P*r-CH₃), 0.89 (d, 6 H, *P*r-CH₃), 0.95 (d, 6 H, ^{*i*}Pr-CH₃), 1.57 (d, 6 H, ^{*i*}Pr-CH₃), 4.77 (m, 2 H, ^{*i*}Pr-CH), 5.66 (m, 2 H, Pr-CH), 6.28 (s, 2 H, CHCH), 6.36 (s, 2 H, CHCH), 6.92-6.96 (m, 4 H, aryl-CH), 7.04-7.06 (m, 2 H, aryl-CH), 7.67-7.69 (m, 4 H, aryl-CH). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 22.7 (s_{br}, ⁱPr-CH₃), 24.9 (s_{br}, ⁱPr-CH₃), 51.3 (s_{br}, ⁱPr-CH), 52.2 (s_{br}, ⁱPr-CH), 116.4 (s_{br}, CHCH), 124.0 (s, aryl-CH_{para}), 127.5 (t, aryl-CH_{meta}), 134.0 (t, N = $|^{2}J_{CP}$ $+ {}^{3}J_{CP}$ = 26.0 Hz), 148.5 (t, N = $|{}^{1}J_{CP} + {}^{2}J_{CP}|$ = 37.0 Hz, aryl- C_{ipso}), 193.9 (t, ${}^{2}J_{CP}$ = 8.3 Hz). ³¹**P NMR** (162.0 MHz, C₆D₆, 298 K): δ = -40.9 (s, *P*). ³¹**P NMR** (162.0 MHz, Toluol d_{8} , 298 K): $\delta = -42.9$ (s, P). $C_{30}H_{42}N_4P_2N_1$ (579.33g/mol): calcd.: 62.20, H 7.31, N 9.67; found: C 62.41, H 7.68, N 9.63. **HRMS LIFDI** (m/z): calculated for C₃₀H₄₂N₄P₂Ni [M⁺]: 578.2233; found: 578.2221. **IR** (ATR[cm⁻¹]): 477 (m), 536 (vw), 570 (vw), 674 (m), 689 (s), 734 (s), 791 (w, δ_{CHoop}), 878 (w, δ_{CHoop}), 1019 (m, δ_{CHip}), 1129 (w), 1211 (vs), 1286 (m), 1366 (m), 1402 (m), 1464 (m), 1574 (m), 1928 (w), 1981 (w), 2022 (w), 2079 (w), 2157 (m), 2179 (w), 2247 (w), 2308 (vw), 2964 (m, vcн), 2974 (m, vcн), 3042 (vw, vcн).

Crystallographic Details

Crystals were immersed in a film of perfluoropolyether oil on a nylon fiber and transferred to a Bruker D8 Apex-1 diffractometer with CCD area detector and graphite-monochromated Mo-K_{α} radiation or a Bruker D8 Apex-2 diffractometer with CCD area detector and graphite-monochromated Mo-K_{α} radiation equipped with an Oxford Cryosystems low-temperature device or a Rigaku XtaLAB Synergy-DW diffractometer with HyPix-6000HE detector and monochromated Cu-*K*_{α} equipped with an Oxford Cryo 800 cooling unit. Data were collected at 100 K. The images were processed with the

Bruker or Crysalis software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. The structures were solved by using the ShelXTL software package.^[45] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were usually assigned to idealized positions and were included in structure factors calculations. Crystal data collection and processing parameter are given in Table 3. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.s CCDC 2041355 (**6**), CCDC 2041356 (**8**), CCDC 2041357 (**12**), CCDC 2041358 (**14**).

Chemical formula	(Me ₄ Im)PMes (6) C ₁₆ H ₂₃ N ₂ P 274 33	(<i>i</i> Pr ₂ Im)PH (8) C ₉ H ₁₇ N ₂ P 184.21	(<i>i</i> Pr ₂ Im)PS ₂ Ph (12) C ₁₉ H ₂₉ N ₂ POS ₂ 396.53	$(i Pr_2 Im) Te (14)$ $C_9 H_{16} N_2 Te$ 279.84			
Temperature [K]	$\frac{1}{2} \frac{1}{2} \frac{1}$		100.00(10)	100(2)			
Wavelength $\begin{bmatrix} \lambda \end{bmatrix}$ 0 71073		0.71073	1.54184	154184			
Crustel system	0.71075	orthorhombic	monoclinic	1.54104			
	crystal system monoclinic		$P2_1/c$				
Space group	C_{c}	8 491(2)	7.99220(10)	P1 7 5231(4)			
	13,032(3)	11 146(3)	15 19500(10)	10.7141(5)			
b [A]	13.032(3)	11.140(3)	17.19500(10)	10.7141(3) 14.6650(8)			
<i>c</i> [A]	12.130(3)	11./94(3)	17.31040(10)	14.0030(8)			
α [°]	90	90	90	85.975(4)			
eta[°]	97.963	90	94.0170(10)	/5.485(4)			
γ [°]	90	90	90	81.3058(4)			
Volume [Å ³]	1512.7(7)	1116.2(5)	2097.76(3)	1128.39(10)			
Ζ	4	4	4	4			
Density [g·cm ⁻³]	1.205	1.096	1.256	1.647			
Abs. coeff. [mm ⁻¹]	0.171	0.202	3.088	20.442			
F (000)	592	400	848	544			
Theta range θ [°]	2.644-26.738	2.514-26.825	2.9040-76.7090	3.120-77.508			
Refl. collected	5893	10509	22314	23066			
Indep. reflections	2319	2402	4281	4713			
Refl. $[I > 2\sigma(I)]$	2212	2134	3973	4260			
R _{int}	0.0296	0.0413	0.0370	0.0604			
Data	2319	2402	4281	4713			
Restraints	2	0	363	0			
Parameter	179	118	306	225			
$\frac{R1}{wR2} \text{ for } [I > 2\sigma(I)]$	0.0289 / 0.0693	0.0438 / 0.1039	0.0304 / 0.0796	0.0405 / 0.1102			
R1/wR2 (all data)	0.0315 / 0.0706	0.0517 / 0.1071	0.0327 / 0.0812	0.0442 / 0.1133			
diff. peak / hole [eÅ ⁻ ³]	0.235 / -0.199	0.982 / -0.218	0.367 / -0.296	1.598 / -1.055			
GooF	1.046	1.064	1.044	1.113			
CCDC	2041355	2041356	2041357	2041358			

Table 3. Crystal data collection and processing parameter for the molecular structure determination of the compounds 6, 8, 12 and 14.

Computational Details

Calculations have been performed using the TURBOMOLE V7.2 program suite, a development of University of Karlsruhe and the Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.^[46] Geometry optimizations were performed using (RI-)DFT calculations^[47] on a m4 grid employing the BP86^[48] functional and a def2-TZVP basis set for titanium and for all other atoms the def2-TZVP basis sets.^[49] Vibrational frequencies were calculated at the same level with the AOFORCE^[50] module and all structures represented true minima without imaginary frequencies. Cartesian coordinates of the compounds are provided in the SI.

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Keywords: N-Heterocyclic Carbenes • Phosphinidenes • Dehydrocoupling • Transition Metal Complexes.

References

[1] a) U. Schmidt, Angew. Chem. 1975, 87, 535-540; Angew. Chem. Int. Ed. 1975, 15, 523-528; b) F. Mathey, Dalton Trans. 2007, 19, 1861-1868.

[2] a) F. Mathey, Angew. Chem. 1987, 99, 285-296; Angew. Chem. Int. Ed. 1987, 26, 275-286; b) H. Aktas, J. C. Slootweg, K. Lammertsma, Angew. Chem. 2010, 122, 2148-2159; Angew. Chem. Int. Ed. 2010, 49, 2102-2113; c) F. Mathey, N. Huy, A. Marinetti, Helv. Chim. Acta 2001, 17, 2938-2957; d) M. Vlaar, K. Lammertsma, Eur. J. Org. Chem. 2002, 7, 1127-1138; e) A. H. Cowley, Acc. Chem. Res. 1997, 30, 445-451.
[3] a) T. Krachko, J. C. Slootweg, Eur. J. Inorg. Chem. 2018, 24, 2734-2754; b) A. Doddi, M. Peters, M. Tamm, Chem. Rev. 2019, 119, 6994-7112; c) R. R. Rodrigues, C. L. Dorsey, C. A. Arceneaux, T. W. Hudnall, Chem. Commun. 2014, 50, 162-164; d) K. Schwedtmann, G. Zanoni, J. J. Weigand, Chem. Asian J. 2018, 13, 1388-1405; e) V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt, S. Inoue, Chem. Rev. 2018, 118, 9678.

[4] a) A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Am. Chem. Soc.* **1982**, *104*, 4484-4485; b) A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Chem. Soc., Chem.*

Commun. **1982**, 667-668; c) D. Rottschäfer, B. Neumann, H.-G. Stammler, D. M. Andrada, R. S. Ghadwal, *J. Org. Chem.* **2020**, *85*, 14351-14359.

[5] a) P. B. Hitchcock, M. F. Lappert, W.-P. Leung, *J. Chem. Soc., Chem. Commun.* **1987**, 1282-1283; b) R. Bohra, P. B. Hitchcock, M. F. Lappert, W.-P. Leung, *Polyhedron* **1989**, *8*, 1884.

[6] a) Z. Hou, T. L. Breen, D. W. Stephan, *Organometallics* 1993, *12*, 3158-3167; b) Z.
Hou, D. W. Stephan, *J. Am. Chem. Soc.* 1992, *114*, 10088-10089; c) J. Ho, Z. Hou, J.
Drake, D. W. Stephan, *Organometallics* 1993, *12*, 3145-3157; d) J. Ho, D. W. Stephan, *Organometallics* 1991, *10*, 3001-3003.

[7] a) J. Ho, R. Rousseau, D. W. Stephan, *Organometallics* 1994, *13*, 1918-1926; b)
T. L. Breen, D. W. Stephan, *J. Am. Chem. Soc.* 1995, *117*, 11914-11921.

[8] D. S. J. Arney, R. C. Schnabel, B. C. Scott, C. J. Burns, *J. Am. Chem. Soc.* **1996**, *118*, 6780-6781.

[9] a) A. T. Termaten, T. Nijbacker, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *Organometallics* 2002, *21*, 3196-3202; b) A. T. Termaten, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *Chem. Eur. J.* 2003, *9*, 3577-3582.

[10] A. Schmidpeter, W. Gebler, F. Zwaschka, W. S. Sheldrick, *Angew. Chem.* 1980, 92, 767-768; *Angew. Chem. Int. Ed.* 1980, 19, 722-723.

[11] a) A. J. Arduengo, J. C. Calabrese, A. H. Cowley, H. V. R. Dias, J. R. Goerlich, W. J. Marshall, B. Riedel, *Inorg. Chem.* **1997**, *36*, 2151-2158; b) A. J. Arduengo, H. V. R. Dias, J. C. Calabrese, *Chem. Lett.* **1997**, *26*, 143-144.

[12] O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem.* **2013**, *125*, 3011-3015; *Angew. Chem. Int. Ed.* **2013**, *52*, 2939-2943.

[13] N. Hayakawa, K. Sadamori, S. Tsujimoto, M. Hatanaka, T. Wakabayashi, T. Matsuo, *Angew. Chem.* 2017, 129, 5859-5863; *Angew. Chem. Int. Ed.* 2017, 56, 5765-5769.

[14] A. Doddi, D. Bockfeld, T. Bannenberg, P. G. Jones, M. Tamm, *Angew. Chem.***2014**, *126*, 13786-13790; *Angew. Chem. Int. Ed.* **2014**, *53*, 13568-13572.

[15] M. Cicač-Hudi, J. Bender, S. H. Schlindwein, M. Bispinghoff, M. Nieger, H. Grützmacher, D. Gudat, *Eur. J. Inorg. Chem.* **2016**, *2016*, 649-658.

[16] a) D. Heift, Z. Benko, H. Grützmacher, *Dalton Trans.* 2014, *43*, 5920-5928; b) Z.
Li, X. Chen, Y. Li, C.-Y. Su, H. Grützmacher, *Chem. Commun.* 2016, *52*, 11343-11346.
[17] F. E. Hahn, D. Le Van, M. C. Moyes, T. von Fehren, R. Fröhlich, E. U. Würthwein, *Angew. Chem.* 2001, *113*, 3241-3244; *Angew. Chem. Int. Ed.* 2001, *40*, 3144-3148.

[18] A. K. Adhikari, T. Grell, P. Lönnecke, E. Hey-Hawkins, *Eur. J. Inorg. Chem.* **2016**, 2016, 620-622.

[19] a) D. Schmidt, J. H. J. Berthel, S. Pietsch, U. Radius, *Angew. Chem.* 2012, *124*, 9011-9015; *Angew. Chem. Int. Ed.* 2012, *51*, 8881-8885; b) H. Schneider, D. Schmidt, U. Radius, *Chem. Commun.* 2015, *51*, 10138-10141; c) S. Würtemberger-Pietsch, H. Schneider, T. B. Marder, U. Radius, *Chem. Eur. J.* 2016, *22*, 13032-13036; d) H. Schneider, M. J. Krahfuß, U. Radius, *Z. Anorg. Allg. Chem.* 2016, *642*, 1282-1286; e) H. Schneider, A. Hock, R. Bertermann, U. Radius, *Chem. Eur. J.* 2017, *23*, 12387-12398; f) H. Schneider, A. Hock, A. D. Jaeger, D. Lentz, U. Radius, *Eur. J. Inorg. Chem.* 2018, *2018*, 644, 1243-1251, h) A. Hock, L. Werner, M. Riethmann, U. Radius, *Eur. J. Inorg. Chem.* 2018, *644*, 1243-1251, h) A. Hock, L. Werner, M. Riethmann, U. Radius, *Eur. J. Inorg. Chem.* 2018, *Chem.* 2020, DOI: 10.1002/ejic.202000720, i) A. Hock, L. Werner, C. Luz, U. Radius, *Dalton Trans.* 2020, *32*, 11108-11119.

[20] a) H. Schneider, D. Schmidt, U. Radius, *Chem. Eur. J.* 2015, *21*, 2793-2797; b) S.
Pietsch, U. Paul, I. A. Cade, M. J. Ingleson, U. Radius, T. B. Marder, *Chem Eur. J* 2015, *21*, 9018-9021; c) S. Würtemberger-Pietsch, U. Radius, T. B. Marder, *Dalton* 2016, *45*, 5880-5895; d) M. Eck, S. Würtemberger-Pietsch, A. Eichhorn, J. H. J. Berthel, R. Bertermann, U. S. D. Paul, H. Schneider, A. Friedrich, C. Kleeberg, U. Radius, T. B. Marder, *Dalton* 2017, *46*, 3661-3680; e) A. F. Eichhorn, S. Fuchs, M. Flock, T. B. Marder, U. Radius, *Angew. Chem.* 2017, *129*, 10343-10347; *Angew. Chem. Int. Ed.* 2017, *56*, 10209-10213; f) U. S. D. Paul, U. Radius, *Eur. J. Inorg. Chem.* 2017, 3362-3375; g) A. F. Eichhorn, L. Kuehn, T. B. Marder, U. Radius, *Chem. Commun.* 2017, *53*, 11694-11696; h) L. Kuehn, M. Stang, S. Würtemberger-Pietsch, A. Friedrich, H. Schneider, U. Radius, T. B. Marder, U. Radius, T. B. Marder, J. 2019, *25*, 11365-11374.

[21] K. Pal, O. B. Hemming, B. M. Day, T. Pugh, D. J. Evans, R. A. Layfield, *Angew. Chem.* **2016**, *128*, 1722-1725; *Angew. Chem. Int. Ed.* **2016**, *55*, 1690-1693.

[22] K. Hansen, T. Szilvási, B. Blom, S. Inoue, J. Epping, M. Driess, *J. Am. Chem. Soc.***2013**, *135*, 11795-11798.

[23] A. M. Tondreau, Z. Benkö, J. R. Harmer, H. Grützmacher, *Chem. Sci.* **2014**, *5*, 1545-1554.

[24] M. Cicač-Hudi, J. Bender, S. H. Schlindwein, M. Bispinghoff, M. Nieger, H. Grützmacher, D. Gudat, *Eur. J. Inorg. Chem.* **2016**, *2016*, 649-658.

[25] M. Bispinghoff, A. M. Tondreau, H. Grützmacher, C. A. Faradji, P. G. Pringle, *Dalton Trans.* **2016**, *45*, 5999-6003.

[26] a) O. Lemp, M. Balmer, K. Reiter, F. Weigend, C. von Hänisch, *Chem. Commun.* **2017**, 53, 7620-7623; b) M. Balmer, Y. J. Franzke, F. Weigend, C. von Hänisch, *Chem. Eur. J.* **2020**, *26*, 192-197.

[27] D. Bockfeld, T. Bannenberg, P. G. Jones, M. Tamm, *Eur. J. Inorg. Chem.* **2017**, 2017, 3452-3458.

[28] K. Verlinden, H. Buhl, W. Frank, C. Ganter, *Eur. J. Inorg. Chem.* 2015, 2416-2425.
[29] a) N. Kuhn, R. Fawzi, T. Kratz, M. Steinmann, G. Henkel, *Phosphorus Sulfur Silicon Relat. Elem.* 2006, *108*, 107-119; b) N. Kuhn, G. Henkel, T. Kratz, Chem. Ber. 1993, *126*, 2047-2049.

[30] a) G. P. Junor, J. Lorkowski, C. M. Weinstein, R. Jazzar, C. Pietraszuk, G. Bertrand, *Angew. Chem.* 2020, *132*, 22212-22217; *Angew. Chem. Int. Ed.* 2020, *59*, 22028-22033; b) A. Merschel, D. Rottschäfer, B. Neumann, H.-G. Stammler, R. S. Ghadwal, *Organometallics* 2020, *39*, 1719-1729.

[31] T. G. Larocque, G. G. Lavoie, New. J. Chem. 2014, 38, 499-502.

[32] A. Doddi, D. Bockfeld, A. Nasr, T. Bannenberg, P. G. Jones, M. Tamm, Chem. *Eur. J.* **2015**, *21*, 16178-16189.

[33] D. Bockfeld, A. Doddi, P. G. Jones, M. Tamm, *Eur. J. Inorg. Chem.* **2016**, 3704-3713.

[34] R. Job, J. Rovang, Synth. React. Inorg. Met. Org. Chem. 1976, 6, 367-371.

[35] a) F. Hering, J. H. J. Berthel, K. Lubitz, U. S. D. Paul, H. Schneider, M. Härterich, U. Radius, *Organometallics* 2016, 35, 2806–2821; b) K. Lubitz, V. Sharma, S. Shukla, J. H. J. Berthel, H. Schneider, C. Hoßbach, U. Radius, *Organometallics* 2018, 37, 1181-1191.

[36] a) S. Dürr, B. Zarzycki, D. Ertler, I. Ivanović-Burmazović, U. Radius, *Organometallics* 2012, *31*, 1730-1742; b) S. Dürr, D. Ertler, U. Radius, *Inorg. Chem.*2012, *51*, 3904-3909; c) B. Zarzycki, F. M. Bickelhaupt, U. Radius *Dalton* 2013, *42*, 7468 – 7481; d) K. Lubitz, U. Radius, *Organometallics* 2019, *38*, 2558-2572.

[37] a) H. Aktas, J. C. Slootweg, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* 2009, *131*, 6666–6667; b) A. T. Termaten, T. Nijbacker, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *Chem. Eur. J.* 2003, *9*, 2200-2208.

[38] a) A. T. Arjan, H. Aktas, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, Organometallics **2003**, *22*, 1827-1834; b) A. Doddi, D. Bockfeld, T.

Bannenberg, M. Tamm, *Chem. Eur. J.* 2020, *26*, 14878-14887; c) M. Peters, A. Doddi,
T. Bannenberg, M. Freytag, P. G. Jones, M. Tamm, *Inorg. Chem.* 2017, *56*, 10785-10793.

[39] see for example: a) J. Zhou, M. W. Kuntze-Fechner, R. Bertermann, U. S. D. Paul, J. H. J. Berthel, A. Friedrich, Z. Du, T. B. Marder, U. Radius, *J. Am. Chem. Soc.* 2016, *138*, 5250-5253; b) Y.-M. Tian, X.-N. Guo, M. W. Kuntze-Fechner, I. Krummenacher, H. Braunschweig, U. Radius, A. Steffen, T. B. Marder, *J. Am. Chem. Soc.* 2018, *140*, 17612-17623; c) U. S. D. Paul, C. Sieck, M. Hähnel, K. Hammond, T. B. Marder, U. Radius, *Chem. Eur. J.* 2016, *22*, 11005-11014; d) U. S. D. Paul, U. Radius, *Chem. Eur. J.* 2016, *22*, 11005-11014; d) U. S. D. Paul, U. Radius, *Chem. Eur. J.* 2016, *22*, 11005-11014; d) U. S. D. Paul, U. Radius, *Chem. Eur. J.* 2017, *23*, 3993-4009; e) U. S. D. Paul, U. Radius, *Organometallics* 2017, *36*, 1398-1407; f) J. H. J. Berthel, L. Tendera, M. W. Kuntze- Fechner, L. Kuehn, U. Radius, *Eur. J. Inorg. Chem.* 2019, 3061-3072; g) L. Kuehn, D. G. Jammal, K. Lubitz, T. B. Marder, U. Radius, *Chem. Eur. J.* 2019, *25*, 9514-9521.

[40] G. Hierlmeier, A. Hinz, R. Wolf, J. M. Goicochea, *Angew. Chem. Int. Ed.* **2018**, *57*, 431-436; *Angew. Chem.* **2018**, *130*, 439-444.

[41] S. Gómez-Ruiz, E. Hey-Hawkins, *Dalton* **2007**, 5678-5683.

[42] T. Schaub, M. Backes, U. Radius, *Organometallics* 2006, 25, 4196-4206. b) T.
Schaub, U. Radius, A. Brucks, M. P. Choules, M. T. Olsen, T. B. Rauchfuss, *Inorg. Synth.* 2011, 35, 78-83.

[43] A. J. Arduengo, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530-5534.

[44] G. R. Fulmer, A. J. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz,J. E. Bercaw, K. I. Goldberg, *Organometallics* 2010, *29*, 2176-2179.

[45] G. M. Sheldrick, Acta Crystallogr. A 2014, 70, C1437.

[46] a) F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. T. Weigend, *Mol. Sci.* 2014, *4*, 91-100; b) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* 1989, *162*, 165-169.

[47] a) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346-354; b) M. Häser, R. Ahlrichs, *J. Comput. Chem.* **1989**, *10*, 104-111.

[48] a) A. D. Becke, *Phys. Rev. A* 1988, *38*, 3098-3100; b) J. Perdew, *Phys. Rev. B* 1986, *34*.

[49] a) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571-2577; b) A.
Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829-5835; c) K. Eichkorn,
O. Treutler, H. Oehm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652-660;

d) F. Weigend, R. Ahlrichs, *Physical Chemistry Chemical Physsics* **2005**, *7*, 3297-3305; e) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1065.

[50] P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2004**, *384*, 103-107.

Entry for the Table of Contents

L. Werner, G. Horrer, M. Philipp, K. Lubitz, M. W. Kuntze-Fechner, U. Radius*

A General Synthetic Route to NHC-Phosphinidenes: NHC-mediated Dehydrogenation of Primary Phosphines



NHC-Phosphinidenes

The dehydrocoupling of primary phosphines with NHCs is a general and convenient synthetic approach to prepare NHC-phosphinidenes in moderate to high isolated yield, as exemplified by the synthesis of different NHC-phosphinidenes. The reactivity of $(iPr_2Im)PPh$ (1) towards chalcogenides and selected transitions metals complexes is presented.