C_7H_8; yield 1.15 g (36% with respect to thiophosgene), m.p. 88–90°C, elemental analysis: calcd: C 36.94, H 6.38%, P 16.81; found: C 37.08, H 6.55, P 16.81; ^{1}H NMR (200 MHz, [D$_6$]acetone, 25°C, TMS): $\delta = 1.28$ (d, ^2J(P,H) = 7.4 Hz, 9H, PCH_3), 1.42 (d, ^2J(P,H) = 9.2 Hz, 9H, PCH_3), 1.98 (d, ^2J(P,H) = 13.7 Hz, 9H, $^+$PCH_3), 2.30 (s, 3H, CCH_3), 7.17 (m, 5H, CH); ^{31}P NMR (81 MHz, [D$_6$]acetone, 25°C, H_3PO_4): $\delta = -9.9$ (d, ^3J(P,P) = 9 Hz, 1P, PCH$_3$), −4.5 (s, 1P, PCH$_3$), 26.9 (s, ^3J(P,P) = 9 Hz, 1P, ^+PCH$_3$).

3: To a solution of **2** (1.45 g, 2.62 mmol) in 40 mL of THF was added a solution of methyllithium in diethyl ether (3.3 mL, 1.6 M, 5.3 mmol) at −80°C with vigorous stirring The mixture turned light brown. Removing the volatile materials in vacuo, extracting the residue with 50 mL of pentane, and cooling to −27°C for 10 h gave brown crystals; yield 0.68 g (62%); m.p. 84–88°C (decomp), elemental analysis calcd for $C_{12}H_{33}Cl_2Ni_2P_3S$ (419.8): C 34.36, H 7.92 , P 22.14; found C 34.33, H 7.86, P 22.10; ^{1}H NMR (200 MHz, [D$_8$]THF, 25°C, TMS): $\delta = -0.78$ (s, 6H, NiCH_3), 1.18 (d, ^2J(P,H) = 6.3 Hz, 18H, PCH_3), 1.66 (d, ^2J(P,H) = 12.9 Hz, 9H, $^+$PCH_3); ^{13}C NMR (75.4 MHz, [D$_8$]THF, 25°C, TMS): $\delta = -24.1$ (s, NiCH$_3$), 15.5 (d, ^1J(P,C) = 55.7 Hz, $^+$PCH$_3$), 17.0 (d, ^1J(P,C) = 9.5 Hz, PCH$_3$); ^{31}P NMR (81 MHz, [D$_8$]THF, 25°C, H_3PO_4): $\delta = -4.8$ (s, PCH$_3$), 23.1 (s, ^+PCH$_3$).

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[2] In toluene **1** is also obtained by treating [NiCl$_2$(PMe$_3$)$_2$] with [Fe$_2$(C$_5$H$_5$)$_2$(CO)$_3$(μ-SnMe$_2$)] or Na$_2$[Fe(CO)$_4$]·1.5 dioxane in 15% and 28% yield, respectively.

[3] Crystal data for **1**: $C_{10}H_{27}Cl_2Ni_2OP_3$, $M_r = 444.6$; crystal dimensions: $0.55 \times 0.45 \times 0.15$, monoclinic, space group $P2_1/c$, $a = 10.902(3)$, $b = 16.923(4)$, $c = 12.323(3)$ Å, $\beta = 115.05(2)°$, $V = 2059(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.434$ g cm^{-3}, $F(000) = 920$; 4611 reflections with $4.8 < 2\Theta < 55.0°$, Siemens R3 diffractometer, Mo$_{K\alpha}$ radiation ($\mu = 2.309$ mm^{-1}), graphite monochromator. The structure was solved with direct methods (SHELXTL V5), refinement with 4413 independent reflections ($R_{int} = 0.0344$) for 173 parameters against $|F^2|$ with SHELXTL V5 gave $R = 0.063$, $wR2 = 0.192$ (all data); max./min. residual electron density 1.143/−0.531 e Å^{-3}. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions.[7b]

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[5] Strong sharp bands were registered at 737 (ν_{as}(PC)) and 671 cm^{-1} (ν_s(PC)).

[6] A nickel complex in which two chelating (Ph$_2$P)$_2$CH$_2$ ligands are attached to a related atomic framework (μ-CO)Ni$_2$Cl$_2$ also shows fluxional behavior.[4]

[7] a) Crystal data for **2**: $C_{10}H_{27}Cl_2Ni_2P_3S \cdot C_7H_8$, $M_r = 552.7$; crystal dimensions: $0.30 \times 0.22 \times 0.20$ mm, monoclinic, space group $P2_1/n$, $a = 11.572(2)$, $b = 9.229(1)$, $c = 25.949(4)$ Å, $\beta = 99.10(1)°$, $V = 2736.4(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.342$ g cm^{-3}, $F(000) = 1152$; 6440 reflections with $5.4 < 2\Theta < 55.1°$, Siemens R3 diffractometer, Mo$_{K\alpha}$ radiation ($\mu = 1.824$ mm^{-1}), graphite monochromator. The structure was solved by direct methods (SHELXTL V5), refinement of 6308 independent reflections ($R_{int} = 0.0445$) for 224 parameters against $|F^2|$ with SHELXTL V5 gave $R1 = 0.063$, $wR2 = 0.171$ (all data); max./min. residual electron density 0.599/−0.424 e Å^{-3}. All non-hydrogen atoms except for the C atoms at P1 were refined anisotropically. Atoms C8–C10 were refined on split positions with mutual half occupation at a fixed distance d(PC). Hydrogen atoms were fixed at calculated positions. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-101260 and -101267. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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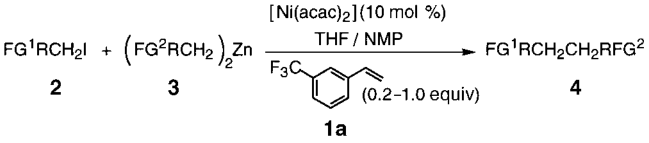
An Efficient Nickel-Catalyzed Cross-Coupling Between sp^3 Carbon Centers

Riccardo Giovannini, Thomas Stüdemann, Gaelle Dussin, and Paul Knochel*

The cross-coupling reaction between an organometallic species and an organic halide is an important method for forming a new carbon–carbon bond. Whereas transition metal catalyzed cross-coupling reactions between sp^2 carbon centers are well established[1] and routinely applied even in complex syntheses,[2] the cross-coupling reaction between two sp^3 carbon centers often requires the use of stoichiometric amounts of organocuprates,[3] which has several drawbacks. A nontransferred or nontransferable functional group is often wasted, and the moderate functional group diversity of lithium or magnesium cuprates[4] often limits their application. Recently, we have shown that the presence of a double bond in the position γ to the carbon–halogen bond considerably facilitates the reductive-elimination step of the cross-coupling.[5] The remote double bond coordinates to the nickel center and in this way removes electron density from the metal atom.[6] Although it is mechanistically interesting, the required presence of the double bond in the iodoalkane reduces the synthetic scope of the reaction. Herein, we report that the addition of catalytic amounts of an unsaturated additive such as **1a** allows an efficient [Ni(acac)$_2$]-catalyzed cross-coupling reaction to be performed between various polyfunctional organic halides **2** and diorganozinc compounds **3** to give the cross-coupling products **4** (Scheme 1); this considerably extends the scope of the reaction.



Scheme 1. Cross-coupling between sp^3 carbon centers in the presence of cocatalysts **1a**. FG = functional group; NMP = N-methylpyrrolidone.

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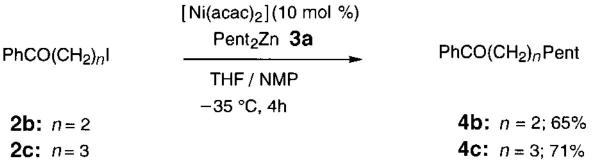
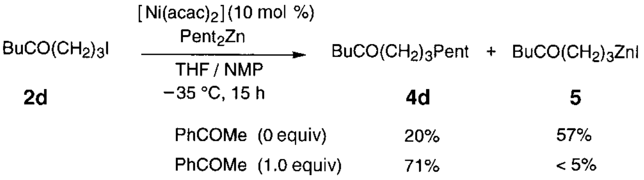
Preliminary results have shown that the Ni-catalyzed cross-coupling between an iodoalkane that does not contain a double bond for complexing to the nickel center could be improved upon adding an external olefin bearing an electron-withdrawing group. Thus, the reaction of 3-phenylpropyl iodide (**2a**) with dipentylzinc ($Pent_2Zn$; **3a**) in the presence of [Ni(acac)$_2$] (7.5 mol%) in THF/NMP (2/1) at 25°C (40 h) provides the cross-coupling product octylbenzene (**4a**) in a modest yield of 34%. Upon addition of ethyl crotonate (**1b**; 1.0 equiv), the product **4a** can be isolated in 64% yield (−25°C, 24 h). Further evidence for cocatalysis by an external unsaturated ligand was obtained in the study of the cross-coupling reaction of 3-keto- and 4-ketoiodoalkanes (**2b**–**d**) with **3a**. The cross-coupling of **2b** and **2c** were fast and yielded the desired products **4b** (65%) and **4c** (71%; Scheme 2).



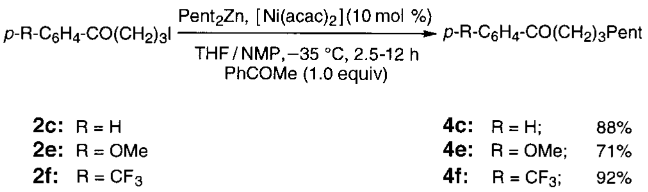
Scheme 2. Cross-coupling with oxygen group containing iodoalkanes **2b** and **2c**.

The reaction of the related iodoalkane **2d** with **3a** was, however, sluggish and provided a mixture of the cross-coupling product **4d** and the organozinc iodide **5**, which results from an iodine–zinc exchange reaction.[7] This result shows that the keto group may play the same coordinating role as a double bond and that the organic group attached to the carbonyl moiety is important. Thus the addition of acetophenone (**1c**; 1.0 equiv) as an external ligand accelerates the reaction considerably and also suppresses completely the iodine–zinc exchange side reaction (less than 5%) and provides the desired product **4d** in a 71% yield (Scheme 3).



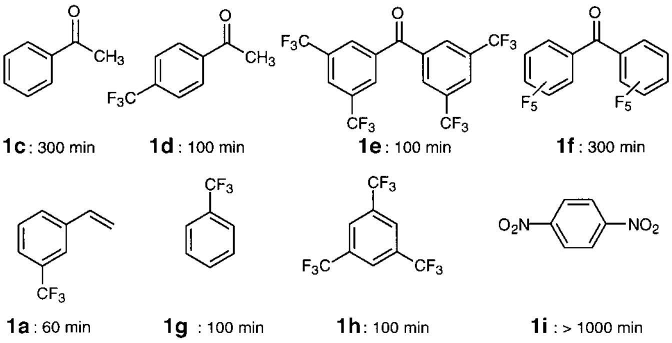
Scheme 3. Influence of acetophenone on the reaction of **2d** under the coupling conditions.

To evaluate the importance of the substitution pattern of the remote arylcarbonyl group, we have submitted the keto-substituted iodides **2c** and **2e**–**f** to our cross-coupling conditions and have observed that the most efficient cross-coupling was obtained with the iodide **2f**, in which the phenyl group bears a strong electron-withdrawing trifluoromethyl group (→**4f**, 92%, Scheme 4). On the other hand, the cross-coupling with a methoxy-substituted phenyl ring was slow, and affords the lowest yield with the longest reaction time (**4e**, 71% yield).



Scheme 4. Influence of the R group on the arylcarbonyl group on the coupling.

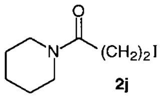
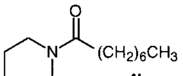
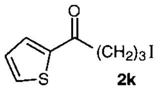
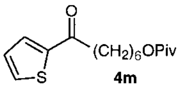
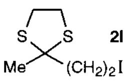
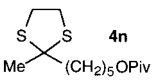
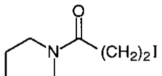
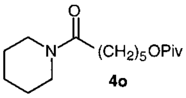
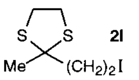
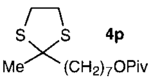
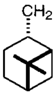
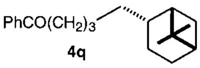
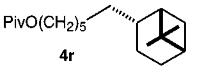
This study encouraged us to study more systematically the nature of the cocatalyst **1** by using the cross-coupling of 1-iodo-4-octanone (**2d**) with **3a** as a test reaction ([Ni(acac)$_2$] (10 mol%), THF/NMP, −35°C) and adding between 0.2 and 1.0 equivalent of the cocatalysts **1a** or **1c**–**i**. The selection criteria for determining the best additive (**1**) was the conversion time and the amount of iodine–zinc exchange (Scheme 5). The introduction of trifluoromethyl substituents increases the reaction rate (compare **1c** with **1d**, **1e**). The use of perfluorinated benzophenone (**1f**) was less efficient than that of various CF_3-substituted benzenes such as **1g**[8] or **1h**. Interestingly, 1,4-dinitrobenzene (**1i**) inhibits the cross-coupling reaction completely, thus indicating a possible radical pathway for the oxidative-addition step of the haloalkane to the nickel catalyst.[9]



Scheme 5. Different cocatalysts and their influence of the cross-coupling of **2d** with **3a**.

Although various additives such as **1d** or **1g** lead to fast cross-coupling reactions, all of these reactions were accompanied by the formation of iodine–zinc exchange products. However, *m*-trifluoromethylstyrene (**1a**) showed an exceptional activity and gave the fastest reactions. Remarkably almost no iodine–zinc exchange could be detected in the presence of **1a**. The use of substoichiometric amounts of the cocatalyst **1a** (20–50 mol%) gave in many cases the same results as when stoichiometric amounts were used. It was now possible to perform a variety of cross-coupling reactions with this optimized catalytic system. All of these reactions were complete within a few hours at −35°C and proceeded very cleanly (see Table 1 and Experimental Section). The presence of a thioether or a thioacetal functionality had a favorable effect on the reaction rate, which may imply that a complexation of the nickel catalyst with the sulfur atom occurs.[10] The cross-coupling with ester-functionalized iodoalkanes with various promotors **1** proved unsatisfactory. However with *m*-trifluoromethylstyrene (**1a**) the desired product was ob-

Table 1. Nickel-catalyzed cross-coupling reaction between dialkylzinc compounds and polyfunctional alkyl iodides in the presence of the cocatalyst **1a** or **1c**.

Entry	Iodalkane **2**	R_2Zn **3**, R =	**4**	Yield [%][a]	Co-cat. (equiv)
1	$PhS(CH_2)_3I$ **2g**	**3a**, Pent	$PhS(CH_2)_7CH_3$ **4g**	71	**1a** (0.5)
2	$PivO(CH_2)_5I$ **2h**[b]	**3a**	$PivO(CH_2)_9CH_3$ **4h**	78	**1a** (0.3)
3	$PhCO(CH_2)_3I$ **2c**	**3b**, $PivO(CH_2)_3$	$PhCO(CH_2)_6OPiv$ **4i**	76	**1a** (0.2)
4	$BuCO(CH_2)_3I$ **2d**	**3b**	$BuCO(CH_2)_6OPiv$ **4j**	68	**1c** (0.5)
5	$BnO_2C(CH_2)_2I$ **2i**[c]	**3a**	$BnO_2C(CH_2)_6CH_3$ **4k**	76	**1a** (1.0)
6	 **2j**	**3a**	 **4l**	70	**1c** (1.0)
7	 **2k**	**3b**	 **4m**	70	**1c** (0.5)
8		**3b**		70	**1a** (0.5)
9	 **2j**	**3b**	 **4o**	68	**1a** (1.0)
10		**3c**, $PivO(CH_2)_5$		67	**1a** (0.3)
11	$PhCO(CH_2)_3I$ **2c**	**3d**, 	 **4q**	66	**1c** (1.0)
12	$PivO(CH_2)_5I$ **2h**	**3d**	 **4r**	74	**1a** (1.0)

[a] Yields of the isolated, analytically pure products. [b] Piv = pivaloyl. [c] Bn = benzyl.

tained (**4k**, 76% yield; entry 5 of Table 1). A similar result was obtained with an iodoalkane bearing an amide functional group **2j**. The test cross-coupling reaction between the ester-containing iodoalkane **2h** with **3a** clearly demonstrates the functional group tolerance of this cross-coupling reaction. The pivaloxy group is too far from the carbon–iodine bond to facilitate the oxidative addition or reductive elimination by coordination; nevertheless the cross-coupling proceeds to furnish **4h** in a satisfactorily yield (78%, entry 2). Various keto-containing iodoalkanes (**2c**, **d**, **j**, **k**) underwent the cross-coupling reaction smoothly with the functionalized zinc reagent ($(PivO(CH_2)_3)_2Zn$ (**3b**); entries 3, 4, 7, and 9). The iodothioketal **2l** reacts as well with the zinc reagent **3b**; (entry 8).

In summary, we have developed a new nickel-catalyzed cross-coupling reaction between polyfunctional primary iodoalkanes and primary diorganozinc compounds in the presence of a promotor. *m*-Trifluoromethylstyrene proves to be an exceptionally active promotor leading to clean and fast cross-coupling reactions. The study of the scope, its mechanistic implications, and further synthetic applications of this reaction are currently being investigated in our laboratory.

Experimental Section

Typical procedure**:** Preparation of benzyl octanoate (**4k**): A 25-mL two-necked flask equipped with an argon inlet and a rubber septum was charged with $[Ni(acac)_2]$ (0.128 g, 0.5 mmol, 10 mol%), THF (3.4 mL), NMP (1.7 mL), *m*-trifluoromethylstyrene (**1a**, 0.15 mL, 1 mmol, 20 mol%), and benzyl 3-iodopropanoate (**2i**; 1.45 g, 5 mmol) at room temperature. The flask was cooled to −78 °C, and dipentylzinc (**3a**, 2 mL, 10 mmol) was added carefully. The reaction mixture was allowed to warm to −35 °C, and stirred for 2.5 h before being poured into an ice-cold saturated aqueous solution of NH_4Cl and extracted with diethyl ether. The organic phase was washed with brine and dried over Na_2SO_4. The resulting crude oil, obtained after evaporation of the solvents, was purified by flash chromatography (hexanes/diethyl ether, 10/1) to give the desired product **4k** (0.89 g, 3.8 mmol, 76% yield) as a colorless oil.

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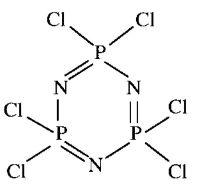
Synthesis and Crystal Structure of a *P*-Hydridophosphoraniminato–Zirconium Complex and Reaction to the First Tris(hydrido)cyclotriphosphazene[**]

Gerold Schick, Michael Raab, Dietrich Gudat, Martin Nieger, and Edgar Niecke*

Dedicated to Professor Heinrich Nöth
on the occasion of his 70th birthday

Cyclophosphazenes belong to the best characterized compounds of main group elements and play a key role in the construction of inorganic polymers.[1] In particular, ring-opening polymerization (ROP) of hexachlorocyclotriphosphazene $(Cl_2PN)_3$ (**I**) and subsequent substitution reactions give way to specifically substituted polymers whose high thermal stability and elastomeric and/or thermoplastic properties have been utilized for various special applications. In contrast, attempts to synthesize hydridocyclophosphazenes and study their reactivity are rare and have been confined to a limited number of compounds containing only a single PH functionality.[2] Here we report on the synthesis of the first representative of a tris(hydrido)cyclotriphosphazene of type **II** (according to our investigations, the previously described[3] compound $[(Me_2N)(H)PN]_3$ is actually not a cyclophosphazene, but a hydridophosphazene polymer; the synthesis and characterization of this and further poly(hydrido)phosphazenes of the type $[(R_2N)(H)PN]_n$ will be reported elsewhere[4]).



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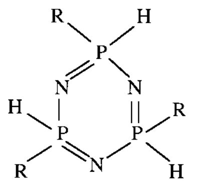
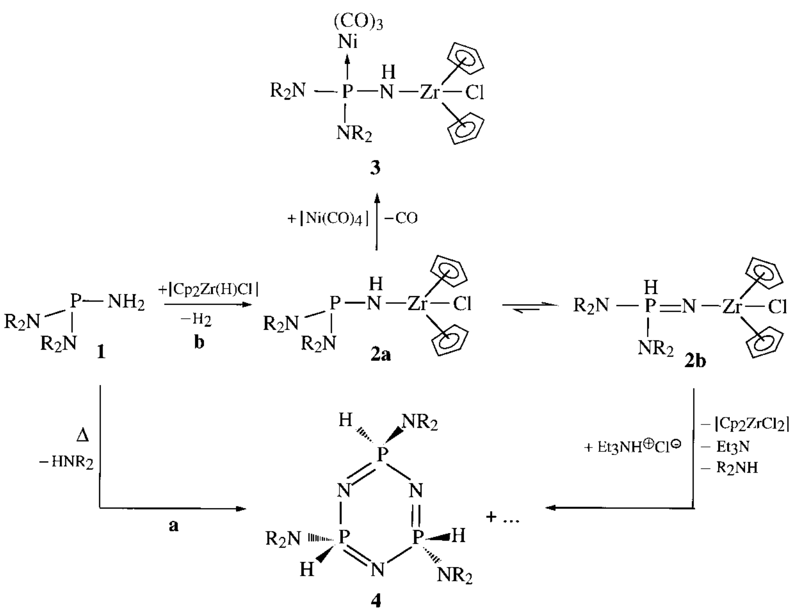


II

In solution the aminophosphane **1**, which is accessible by ammonolysis of the corresponding diaminochlorophosphane,[5] decomposes at ambient temperature under cleavage of dicyclohexylamine to give mixtures of oligomeric and polymeric amino(hydrido)phosphazenes (Scheme 1, path a).[4] Chromatographic separation affords the *cis,trans,trans*-configurated cyclic trimer **4** in low yields (ca. 10%).[6] The tris(hydrido)cyclophosphazenes are obtained in higher yields by controlled cleavage of the *P*-hydridophosphoraniminato–zirconium complex **2b** with triethylammonium chloride (Scheme 1, path b).



Scheme 1. R = *cyclo*-Hexyl.

Complex **2b** is easily accessible by treatment of **1** with $[Cp_2Zr(H)Cl]$. The reaction proceeds by elimination of H_2 and formation of a Zr–N bond, and affords primarily a mixture of the two tautomers **2a** and **2b** in a ratio of 1:20. Compound **2b** can be isolated in pure form by crystallization at low temperature. Its reaction with tetracarbonylnickel affords in quantitative yield the phosphanylamido–$Ni(CO)_3$ complex **3**, whose formation is presumably preceeded by conversion of **2b** into the thermodynamically less favored tautomer **2a**. An intramolecular cyclization of **2a** under formation of a zirconaazaphosphirane as was recently reported by Majoral et al.[7] is not observed in this case.

The composition and constitution of **2b** and **3** follow from high-resolution mass spectra and ^{31}P, ^{1}H, and ^{13}C NMR spectra. The presence of a hydridophosphorane moiety in **2b** is proven in the ^{31}P NMR spectrum by the significant shielding of the phosphorus atom with respect to that in **1**, and by the

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