

and polynuclear complexes in radical-driven carbonylation reactions, are in progress.

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New Palladium Complexes of Cis-Fixed Bidentate Nitrogen Ligands as Catalysts for Carbon–Carbon Bond Formation

Rob van Asselt and Cornelis J. Elsevier*

Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, Nieuwe Achtergracht 166,
1018 WV Amsterdam, The Netherlands

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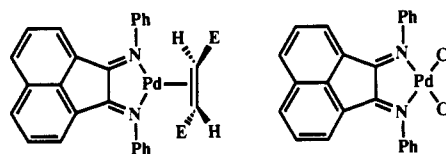
Summary: New palladium complexes of the cis-fixed bidentate nitrogen ligand bis(phenylimino)acenaphthene (Ph-BIAN) are excellent catalysts for the carbon–carbon coupling reactions between various organic halides and organomagnesium, -zinc, and -tin reagents.

The palladium-catalyzed cross-coupling reaction has become a versatile tool in organic synthesis, and a wide variety of organic electrophiles and transmetalating reagents can be used.¹ The nature of the ligands coordinated to the palladium center is expected to have a pronounced influence on the carbon–carbon coupling reaction, because it has been shown that oxidative addition² and reductive elimination³ (and probably also transmetalation) are strongly dependent on the type of ligands coordinated to the metal center. So far, in such catalytic reactions, mainly monodentate phosphine complexes of palladium have been employed. Bidentate chelating phosphine ligands have been used in Grignard cross-coupling reactions,^{1a} but in tin cross coupling they usually slow down the reaction rate,⁴ although improved rates have also been reported.⁵

The few reports dealing with carbon–carbon bond formation catalyzed by palladium complexes of bidentate nitrogen ligands include nucleophilic allylic substitution⁶ and coupling reactions of organic halides with organotin reagents catalyzed by Pd(2,2'-bipyridine)⁷ or Pd(bis(2-pyridyl)silane).⁸ Stoichiometric formation of a carbon–carbon-coupled product from various Pd(α -diimine)(η^3 -allyl) complexes⁹ and (isolated) Pd(IV) complexes¹⁰ has

also been reported.

We recently started investigations concerning the reactivity and catalytic activity of zerovalent (1) and divalent (2) palladium complexes containing the cis-fixed bidentate nitrogen ligands bis(arylimino)acenaphthene (e.g. Ph-BIAN).¹¹ Because of their good σ -donor and π -acceptor



1 (E = CO₂CH₃)

2

capacities and their rigidity, imposing a fixed cis orientation of both nitrogen atoms, we expected these ligands to endow properties upon the palladium center which might be favorable in carbon–carbon cross-coupling reactions. Both higher and lower oxidation states, necessary in an alternating sequence of oxidative addition and reductive elimination, can be stabilized. Furthermore, the diorganopalladium(II) complex formed after transmetalation has both organic groups in a fixed cis orientation, facilitating reductive elimination from this type of complex. Apart from the anticipated behavior it appears, to our surprise, that zerovalent [Pd(Ar-BIAN)(alkene)] complexes are also active as catalysts in the homogeneous hydrogenation of electron-poor alkenes.¹²

We wish to report that palladium complexes of the types 1 and 2 are indeed active in a variety of carbon–carbon bond-forming reactions under mild conditions using several organic electrophiles (including acyl, aryl, benzyl, vinyl, and 1,2-dienyl halides) with organomagnesium, -zinc, and -tin reagents.^{13,14}

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Table I. Pd(Ph-BIAN)-Catalyzed Coupling between Organic Electrophiles and Organomagnesium and -zinc Reagents^a

organic halide	Mg/Zn reagent ^b	conditions	products ^c	yield, ^d %
(pTol)I	PhCH ₂ MgCl	20 °C, 16 h	(pTol)CH ₂ Ph (98%), (PhCH ₂) ₂ (2%)	85
PhI	PhCH ₂ MgCl	20 °C, 16 h	PhCH ₂ Ph (98%), (PhCH ₂) ₂ (2%)	99
PhCH(Me)Br	(allyl)MgCl	20 °C, 2 h	PhCH(Me)CH ₂ CH=CH ₂ (85%), (PhCH(Me)) ₂ (15%)	88
Me ₂ C=C=CHBr	(pTol)MgBr	20 °C, 2 h	Me ₂ C=C=CH(pTol) (64%), (pTol) ₂ ^e (36%)	49
Me ₂ C=C=CHBr	(pTol)ZnCl	20 °C, 3 h	Me ₂ C=C=CH(pTol) (77%), (pTol) ₂ ^e (23%)	66
PhCH=CHBr	(pTol)MgBr	67 °C, 2 h	Ph-CH=CH(pTol) (67%), (pTol) ₂ (33%)	99
PhCH=CHBr	(pTol)ZnCl	67 °C, 2 h	Ph-CH=CH(pTol) (88%), (pTol) ₂ (12%)	98

^a Conversion of the starting halide is complete in all cases within the indicated time (GC/NMR). The reactions are carried out in THF with 1% of Pd(Ph-BIAN)(dimethyl fumarate) or Pd(Ph-BIAN)Cl₂ as the catalyst. Abbreviations used are as follows: Ph = C₆H₅, pTol = 4-CH₃C₆H₄, allyl = CH₂=CHCH₂, Me = CH₃. ^b (pTol)ZnCl solutions are prepared in situ by the addition of 1 equiv of (pTol)MgBr to a ZnCl₂ solution in THF and contain equimolar amounts of MgClBr. ^c The relative amounts of the products in the crude reaction mixture (i.e. before chromatographic workup) are indicated after the formulas. ^d Total yield of the organic product(s) after chromatographic workup. ^e No propargyl compound, arising from attack at C(3), was observed in the reaction product.

Table II. Pd(Ph-BIAN)-Catalyzed Coupling of Organic Electrophiles with Organotin Reagents^a

organic halide	Sn reagent	conditions ^b	time, h	products ^c	yield, ^d %
PhCH ₂ Br	SnMe ₄	DMF, 50 °C or HMPA ^e	20	PhCH ₂ CH ₃ (90%), (PhCH ₂) ₂ (10%)	84 ^f
PhCH ₂ Br	SnMe ₄	Pd(II)-cat. ^g in DMF	16	PhCH ₂ CH ₃ (19%), PhCH ₂ Br (81%)	nd
PhCH ₂ Br	(pTol)SnBu ₃	DMF, 50 °C ^h or HMPA	20	PhCH ₂ (pTol) (>99%)	76
PhCH ₂ Br	SnMe ₄	HMPA, 1 bar CO	20	PhCH ₂ C(O)CH ₃ (>99%)	88
PhC(O)Cl	SnMe ₄	DMF, 50 °C	16	PhC(O)CH ₃ (>99%)	98

^a Pd(Ph-BIAN)(dimethyl fumarate) was used as the catalyst in a relative amount of 1%, under the conditions indicated in the table. After the time indicated in the table, conversion of the organic halide was complete (GC/NMR), unless noted otherwise (Bu = *n*-butyl). ^b Reactions were carried out at 20 °C, unless stated otherwise. ^c The relative amounts of the products in the crude reaction mixture (before chromatographic workup) are indicated after the formulas. ^d After chromatographic workup (nd = not determined). ^e In THF, CHCl₃, or DMSO no or only minor conversion occurred (ca. 1%). ^f GC yield. ^g Pd(Ph-BIAN)Cl₂ was used as the catalyst in a relative amount of 2%. Raising the temperature to 50 °C with 1% of the Pd(II) catalyst gave 27% conversion to the cross-coupled product. ^h When Pd(Ph-BIAN)Cl₂ was used as the catalyst, only 37% conversion of benzyl bromide was achieved.

The cross-coupling reaction between organic halides and organomagnesium and -zinc reagents readily takes place in tetrahydrofuran (THF) at 20 °C, and conversion of the organic electrophile is generally complete within several hours with 1% of compound 1 or 2 as the catalyst. Yields of isolated products after chromatographic workup are good (85–99%), except for 1,2-dienyl bromides, which give only 49–66% yield.

The results, summarized in Table I, clearly indicate that the ratio of cross coupling to homo coupling strongly depends on the reagents. Aryl iodides couple with benzylmagnesium chloride to give the cross-coupled products almost exclusively, whereas (*E*)-β-bromostyrene reacts with *p*-tolylmagnesium bromide in refluxing THF to give the substituted stilbene derivative as the main reaction product together with a considerable amount of homo-coupled bitolyl. In the latter case no cross coupling occurred in the absence of the Pd(Ph-BIAN) catalyst, but ca. 35% bitolyl is formed. The coupling of 1-phenylethyl bromide with allylmagnesium chloride predominantly leads to the cross-coupled product, and less than 1% styrene is observed, indicating that transmetalation is fast compared to β-elimination.

The use of organozinc reagents in the cross-coupling reactions is advantageous, because the amount of homo-coupling is considerably lower than in comparable reactions with organomagnesium reagents. The greater affinity of organozinc reagents for cross coupling, as compared to

organomagnesium reagents, has been observed before¹⁵ and might point to a different mechanism operating in these cases.

As in Pd-phosphine-catalyzed reactions, the Pd(Ph-BIAN)-catalyzed cross-coupling reactions using organotin reagents proceed with higher selectivity than the reactions with organomagnesium and -zinc reagents (see Table II). There is a high preference for cross coupling and no or only small amounts of homo-coupled products are observed in the described reactions.

The coupling reactions employing organotin reagents proceed best with Pd(Ph-BIAN) catalysts of type 1 in polar aprotic solvents such as *N,N*-dimethylformamide (DMF) at 50 °C or hexamethylphosphoric triamide (HMPA) at 20 °C, whereas in THF, dimethyl sulfoxide (DMSO), or chloroform at 20 °C only trace amounts of cross-coupled products were formed. When the reaction was carried out in THF at 50 °C, the amount of cross-coupled product increased somewhat but conversion was still very low (6% after 16 h). A separate study showed that the oxidative addition of the organic halides employed in this work is faster than cross coupling in all solvents studied. Furthermore, in the stoichiometric reactions of the oxidative-addition products with 1 equiv of the organotin compound, no intermediate diorgano-Pd(II) complex could be observed, only cross-coupling products.¹⁶ This suggests that transmetalation is the rate-determining step in the Pd(Ph-BIAN)-catalyzed coupling of organic halides with organotin reagents, in agreement with other studies which showed that transmetalation is the rate-determining step in palladium-catalyzed cross coupling with organotin reagents.^{1c,4b} The results indicate that the transmetalation step is faster in the more polar solvent, which points to a polar mechanism, probably an electrophilic attack of the

(14) In a typical procedure 2.0 mmol of the organic electrophile and 2.0 mmol of the organometallic (Grignard, organozinc, or organotin) reagent were added to a solution of 0.02 mmol (10–15 mg, 1 mol %) of the Pd(Ph-BIAN) catalyst of type 1 or 2. After the reaction mixture was stirred under the indicated conditions, 30 mL of water was added and the organic products were extracted from the reaction mixture using diethyl ether or *n*-hexane (3 × 30 mL). The organic layer was back-extracted with brine (20 mL), dried on MgSO₄, and evaporated to dryness, and the crude product was analyzed by NMR spectroscopy. In the case of volatile products the organic phase was filtered over neutral alumina to remove traces of the metal complex and the filtered solution was analyzed by gas chromatography.

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palladium on the tin-bound carbon atom.^{1c}

The possibility of synthesizing ketones by using Pd(Ph-BIAN) catalysts was demonstrated by the coupling of benzoyl chloride with Sn(CH₃)₄ and reaction of benzyl bromide with Sn(CH₃)₄ under 1 bar of CO pressure. These reactions are highly selective, since in both cases the ketone was formed as the only product in good chemical yield (88–98%). In a separate experiment it was shown that [Pd(Ph-BIAN)Br(CH₂Ph)] in THF or CDCl₃ reacts rapidly with CO at atmospheric pressure and room temperature to yield the Pd-acyl complex [Pd(Ph-BIAN)Br(C(O)-CH₂Ph)] quantitatively,¹⁷ which explains the high efficiency and selectivity of the carbonylative coupling.

We conclude that the new palladium complexes of type 1 and 2, containing the cis-fixed bidentate nitrogen ligand Ph-BIAN, are active catalysts in a variety of selective carbon-carbon bond-forming reactions which can be carried out under mild reaction conditions using small amounts of catalyst (generally 1 mol %).

(17) NMR (in CDCl₃): 3.40 ppm, Pd(CH₂Ph); 4.14 ppm, Pd(C(O)-CH₂Ph). IR (CH₂Cl₂): 1715 cm⁻¹, Pd(C(O)CH₂Ph).

Further studies, involving the scope and limitations of the Pd(Ph-BIAN)-catalyzed carbon-carbon bond-forming reactions as well as mechanistic investigations and comparison with other ligands (e.g. other (cis-fixed) bidentate nitrogen ligands and phosphines), are currently in progress.

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Registry No. 1 (E = CO₂CH₃), 141062-94-4; (*p*-Tol)I, 624-31-7; PhI, 591-50-4; PhCH(Me)Br, 585-71-7; Me₂C=C=CHBr, 6214-32-0; PhCH=CHBr, 103-64-0; PhCH₂MgCl, 6921-34-2; (allyl)-MgCl, 2622-05-1; (*p*-Tol)MgBr, 4294-57-9; (*p*-Tol)ZnCl, 90252-89-4; (*p*-Tol)CH₂Ph, 620-83-7; (PhCH₂)₂, 103-29-7; PhCH₂Ph, 101-81-5; PhCH(Me)CH₂CH=CH₂, 10340-49-5; (PhCH(Me))₂, 5789-35-5; Me₂C=C=CH(*p*-Tol), 141062-93-3; (*p*-Tol)₂, 613-33-2; PhCH=CH(*p*-Tol), 4714-21-0; PhCH₂Br, 100-39-0; PhC(O)Cl, 98-88-4; SnMe₄, 594-27-4; (*p*-Tol)SnBu₃, 31614-66-1; PhCH₂CH₃, 100-41-4; PhCH₂C(O)CH₃, 103-79-7; PhC(O)CH₃, 98-86-2.

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Retro-Alkyne Cyclotrimerization in Thermal Gas-Phase Metal Ion-Arene Reactions

R. Marshall Pope, Steven L. VanOrden, Brian T. Cooper, and Steven W. Buckner*

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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Summary: The thermal energy reactions of Ta⁺, Nb⁺, and NbL⁺ (L = O, N) with arenes in the gas phase result in cleavage of the aromatic rings with formation of metallocyclopentadiene ion complexes via a retro-alkyne cyclotrimerization mechanism. The ring cleavage reactions are proposed to involve bent arene intermediates, analogous to recently observed Ta- and Nb-benzene complexes generated in solution by alkyne cyclotrimerization. The d⁰ system NbO₂⁺ reacts with pyridine exclusively via C-H bond activation involving a σ -metathesis transition state.

The interaction of arenes with transition-metal systems has clear implications for the metal-catalyzed [2 + 2 + 2] cycloaddition reactions of alkynes and nitriles and for the activation of C-H bonds in aromatic systems.^{1,2} In accord with this interest, the reactions of benzene and its halogen-substituted analogues with gas-phase atomic metal ions have been the subject of numerous recent investigations.³⁻⁶ Some of the most reactive gas-phase metal ions

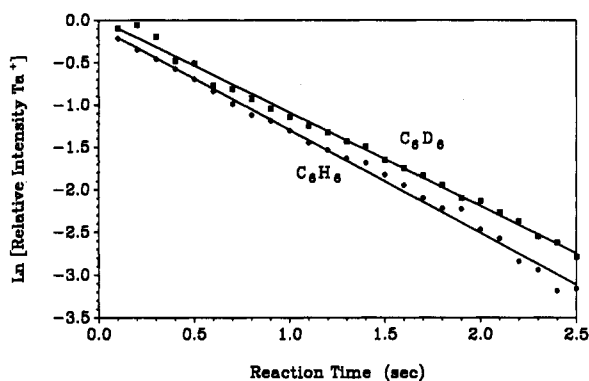


Figure 1. Plot of the decay of ln(Ta⁺) as a function of time in the reaction of thermalized Ta⁺ with (i) C₆H₆ and (ii) C₆D₆. The ratio of the slopes yields a kinetic isotope effect of $k_H/k_D = 1.1 \pm 0.1$.

react directly with benzene to generate benzyne complexes,⁴ and subsequent reactions for some metals produce coordinated polyphenylenes.²⁻⁵ We report here on the unusual thermal reactions of Nb⁺ and Ta⁺ with benzene and pyridine, including ring cleavage by a retro-alkyne

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