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Generation of Organozinc Reagents by Nickel-Diazadiene-Complex Catalyzed Zinc Insertion into Aryl Sulfonates

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Abstract: The generation of arylzinc reagents (ArZnX) by direct insertion of zinc into the C–X bond of ArX electrophiles has typically been restricted to iodides and bromides. The insertions of zinc dust into the C–O bonds of various aryl sulfonates (tosylates, mesylates, triflates, sulfamates), or into the C–X bonds of other moderate electrophiles (X = Cl, SMe) are catalyzed by a simple NiCl₂–1,4-diazadiene catalyst system, where 1,4-diazadiene (DAD) stands for diacetyl diimines, phenanthroline, bipyridine and related ligands. Catalytic zincation in DMF or NMP solution at room temperature now provides arylzinc sulfonates, which undergo typical catalytic cross-coupling or electrophilic substitution reactions.

The insertion of zinc or magnesium metal (M) into the carbon-halogen bond (C-X) of RX affords valuable organometallic reagents (RMX) for use in C-C- and other bond-forming reactions.^[1,2] Such methods, connected with Grignard (Mg)^[3] and Frankland (Zn),^[4] are widely utilized and show distinct scope and limitation profiles. The ease of metal insertion into RX decreases in the order I > Br > CI for X, with alkyl > aryl/vinyl for R, and with Mg > Zn for M. While magnesiation of ArCl demands specific conditions and fails with certain substrates,^[5] zincation of ArCl typically fails^[6] and is sluggish with unactivated ArBr.^[7] Such limitations can be overcome by catalysis, as shown by Bogdanović et al for magnesiation of ArCl with iron catalysts,^[8] or by Gosmini^[9] and Yoshikai^[10] et al for zincation of ArBr and ArCl under cobalt catalysis. However, metal insertion into non-halogenated electrophiles is less common^[11,12] and not synthetically viable for simple aryl sulfonates as obtained from phenols.[13-15]

To examine the feasibility of catalytic metalation of aryl sulfonates,^[13] 1-naphthyl tosylate (**1a**) was stirred with zinc dust and Nal in the presence of various transition metal complexes and ligands in hot tetrahydrofuran (THF) solution (Scheme 1).



Scheme 1. Reaction design to screen for catalytic zincation of aryl sulfonates.

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lodolysis of the reaction mixture will transform any arylzinc **2a** present to iodide **3a**, recovered next to naphthalene (**4a**) and homo-coupled 1,1'-binaphthyl (**5a**)^[16] (Scheme 1).^[17] Initial semiquantitative experiments substantiated this approach and pointed, among various metal-ligand-combinations, to Ni(II)–DAD (DAD = 1,4-diaza-1,3-diene) combinations as promising catalyst systems (Tables S1–S5).^[18] We have now reinitiated those studies by means of a refined experimental design, and the reaction conditions soon channelled towards those in Table 1.

Table 1. Screening of reaction conditions for catalytic zincation of 1a.[a]

	1. <mark>Zn</mark> (4.0 eq.), DBE (0.2 eq.) DMF, 60 °C, 20 min			
	 NiCl₂(dme)–L1 (5+10 mol%) r.t., 30 min 	<mark>ا</mark> ء (4.0 eq	.)	
1-NapO	Ts → 1-NapZn	OTs	 1-Napl 	
1a	r.t., 20 h 2a	10 min	3a	
Entry	Deviation from standard conditions		Yield ^[b] (%)	
1	none	9	96	
2	I_2 (0.5) replacing DBE in activation	:	84	
3	I_2 (0.5) for DBE, solvent NMP	9	91	
4	I_2 (0.5) for DBE, solvent THF, 50 $^\circ\text{C}$:	85	
5	$I_2 \left(0.5 \right)$ for DBE, 10 mol% [Ni], solvent THF	:	86	
6	$I_2~(0.5)$ for DBE, Mg (1.5) + ZnCl_2 (2.0) for Zr mol% [Ni], solvent THF	n, 10 a	83	

[a] Reaction conditions: **1a** (1 mmol), solvent (3 mL). Activation with DBE as indicated above; activation with l_2 (0.5 eq.) involved stirring at r.t. until decoloration was reached. [b] Spectral yield of **3a** by qNMR. DBE = 1,2-dibromoethane; NMP = *N*-methyl-2-pyrrolidone; DMF = *N*,*N*-dimethylformamide.

Combining the precursors NiCl₂(dme) or NiCl₂(diglyme) with ligand IPr-^{Me}DAD (**L1**)^[19] and zinc dust in DMF solution provides a medium that transforms aryl tosylate **1a** into organozinc reagent NapZnOTs (**2a**) at ambient temperature (entry 1). Zinc was activated by iodine or dibromoethane. The presence of iodide is facultative (entry 1 vs 2–6), precluding a reaction pathway via catalytic iodination^[12a] (**1a**→**3a**) and zinc insertion.^[20] The reaction is feasible in THF at 50 °C, or at room temperature with higher catalyst loading (entries 4, 5). Amidic solvents DMF or *N*methyl-pyrrolidone (NMP; entry 3) are nevertheless preferred, as they facilitate high conversion at ambient temperature and suppress homocoupling to **5a**. Metalation with magnesium in the presence of ZnCl₂ was also possible (entry 6).^[21]

Suitable ligands were found among open-chain DADs (L1–L4)^[19] or related Schiff bases (L5, L6), whose simple syntheses and amenability to structural variation render them more versatile for optimization than the similarly successful phenanthroline-type ligands (L7–L9; Figure 1, Table S9).^[22]

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Figure 1. Ligand variation in the nickel-catalytic zincation of **1a** by the standard procedure (Table 1). The spectral yield of **3a** after iodolysis and catalyst loading (mol%, in brackets) are indicated. ^a Zinc was activated with I₂ (0.5 equiv.). ^b 1:1 ratio of [Ni]:L used; else, it was 1:2.

Notably, **L2** and more so **L7** profit from iodine activation of zinc powder, which is not required with **L1** (Figure 1).^[23] The promising catalyst incorporating **L7** fully converted **1a** at the 3 mol% level, but was not the first choice for subsequent experiments in view of the iodide activation requirement.

The substrate scope of catalytic zincation was further explored by applying the simple $NiCl_2(dme)-L1$ catalyst system to a range of aryl tosylates, including functionalized ones (Table 2). The efficiency of metalation was determined through iodolysis of the reaction mixture, with subsequent qNMR analysis of aryl iodide **3**, and the result was confirmed by isolation of the latter in near identical yield (Table 2).

Table 2. Substrate scope of the nickel-diazadiene-complex catalyzed zincation of aryl tosylates with follow-up iodolysis.^[a]

	R II	a) Zn (4.0 eq b) NiCl ₂ (dme c) 1, DMF; r.t <u>Metalati</u>), DBE (0.2 eq.))– L1 (1:2) , 20 h		$\frac{l_2 (4.0 \text{ eq.})}{0 \text{ °C, } 10 \text{ min}}$		
Entry	Substrate	[Ni] (mol%)	Yield of 3 (%) ^[b]	Entry	Substrate	[Ni] (mol%)	Yield of 3 (%) ^[b]
1	OTs	5	96 ^[c] (96)	11	Me Me Me OTs	10	77 (77)
2	OTs	5	88 ^[d] (92)	12	tBu tBu	10	0
3	OTs	5	98 (99)	13	MeO	5	83 (88)
4	-OTs	5	(21)	14 ^[e]	Et ₂ N OTs	5	96 (99)
5	OTs	5	85 (88)	15	CO ₂ Me OTs	10	96 (96)
6	OTs Me	5	95 (96)	16	MeO ₂ C	10	75 (78)
7	MeOTs	5	85 (90)	17		5	86 (85)
8	Me	5	90 (93)	18	OTs	10	56 (54)
9	<i>t</i> Bu OTs	10	76 (80)	19	CI	5	77 ^[f] (77)
10	OTs iPr	10	80 (85)	20 ^[g]	OTs	15	88 (89)

[a] Reaction conditions: Zn (4.0 equiv.) and DBE (0.2 equiv.) activated for 20 min at 60 °C in DMF (3 L/mol); NiCl₂(dme) and L1 ([Ni]:L1 = 1:2) added at r.t. and stirred for 30 min; ArOTs added and mixture stirred for 20 h. [b] ArZnOTs was quantified as ArI after iodolysis (l_2 , 0 °C, 10 min); isolated yields of chromatographically purified material; numbers in brackets are spectroscopic yields by quantitative ¹H-NMR against internal standard. [c] ArI/ArH = 98:2. [d] ArI/ArH = 95:5. [e] 1.2 equiv. of l_2 used for quenching with short (1 min) stirring at 0 °C. [f] IC₆H₄Cl/C₆H₄l₂/PhI 91:6:3. [g] NMP was used as solvent.

Like 1a, the regioisomeric 2-naphthyl- (entry 2) and orthobiphenyl- (entry 3) derived sulfonates show excellent zincation yields. The low yield of the *p*-biphenyl derivative is due to the low solubility of both starting material and the zinc reagent, which stopped the conversion (entry 4). Core-alkylated aryl sulfonates were efficiently metalated (entries 5-9), although a larger group like isopropyl next to the reaction center diminishes the reaction efficiency (entries 10, 11), and tert-butyl blocks it entirely (entry 12). Electron-rich substrates (entries 13, 14) were well tolerated, as were acceptor substrates of the nitrile and ester type (entries 15-17), whose functional groups remained untouched. The potentially coordinating quinolinyl sulfonate reacted moderately well (entry 18). With 4-chlorophenyl tosylate, the catalyst prefers C-OTs over C-Cl activation, and a trace of para-diiodobenzene stems from double metalation (entry 19). Twofold zincation was pursued and obtained with naphthalene-1,5-ditosylate (entry 19).

Although the organozinc reagents were most conveniently quantified after iodolysis, we wished to support the generation of ArZnOTs (2) reagent by its direct observation in solution. Hence, a catalytic metalation of **1a** was performed in (D₇)-DMF, and the solution scrutinized with 2D NMR methods. The presence of zinc insertion product **2a** was revealed by complete ¹H and ¹³C NMR signal sets, including a quaternary signal at & 156.3 (C–Zn) (Table S10). Minor amounts of naphthalene and ligand **L1** were observed in the reaction mixture,^[24] and the former rose in intensity after addition of a little water to the sample, with those of **2a** disappearing.

Since counter-ions X affect the reactivity of arylzinc reagents ArZnX,^[25] evaluation of the synthetic utility of the new arylzinc sulfonates beyond iodolysis was vital. 1-Naphthyl- (**1a**) and 2-biphenyl tosylate (**1b**) were zincated as usual (Table 1), and the reagents exposed to electrophiles (Table 3). Quenching of **1a** with D₂O gave (1-D)-naphthalene (entry 1). Halogenation of **1b** with NBS returned *ortho*-bromobiphenyl near quantitatively (entry 2). Cross-coupling of organozincs **2a/b** was realized with Buchwald's Pd–S-Phos catalyst system:^[26] allylation with allyl bromide (entry 4), methylation with (¹³C)-methyl iodide (entry 5), and Negishi coupling with aryl halides (entries 6 and 7) proceed at ambient temperature in >90% yield. The incompatibility of DMF with acid chlorides initially prevented acylations of **1a/b**, however, a Fukuyama-type acylation^[27] of a thioester electrophile provided the ketone cleanly (entry 8).

Our work had focussed on catalytic zinc insertion into aryl tosylates which are among the most readily available derivatives of phenols. We were also keen to examine the scope of Ni–DAD catalysts towards other electrophiles. A cursory evaluation of naphthyl electrophiles bearing various leaving groups is shown in Table 4.

Compared with tosylate **1a**, the mesylate and 1-/2-naphthyl triflates were efficiently zincated, as were aminosulfonate electrophiles. A systematic variation of halides showed that while 1-fluoronaphthalene is unreactive, both 1-bromo- and 1-chloronaphthalene were successfully zincated under catalytic conditions. Combined with the previous experiment involving 1-chloro-4-tosyloxybenzene (Table 2, entry 19), opportunities for chemoselective activation arise. Remarkably, the feebly

activated 1- and 2-methylthionaphthyl ethers were also zincated by the Ni–DAD catalyst,^[28] pointing to new reaction opportunities for accessing organometallic reagents from less activated electrophiles.^[29]

Table 3. Reactions of ArZnOTs with electrophiles.^[a]



[a] Reaction size: ArOTs (1; 2 mmol), DMF (6 mL). [b] Isolated yields of chromatographically purified material; numbers in brackets are qNMR yields. [c] 95% D-incorporation at C-1. [d] Pd(OAc)₂–S-Phos 1:2 (mol% loading given in brackets). [e] ArAll–ArH 95:5. [f] Ar¹³CH₃–ArH 87:13, ArH due to acid traces in ¹³CH₃. [g] 1.5 equiv. of ArZnOTs (2) used. All = allyl; NBS = *N*-bromosuccinimide.

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Table 4. Propensity of substrates with various leaving groups for nickel-catalyzed zincation. $^{\left[n\right] }$



[a] Reactions performed at the 1 mmol scale. Solvent and yield of ArZnX (in brackets) indicated for each substrate. ArZnX was quantified after iodolysis as 1-Napl (**3a**) or 2-Napl (**3c**) by qNMR.

Based on the experimental observations in hand and with reference to previous work on catalytic zincations^[9] or Ni–bipy catalyzed reductive carboxylation,^[22d] we formulate a likely catalytic cycle for the nickel-catalyzed reaction as in Scheme 2.



Scheme 2. Proposed catalytic cycle. L = IPr.^{Me}DAD (L1); dme = dimethoxyethane;

(L)Ni^{II}Cl₂ (L = L1, IPr-^{Me}DAD) formed in situ is reduced to (L)Ni⁰, presumably stabilized as (L)₂Ni with additional ligand,^[19] that oxidatively adds aryl tosylate to afford an arylnickel(II)

species. A pool of zinc (pseudo)halide (X = CI, OTs) accumulates through activation and SET-reduction events, and transmetalation of aryl from (L)Ni^{II}ArX to ZnX₂ can be considered to generate ArZnX. Such a step appears unfavorable with Ni^{II}, however, since the usual course of transmetalation is transfer of aryl from electropositive (Zn, Mg) to less electropositive metal centers (Ni^{II}, Pd^{II}, Pt^{II}).^[30] By SET-reduction of Ni^{II}, a more nucleophilic (L)Ni^IAr species is obtained instead, with higher propensity to transfer aryl to ZnCI(OTs), releasing ArZnOTs and (L)Ni^ICl in the process.^[31] The latter is reduced by another SET from zinc metal to regenerate (L)_nNi⁰.

Reductive coupling of ArOTs (1) to biaryl (5) is a potential side-reaction,^[16] and while the latter is preferred with Niphosphane catalyst systems^[16b] and ascribed to a Ni^I–Ni^{III} cycle with oxidative addition of ArX to Ni(I)Ar,^[16], the DAD-type ligands of the current catalyst system apparently disallow this route. Besides the preparative opportunities that the catalytic zincation of aryl sulfonates offers, our results imply that mechanistic pathways involving transmetalation with temporary release of organometallics ArMX enable additional options in Ni-catalyzed reductive coupling reactions, which have previously been assumed to take place at the Ni-center exclusively.^[22]

In summary, we have developed a generally applicable method to catalytically zincate aryl sulfonates and other deactivated electrophiles that provides synthetically useful arylzinc reagents. The DAD ligands used are readily available and easy to modify synthetically. As such, the Ni–DAD catalyst systems introduced by tom Dieck^[19] may yet find more widespread application in reductive transformations.

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Keywords: aryl sulfonates • catalysis • nickel • metalation • organozinc reagents

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Unlike aryl halides, common aryl sulfonates do not undergo metal insertion to give organometallic reagents. A nickel-diazadiene complex has been found to catalyze zincation of aryl sulfonates and provide synthetically valuable arylzinc sulfonates.



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Generation of Organozinc Reagents by Nickel-Diazadiene-Complex Catalyzed Zinc Insertion into Aryl Sulfonates