

Catalysis | Hot Paper |

Dumbbell-Shaped 2,2'-Bipyridines: Controlled Metal Monochelation and Application to Ni-Catalyzed Cross-Couplings

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Abstract: 2,2'-Bipyridine ligands (dsbpys) with dumbbell-like shapes and differently substituted triarylmethyl groups at the C5 and C5' positions showed high ligand performance in the Ni-catalyzed cross-electrophile coupling and the Ni/photoredox-synergistically catalyzed decarboxylative coupling reactions. The superior ligand effects of dsbpys compared to the conventional bpy ligands were attributed to the monochelating nature of dsbpys.

2,2'-Bipyridine (bpy) has been established as a prime ligand scaffold for Ni catalysis involving a single-electron redox process, which enables novel molecular transformations.^[1,2] For instance, Weix and co-workers utilized 4,4'-di-*tert*-butyl-2,2'-bipyridine (4,4'-*t*Bu₂bpy) or 4,4'-dimethoxy-2,2'-bipyridine (4,4'-(MeO)₂bpy) for the cross-electrophile coupling between aryl bromides and alkyl bromides in the presence of Mn or Zn reductants,^[3,4] while Doyle, MacMillan and co-workers disclosed photochemical decarboxylative coupling between aryl bromides and alkyl carboxylic acids using 4,4'-*t*Bu₂bpy.^[5] Metallaphotoredox catalysis for the cross-coupling between aryl bromides and potassium alkyltrifluoroborates using 4,4'-*t*Bu₂bpy was reported by Molander and co-workers.^[6,7] More recently, Baran and co-workers reported electrochemical aryl amination using a Ni-bpy catalyst system.^[8–10] Despite significant advances made by these pioneering works, high catalyst loadings and limited substrate scope still remain problems in the reported Ni systems. In these Ni-bpy catalyses, catalytically active species are likely to be in the form of bpy-monochelated Ni complexes [Ni(bpy)], but dynamic coordination equilibria perturb the number of bpy ligands on the Ni atom. These coordination behavior may lead to a decrease in catalytic efficiency

(Figure 1 a).^[8b] We envisioned that distal steric effects of bpy C5 and C5'-substituents, which do not hamper the catalytic reactions by steric hindrance in the vicinity of the metal but develop outside the boundary of the catalytic space to allow selective monochelation to the metal center, could be an effective approach to improve the efficiency of the Ni catalysis (Figure 1 b).^[11,12]

Herein, we report the synthesis of a new class of 2,2'-bipyridine ligands (dsbpys, structures shown in Scheme 1) having dumbbell-like shapes with differently substituted triarylmethyl groups at the C5 and C5' positions and their applications as favorable ligands for the Ni-catalyzed cross-electrophile coupling and the Ni/photoredox-synergistically catalyzed decarboxylative coupling. Analysis of metal coordination behaviors of the bpy ligands by UV-vis absorption spectroscopy indicated the apparent monochelating nature of the dumbbell-shaped bpy ligands.

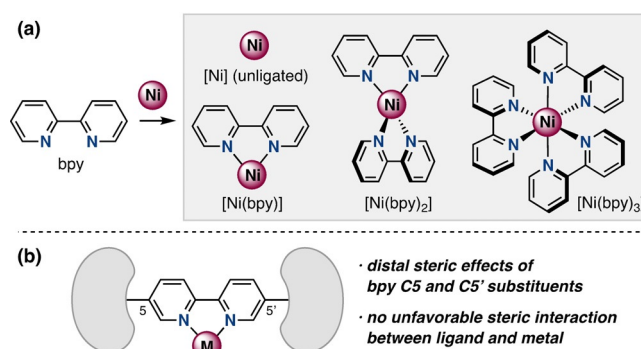
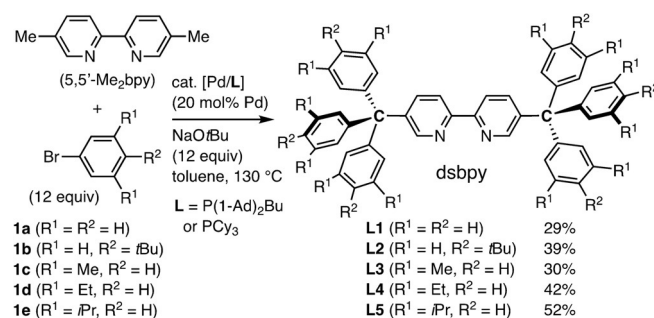


Figure 1. (a) Dynamic coordination equilibrium of Ni-bpy complexes and (b) design for controlled bpy monochelation.



Scheme 1. Synthesis of dsbpys through the Pd-catalyzed six-fold deprotonative C(sp³)-H arylation of 5,5'-Me₂bpy.

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The dsbpy ligands were synthesized in one step by applying the Pd-catalyzed deprotonative C(sp³)–H arylation of heteroarylmethanes, which was recently reported by Walsh and co-workers.^[13] Thus, six-fold C(sp³)–H arylation of commercially available 5,5'-dimethyl-2,2'-bipyridine (5,5'-Me₂bpy) with aryl bromides (**1**) in the presence of a Pd catalyst afforded the corresponding dsbpy ligands in reasonable yields (Scheme 1; **L1–L5** from **1a–e**, respectively).^[14,15] The molecular structure of the dsbpy (**L5**) with the most pronounced steric demand was determined by X-ray diffraction analysis. Some of the *meta*-isopropyl groups form the side walls at the ends of the bipyridyl center axis, leaving a substantial accessible space around the bipyridyl scaffold (Figure 2).

To evaluate the substituent effects at the 5,5'-positions of the bpy ligands on Ni^{II}-bpy coordination equilibria, titrations between NiBr₂·DME (DME: 1,2-dimethoxyethane) and bpy ligands (5,5'-Me₂bpy, **L1–L5**) were conducted in *N,N*-dimethylacetamide (DMA) at room temperature while monitored by UV-vis absorption spectroscopy (270–350 nm). To quantify the coordination equilibria, the concentration profiles for each Ni species and the free ligand were constructed with the equilibrium-restricted factor analysis aided by the *Sivvu* program.^[16] The results are summarized in Figure 3.

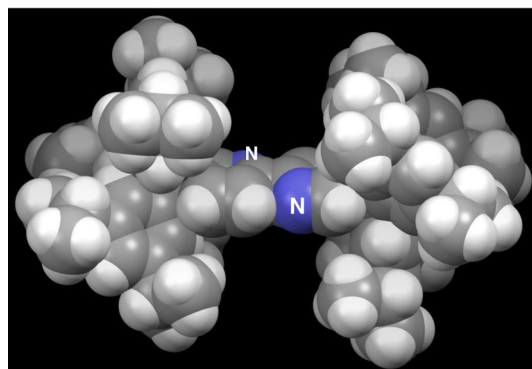


Figure 2. A space-filling model of **L5** determined by X-ray diffraction analysis (solvents are omitted for clarity).

With 5,5'-Me₂bpy, continuous addition of the Ni salt until a 0.5:1 Ni/ligand ratio was reached led to the exclusive formation of a bischelated complex [Ni(5,5'-Me₂bpy)₂] (Figure 3a).^[17] The reaction at a 1:1 Ni/ligand ratio afforded a mixture of a monochelated complex [Ni(5,5'-Me₂bpy)], the bischelated complex [Ni(5,5'-Me₂bpy)₂], and an unligated Ni species. Even with excess Ni (Ni/ligand 1.5:1), the bischelated complex [Ni(5,5'-

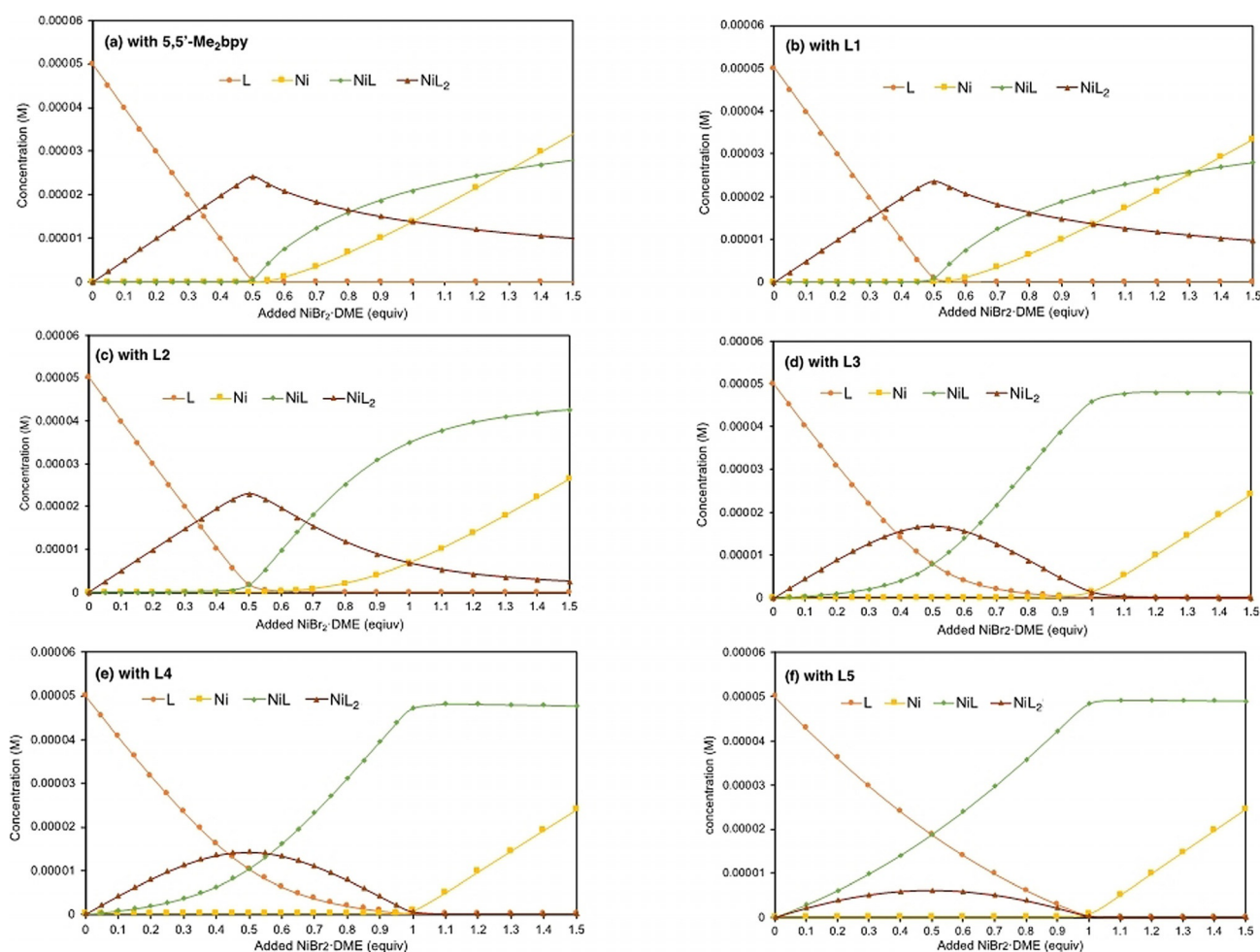


Figure 3. The concentration profiles for Ni species with (a) 5,5'-Me₂bpy, (b) **L1**, (c) **L2**, (d) **L3**, (e) **L4**, and (f) **L5**.

Me₂bpy)₂] still remained in the solution, indicating a strong tendency of 5,5'-Me₂bpy to cause a second chelation as demonstrated in the literature for the parent bpy ligand and 4,4'-dimethyl-2,2'-bipyridine.^[8b, 16] While the simplest dsbpy (L1) substituted with trityl groups provided a coordination profile similar to that of 5,5'-Me₂bpy (Figure 3b), the *para*-*t*Bu-substituted dsbpy (L2) gave a higher distribution for monochelated Ni complex [Ni(L2)] at a 1:1 Ni^{II}/ligand ratio, albeit with the substantial coexistence of a Ni species [Ni(L2)₂] with participation of the second L2 molecule (Figure 3c). More selective monochelation was achieved by dsbpys (L3–L5) with the 3,5-disubstituted trityl groups (Me, Et, *i*Pr; Figures 3d–3f). Notably, the bulkiest dsbpy ligand L5 was most effective for controlled monochelation. Gibbs free energy differences between the first ([Ni] to [NiL], ΔG_1) and second ([NiL] to [NiL₂], ΔG_2) ligand binding (L = 5,5'-Me₂bpy, L1–L5) are summarized in Figure 4.^[18]

The dsbpys exhibited high ligand performance in the Ni-catalyzed cross-electrophile coupling between aryl bromides and alkyl bromides, developed by Weix.^[3a] The reported protocol required substantial Ni loading (5–10 mol%) and the use of additives such as NaI and pyridine for attaining acceptable yields of the desired cross-coupling product. Indeed, we observed that the reaction between bromobenzene (**1a**, 0.5 mmol) and 1-bromododecane (**2a**, 0.6 mmol) in DMA (0.25 M) at 60 °C for 14 h in the presence of Zn as a reductant (2 equiv) and a Ni catalyst (1 mol%) prepared in situ from NiBr₂·DME (1 mol%) and 2,2'-bipyridine (bpy) (1.1 mol%) resulted in only 34% yield of dodecylbenzene (**3a**) with the formation of homocoupling product biphenyl (**4**) as the major product (57%; Table 1, entry 1).^[19] Under the same conditions, the simplest dsbpy ligand (L1) substantially suppressed the formation of **4** with a slightly improved yield of the cross-coupling product (49% of **3a**, entry 2). While the *para*-*t*Bu-substituted dsbpy (L2) showed a similar but less favorable ligand performance (entry 3), much improved cross-coupling efficiencies were observed with the bulkier series of dsbpy ligands (L3–L5), giving **3a** in 83–86% yields, respectively (entries 4–6).

Reported substituted bpy ligands such as 4,4'-*t*Bu₂bpy, 4,4'-(MeO)₂bpy, 5,5'-Me₂bpy, and 5,5'-Me₂bpy (structures shown in Table 1) gave unfavorable product distributions similar to that with the parent bpy ligand (Table 1, entries 7–10). The 6,6'-dis-

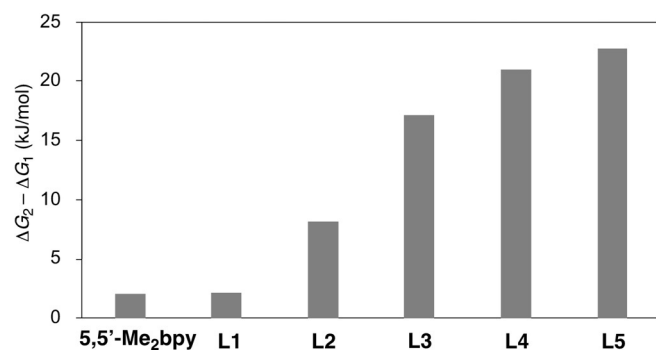


Figure 4. Gibbs free energy differences between the first ([Ni] to [NiL], ΔG_1) and second ([NiL] to [NiL₂], ΔG_2) ligand binding (L = 5,5'-Me₂bpy, L1–L5).

Entry	Ligand	3a [%] ^[b]	4 [%] ^[b]
1	bpy	34	57
2	L1	49	9
3	L2	38	12
4	L3	83	14
5	L4	84	5
6	L5	86 (85)	6
7	4,4'- <i>t</i> Bu ₂ bpy	17	31
8	4,4'-(MeO) ₂ bpy	12	17
9	5,5'-Me ₂ bpy	31	69
10	5,5'-Me ₂ bpy	39	57
11	6,6'-Me ₂ bpy	0	0

^[a] Conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), NiBr₂·DME (1 mol%), ligand (1.1 mol%), Zn (1 mmol), DMA (2 mL), 60 °C, 14 h. ^[b] Yields determined by ¹H NMR analysis. Isolated yield shown in parentheses.

substituted ligand (6,6'-Me₂bpy) induced no conversion of the substrates (entry 11).

The superior ligand effects of the dsbpys (L1–L5) compared to the conventional bpy ligands are attributable to the apparent monochelating nature of dsbpys indicated by the UV-vis analysis of the Ni^{II}-bpy coordination equilibria. The distal steric effects of the triarylmethyl substituents at the C5 and C5' positions may also contribute to the suppression of the aryl homocoupling of the aryl bromides through inhibiting a bimolecular disproportionation reaction of the putative aryl bromide oxidative addition product [Ar-Ni-Br]. These effects are significant with dsbpys (L3–L5) having the 3,5-disubstituted trityl groups.

As shown in Table 2, the Ni catalyst systems with high performing ligands L3–L5 improved the efficacy of cross-electrophile coupling between several aryl bromides and alkyl bromides compared to that with bpy. Specifically, an electronically challenging aryl bromide 4-bromoanisole (**1f**) coupled with ethyl 4-bromobutanoate (**2b**) to afford **3b** in 82% yield using L3, while bpy gave **3b** in a low yield (25%) along with the biaryl homocoupling product (31% based on **1f**). The reaction of an electron-deficient aryl bromide 4-bromobenzonitrile (**1g**) occurred most efficiently with L5 (**3c**, 83%). While the cross-coupling was hampered by the *ortho*-substituent of *o*-tolyl bromide (**1h**), an acceptable yield was obtained with L3 (**3d**, 47%). The dsbpys L3–L5 allowed the cross-coupling of the alkenyl bromide, 2-bromopropene (**1i**), with benzyl 4-bromobutanoate (**2c**) in good yields (**3e**, 58–71%). Cyclic secondary alkyl bromides such as bromocyclopentane (**2d**) and 4-bromo-*N*-tosylpiperidine (**2e**) participated in the reaction using L3–L5, giving the corresponding products **3f** and **3g** in good to high yields.

Table 2. Scope of aryl/alkenyl bromides (**1**) and alkyl bromides (**2**) with Ni catalyst systems.^[a]

Ligand	bpy	25	44	14	34	36
	L3	82 (71)	51	47 (44)	58	63 (48)
	L4	75	62	41	68	60
	L5	47	83 (61)	29	71 (62) ^[d]	56

[a] Conditions: **1** (0.5 mmol), **2** (0.6 mmol), NiBr₂·DME (1 mol%), ligand (1.1 mol%), Zn (1 mmol), DMA (2 mL), 60 °C, 14 h. [b] Yields determined by ¹H NMR analysis. Isolated yield shown in parentheses. [c] **1a** (0.75 mmol), **2e** (0.5 mmol). [d] The isolated product **3e** was contaminated with benzyl butyrate (**3e**/benzyl butyrate = 90:10, based on ¹H NMR analysis).

Furthermore, dsbpy was applicable to the Ni/photoredox-synergistically catalyzed decarboxylative cross-coupling of aryl bromides and alkyl carboxylic acids, developed by Doyle, Mac-Millan and co-workers.^[5a] The reaction of unactivated aryl bromides still remains a challenge with the reported system. As shown in Table 3, **L3**–**L5** showed better ligand performance than 4,4'-tBu₂bpy in the reaction between electronically unbiased **1a** and *N*-Boc-proline (**5**) with 5 mol% Ni loading in the presence of Ir[dF(CF₃)ppy]₂(4,4'-tBu₂bpy)PF₆ (1 mol%) as a photocatalyst, giving **6a** in good-to-high yields.^[20] More challenging substrate **1f** underwent efficient coupling reaction with **L3** to afford **6b** in 72% yield. Similar ligand effects were observed in the reaction of alkenyl bromide (**1i**) to produce **6c**.

In conclusion, dumbbell-shaped 2,2'-bipyridines (dsbpy)s bearing triarylmethyl substituents at the C5 and C5' positions were synthesized through Pd-catalyzed six-fold deprotonative C(sp³)–H arylation of commercially available 5,5'-dimethyl-2,2'-

bipyridine. The dsbpy–Ni^{II} titration monitored by UV absorption spectroscopy showed monochelation properties of the dsbpy (**L3**–**L5**). These ligands showed improved ligand performance compared to conventional bpy-type ligands in the Ni-catalyzed cross-electrophile coupling between aryl bromides and alkyl bromides and the Ni/photoredox-synergistically catalyzed decarboxylative coupling between aryl bromides and alkyl carboxylic acids. Further investigations of the catalytic application of dsbpy ligands are ongoing in our laboratory.

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Conflict of interest

The authors declare no conflict of interest.

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Table 3. Ni/photoredox-synergistically catalyzed decarboxylative cross-coupling of aryl/alkenyl bromides (**1**) and alkyl carboxylic acids (**5**).^[a]

Ligand	4,4'-tBu ₂ bpy	34	17
	L3	87 (77) ^[c]	72 (71) ^[c]
	L4	84	59
	L5	74	41

[a] Conditions: **1** (0.1 mmol), **5** (0.3 mmol), NiBr₂·DME (5 mol%), ligand (5.5 mol%), Ir[dF(CF₃)ppy]₂(4,4'-tBu₂bpy)PF₆ (1 mol%), DMA (2 mL), 40 W blue LED, room temperature, 22 h. [b] Yields determined by ¹H NMR analysis. Isolated yield shown in parentheses. [c] The isolated products **6a**–**c** were existed as 2.2:1, 2:1, 1.3:1 mixture of rotamers, respectively.

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- [18] Cyclic voltammetry analysis was carried out to examine the electrochemical characteristics of [Ni-(5,5'-Me₂bpy)] and [Ni-(L5)] systems. See the Supporting Information for details.
- [19] The use of *N,N'*-dimethylpropyleneurea (DMPU), which had proved to be an effective solvent in the Weix's report (ref 3a), gave ligand effects similar to those with DMA. The reaction using L5 in DMPU gave **3a** in 85% yield along with 3% of **4**. When bpy was used as a ligand, the formation of **4** (29%) was substantially suppressed although the yield of **3a** was as moderate as 40%.
- [20] No ligand exchange was observed by ¹H NMR spectroscopy after Ir[dF(CF₃)ppy]₂(4,4'-tBu₂bpy)PF₆ was treated with L3 (1:1 ratio) in CDCl₃ at room temperature for 2 h.

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