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PAPER

Dinickel(II) complexes: Preparation and catalytic activity†

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Ligands ($\mathbf{L_{a-c}}$) based on 2,7-bis(3,5-di-R-pyrazol-1-yl)-1,8-naphthyridine (**a**, R = H; **b**, R = CH_3; **c**, R = Ph) were prepared for the construction of a series of dinickel complexes. Treatment of $\mathbf{L}_x$ with $NiCl_2$ in an anhydrous methanol/THF solution resulted in the formation of dinuclear complexes [($\mathbf{L}_x$)(μ-Cl)$_2$Ni$_2$Cl$_2$(CH$_3$OH)$_2$] (**3**, x = **a**; **4**, x = **b**; **5**, x = **c**). These new complexes were characterized by elemental analysis, IR and UV–Vis spectroscopic techniques. The structures of complexes **3** and **4** were further confirmed by X-ray diffraction studies. Interestingly, crystals of **4** were obtained as a co-crystallization of **4** and the methanol substituted species [{($\mathbf{L_b}$)(μ-Cl)$_2$Ni$_2$Cl(CH$_3$OH)$_3$}Cl] (**4′**). These dinickel complexes have been tested in the catalytic homo-coupling of terminal alkynes with the use O_2 as the oxidant, showing excellent activities. A clear improvement on the catalytic activity of these complexes is observed as compared to the mono-nuclear species.

Introduction

Dinickel complexes have received considerable attention over the past several decades,[1–4] especially as they are model compounds for dinuclear metalloenzymes,[5–7] and are catalysts for cross coupling and oxidations.[8,9] They have also been studied in an attempt to understand and control the dinuclear metal reactivity.[10] The structural analysis of urease, which is a typical dinickel based enzyme, reveals that two nickel ions are separated by a distance of *ca.* 3.5 Å.[11] To meet this demand, many model systems use either a bridging donor or a bi-nucleating ligand to confine the metal ions in close proximity.

2,7-Bis(3,5-dimethylpyrazol-1-yl)-1,8-naphthyridine $\mathbf{L_b}$ (Chart 1) reported by Chen and co-workers is a rigid tetradentate,[12] which is suitable to accommodate two metal ions. However, there is no report concerning the complexation of this chelating ligand. As part of our ongoing research project on the coordinating capability of polytridentates,[13] we are interested in these naphthyridine based donors because of their use as binding units in the construction of di- or poly-nuclear systems. This work describes the synthesis of a series of pyrazolyl substituted naphthyridine ligands ($\mathbf{L_{a-c}}$) and their dinickel complexes. Furthermore, these dinickel species show good catalytic activities on homo-coupling of terminal alkynes.

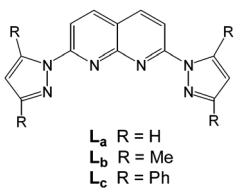
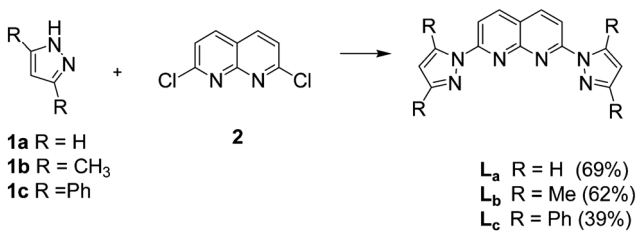


Chart 1 Bis(pyrazol-1-yl)-1,8-naphthyridine ligands.



Scheme 1 Preparation of ligands $\mathbf{L_a}$–$\mathbf{L_c}$.

Results and discussion

Ligand synthesis

Substituted 1,8-naphthyridine ligands $\mathbf{L_a}$–$\mathbf{L_c}$ were prepared by modification of a reported method (Scheme 1).[12] Substituted pyrazole **1b–1c** was obtained from the condensation of 1,3-diketone with hydrazine, whereas 2,7-dichloro-1,8-naphthyridine **2** was prepared according to the literature reported method.[14] It has been reported by Chen *et al.* that the C–N bond formation between pyrazole and **2** should be carried out under the palladium-mediated cross coupling conditions.[12] However, we found that the direct substitution of **2** with pyrazole or 3,5-dimethylpyrazole to yield $\mathbf{L_a}$ or $\mathbf{L_b}$ could be accomplished under heating conditions, but not $\mathbf{L_c}$. Typically, a sealed tube loaded with a

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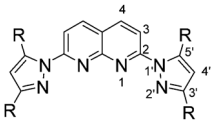
†Electronic supplementary information (ESI) available: Plots of inverse magnetic susceptibilities (1/χM) *versus* temperature for complexes **3**–**5**. CCDC reference number for **3** and (**4**+**4′**): 835817–835818. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt11398h

Table 1 Selected ^{1}H NMR data of ligands



Ligand	^{1}H NMR shift in ppm (multiplicity)				
	H-5′	H-4′	H-3′	H-4	H-3
$\mathbf{L_a}$	8.86 (d)	6.65 (dd)	7.87 (d)	8.61 (d)	8.29 (d)
$\mathbf{L_b}$	—	6.14 (s)	—	8.44 (d)	8.19 (d)
$\mathbf{L_c}$	—	7.08 (s)	—	8.65 (d)	8.19 (d)

Table 2 UV-vis absorption data for ligands $\mathbf{L_{a-c}}$ and complexes **3–5**

Compound	λ_{max} in nm (ε)
$\mathbf{L_a}$	352 (4.9×10^4), 337 (3.7×10^4), 256 (7.1×10^4)
$\mathbf{L_b}$	352 (3.4×10^4), 338 (2.6×10^4), 256 (4.7×10^4)
$\mathbf{L_c}$	355 (2.0×10^4), 247 (4.0×10^4)
3	672 (7), 360 (3.6×10^4), 352 (3.6×10^4), 257 (3.8×10^4)
4	668 (6), 371 (2.2×10^4), 352 (5.7×10^4), 254 (7.9×10^4)

mixture of **2** and pyrazole (mol ratio = 1 : 2) in DMF was heated at 140 °C for 12 h and ligand $\mathbf{L_a}$ was obtained in 69% isolated yield upon re-precipitation purification. This approach appears to be a more green way as compared to a metal-catalyzed reaction. Direct displacement did not proceed smoothly with 3,5-diphenylpyrazole, which maybe due to the steric hindrance of the nucleophile. Nevertheless, with the assistance of copper ion and microwave heating, the coupling reaction of **2** with **1c** did provide $\mathbf{L_c}$ in low yield.

Ligands $\mathbf{L_{a-c}}$ have been fully characterized by ^{1}H and ^{13}C NMR spectroscopy (Table 1). These data show with no ambiguity that ligands $\mathbf{L_{a-c}}$ are a 2,7-di-pyrazolyl substituted compound as expected. The ^{1}H NMR spectra for ligands $\mathbf{L_{a-c}}$ exhibit signals diagnostic of the naphthyridine ring C–H protons which appear as two sets of doublet over the range δ 8.0–8.7. The pyrazole protons of $\mathbf{L_b}$ and $\mathbf{L_c}$ show their NMR shifts as a singlet at δ 6.14 and 7.98, respectively, while the pyrazole protons of $\mathbf{L_a}$ appear as three sets of signals at δ 7.95 (H-3′), 6.69 (H-4′) and 8.84 (H-5′). ^{13}C NMR shifts are also consistent with the proposed structures.

Dinickel complexes and characterization

Treatment of nickel(II) chloride with $\mathbf{L_{a-c}}$ in a 2 : 1 molar ratio gave excellent yields of chloride-bridged dinickel complexes **3–5**, respectively (eqn (1)). All complexes obtained were green solids, and complexes **3** and **4** were further re-crystallized from a MeOH/CH_2Cl_2 solution. These complexes were characterized by elemental analysis, IR and UV-Vis spectroscopy. In comparison with the absorption spectrum of the free organic ligand (Table 2), the absorption bands of complexes were red-shifted, indicating the coordination effects. Both complexes **3** and **4** show their weak d–d transitions at 672 and 668 nm, respectively. To confirm their real structures, the single crystals of complexes **3** and **4** were determined by a SMART CCD X-ray diffractometer. The detail structures are discussed with their structural features, while their selected bond lengths and angles are collected in Tables 3–5.

Table 3 Selected bond lengths (Å) and angles (°) for complex **3**

Ni(1)–N(1)	2.043(5)	Ni(1)–Cl(3)–Ni(2)	85.51(5)
Ni(1)–N(3)	2.168(5)	Ni(2)–Cl(2)–Ni(1)	84.79(5)
Ni(2)–N(4)	2.162(5)	N(1)–Ni(1)–N(3)	76.3(2)
Ni(2)–N(6)	2.035(5)	N(6)–Ni(2)–N(4)	76.5(2)
Ni(1)–Cl(3)	2.371(2)	N(1)–Ni(1)–Cl(2)	178.4(2)
Ni(1)–Cl(1)	2.388(2)	N(6)–Ni(2)–Cl(3)	178.3(1)
Ni(1)–Cl(2)	2.414(2)	N(1)–Ni(1)–Cl(1)	87.7(1)
Ni(2)–Cl(2)	2.392(2)	N(6)–Ni(2)–Cl(4)	87.9(1)
Ni(2)–Cl(3)	2.402(2)	O(2)–Ni(2)–N(4)	164.3(2)
Ni(2)–Cl(4)	2.394(2)	O(1)–Ni(1)–N(3)	165.7(2)

Table 4 Selected bond lengths (Å) and angles (°) for **4′**

Ni(1)–N(1)	2.065(5)	Ni(1)–Cl(1)	2.358(2)
Ni(1)–N(3)	2.122(5)	Ni(1)–Cl(2)	2.417(1)
Ni(2)–N(4)	2.130(4)	Ni(2)–Cl(2)	2.349(1)
Ni(2)–N(6)	2.024(5)	Ni(2)–Cl(3)	2.366(2)
Ni(1)–Cl(3)	2.422(2)	Ni(2)–O(2)	2.052(4)
Ni(1)–O(1)	2.041(4)	Ni(2)–O(3)	2.157(4)
Ni(1)–Cl(3)–Ni(2)	84.73(5)	N(1)–Ni(1)–N(3)	77.6(2)
Ni(2)–Cl(2)–Ni(1)	85.20(5)	N(6)–Ni(2)–N(4)	77.7(2)

Table 5 Selected bond lengths (Å) and angles (°) for **4**

Ni(3)–N(7)	2.054(5)	Ni(3)–Cl(4)	2.3866(16)
Ni(3)–N(9)	2.117(5)	Ni(3)–Cl(5)	2.4071(18)
Ni(3)–O(4)	2.077(5)		
N(7)–Ni(3)–N(9)	76.9(2)	N(9)–Ni(3)–O(4)	170.6(2)
N(7)–Ni(3)–Cl(4)	175.8(1)	Cl(5)–Ni(3)–Cl(4A)	176.30(6)

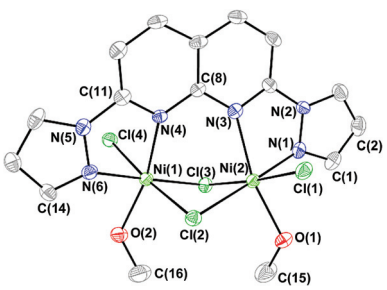
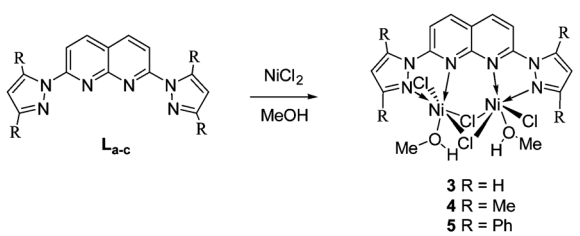


Fig. 1 ORTEP plot of **3** at the 30% probability level. Labels of aromatic carbons are omitted for clarity.



(1)

The molecular structure of **3** reveals a dinickel complex, in which two metal centers are bridged by two chloride ligands (Fig. 1). The geometry around the nickel centers can be

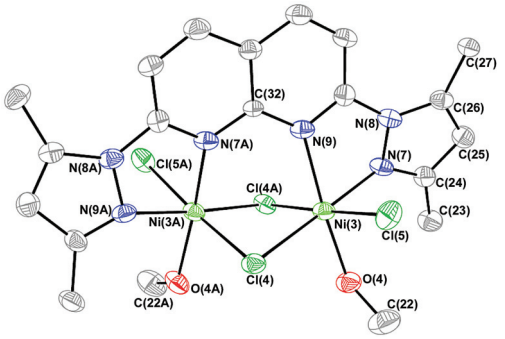


Fig. 2 ORTEP plot of **4** at the 30% probability level.

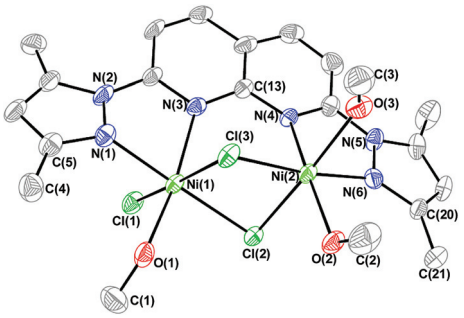
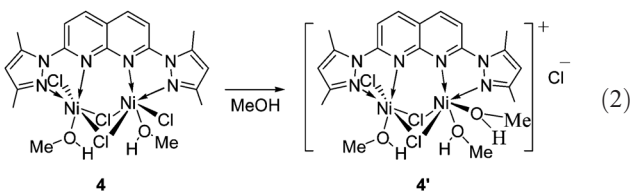


Fig. 3 ORTEP plot of cationic part of **4′**at the 30% probability level.

described as a distorted octahedron. Each nickel ion is coordinated by two pyridinyl nitrogen donors, three chlorides and a solvent molecule (methanol). The distance between nickel atoms [Ni(1)–Ni(2)] is 3.240 Å, which is shorter than that in the urease. The average distances of Ni–N and Ni–Cl bonds are 2.10 Å and 2.39 Å, respectively, which are normal for these bond lengths (Table 2). Other bond distances and angles are in normal ranges.

Crystallization of **4** in a mixture of methanol/CH_2Cl_2 occurred very slowly and ligand substitution of chloride by methanol in **4** leading to **4′** (eqn (2)) proceeded during crystallization. Thus co-crystallization of **4** and **4′** took place to yield single crystals suitable for X-ray diffraction analysis. The asymmetric unit of the crystal contains one molecule of **4′**, half of **4**, and one CH_2Cl_2 and two methanol lattice molecules. Fig. 2 and 3 depict the ORTEP plot of cationic part of **4** and **4′**, respectively.



(2)

Analogous to the structural feature of **3**, both **4** and **4′** are also chloride-bridged dinuclear species with each nickel ion possessing a distorted octahedral geometry. Relevant structural parameters for **4′**and **4** are reported in Tables 4 and 5, respectively. The distances between Ni ions are 3.222 Å in **4** and 3.226 Å in **4′**, which are essentially similar to that in **3**, showing that these

Table 6 Homo-coupling of phenylacetylene catalyzed by **3**[a]

Entry	Base	Solvent	Temp. (°C)	Yield[b]
1	—	toluene	25	0%
2	KO-*t*-Bu	toluene	25	65%
3	KO-*t*-Bu	MeOH	25	3%
4	KO-*t*-Bu	DMF	25	58%
5	KO-*t*-Bu	1,4-dioxane	25	59%
6	KO-*t*-Bu	hexane	25	36%
7	KO-*t*-Bu	toluene	30	79%
8	K_2CO_3	toluene	30	32%
9	Cs_2CO_3	toluene	30	53%
10	DBU[d]	toluene	30	70%
11	NaO-*t*-Bu	toluene	30	90%
12	NaO-*t*-Bu	toluene	35	100%
13[c]	NaO-*t*-Bu	toluene	35	81%
14[e]	KO-*t*-Bu	toluene	25	74%
15[f]	KO-*t*-Bu	toluene	25	43%

[a] Reaction conditions: phenylacetylene (0.5 mmol), **3** (1.2×10^{-2} mmol), and base (1 mmol) in solvent (0.6 ml) under O_2 (1 atm) for 15 h. [b] GC yields. [c] In air. [d] DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene. [e] Catalyst **3** (2.4×10^{-2} mmol). [f] Catalyst **3** (5×10^{-3} mmol).

naphthyridine based ligands readily accommodate the two metal ions in close proximity.

Catalytic oxidative coupling of terminal alkynes

It has been revealed that dinickel complexes might be suitable for the model study of urease.[5–7] However, we found that complexes **3–5** do not show good catalytic activity towards the hydrolysis of urea or small amide substrates under mild conditions. In the further study, we learned that these dinickel complexes could act as pre-catalysts for the homo-coupling of terminal alkynes. The direct coupling of terminal alkynes is an interesting process because diynes are an important class of compounds for many application such as synthetic starting materials, biological, and polymers. Oxidative coupling of terminal alkynes appears to be a direct way to prepare this type of derivatives.[15] One of the main challenges in this type of reaction is the preparation of highly effective catalysts capable of affording good conversion under mild conditions and using O_2 as the oxidant.

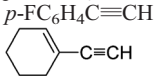
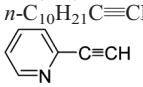
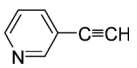
Initially, the coupling of phenylacetylene catalyzed by the dinickel complex **3** to yield 1,4-diphenyl-1,3-butadiyne was examined to screen the best catalytic system. The reactions were carried out with phenylacetylene, base and a fixed amount of catalyst (2.5 mol%) in an organic solvent. The yields of the product were determined by the GC analysis. Efforts were focused on optimizing the reaction conditions, and the results of the coupling reactions are summarized in Table 6. As observed, good conversions are achieved in various organic solvents except methanol and hexane. Among them, toluene is the best choice. In the screening of bases, *tert*-butoxide appears to be the good one to promote the coupling reaction. However, we noticed that the cation also plays a role in the reaction. Sodium *tert*-butoxide provides the yield in 90% in dimerization of phenylacetylene at 30 °C (Table 6, entry 11), while potassium salt affords 79% yield under the same conditions (Table 6, entry 7). Finally, the quantitative conversion of the substrate can be achieved by

Table 7 Preliminary survey of catalysts on the coupling of PhC≡CH[a]

Entry	Complex	Time (h)	Yield[b]
1	—	15	0%
2	$NiCl_2$	15	11%
3	**3**	15	100%
4	**3** + with trace moisture	15	52%
5	**4**	15	87%
6	**5**	8	100%
7	[(bipy)$NiCl_2$][c]	15	73%
8	$NiCl_2$ + $Me_2N(CH)_2NMe_2$	15	73%
9	$NiCl_2$ + cyclam[d]	15	67%
10	$NiCl_2$ + (**P∼N**)[e]	15	44%
11	$NiCl_2$ + (PhC=NCH_2-)$_2$	15	73%
12	**5**	2	58%
13	**5**	5	88%

[a] Reaction conditions: phenylacetylene (0.5 mmol), [Ni] (1.25×10^{-2} mmol, 2.5 mol%), and NaO-*t*-Bu(1 mmol) in toluene (0.6 ml) under O_2(1 atm) [b] GC yields. [c] bipy = 2,2′-bipyridine. [d] cyclam = 1,4,8,11-tetraazacyclotetradecane. [e] **P∼N** = *o*-(diphenylphosphino)aniline.

Table 8 Results of the coupling of various terminal alkynes[a]

Entry	Substrate	Yields[b]
1	$C_6H_5C{\equiv}CH$	93 (92)
2	*p*-$MeC_6H_4C{\equiv}CH$	91 (93)
3	*p*-*tert*-$BuC_6H_4C{\equiv}CH$	89 (87)
4	*p*-$MeOC_6H_4C{\equiv}CH$	86 (81)
5	*p*-$FC_6H_4C{\equiv}CH$	72 (79)
6		66 (61)
7	*tert*-Bu$C{\equiv}CH$	77 (87)
8	*n*-Bu$C{\equiv}CH$	66 (78)
9	*n*-$C_6H_{13}C{\equiv}CH$	58 (55)
10	*n*-$C_8H_{17}C{\equiv}CH$	47 (51)
11	*n*-$C_{10}H_{21}C{\equiv}CH$	59 (68)
12		NR[c]
13		NR[c]

[a] Alkyne (0.5 mmol), complex **5** (2.5 mol% base on alkyne), NaO-*t*-Bu (1.0 mmol) in toluene (0.6 ml) under O_2 (1 atm) at 35 °C for 8 h. [b] Isolated yields; yields given in parentheses are the reactions using **3** as catalyst for 15 h. [c] NR: no reaction.

raising the reaction temperature to 35 °C (Table 6, entry 13). It is worthy to mention that carrying out the coupling reaction under dioxygen atmosphere is faster than in air (Table 6, entry 14).

The catalytic activities of nickel complexes are slightly affected by their ligands. As shown in Table 7, the coupling activity varied slightly in the order **5** > **3** > **4**. The higher activity of **5** is presumably due to the steric factor. The phenyl groups cause the steric congested environment around the active metal center, which might accelerate the reductive elimination step. The lower activity of **4** might be due to the larger content of methanol in the complex. In a separate experiment, we found that moisture affects the conversion of the coupling. The catalytic activities of various mono-nuclear nickel complexes on this homo-coupling reaction are less active than those of the dinuclear ones (Table 7, entries 7–11). This observation reveals that these bimetallic species could exhibit a cooperative effect in the homo-coupling reaction, partially due to the coordination of the alkyne moiety toward the adjacent metal center.

In view of the above results, the catalytic system rendered the best yield in coupling of alkyne into diyne and was followed in the subsequent studies for various terminal alkynes as illustrated in Table 8. As observed, high conversions were achieved in all cases except pyridinyl-substituted alkynes. Substituent variation on the aromatic ring of phenylacetylene does slightly influence the efficiency. The results obtained for dinickel complex **3** compare well with the activity of **5**, except for the longer reaction times.

Summary

We have prepared a set of dinickel complexes with 2,7-bis(pyrazol-1-yl)-1,8-naphthyridines as the bi-nucleating ligand. The distance between nickel atoms in this series of complexes is *ca.* 3.2 Å, which is significantly shorter than that in urease. This might be one of the reasons for these complexes being poor catalytic activity on hydrolysis of urea. However, our results prove that the dinickel species are highly effective catalysts for homo-coupling of 1-alkynes. Investigation on the modification of the topologies of this type of donors and their coordination to other potential catalytically active metal ions is currently in progress.

Experimental

General information

All reactions, manipulations and purification steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane was dried over CaH_2 and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used after a degassed process. 2,7-Dichloro-1,8-naphthyridine, 3,5-diphenyl-1*H*-pyrazole and 3,5-dimethyl-1*H*-pyrazole were prepared accordingly to the method reported previously.[14]

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ on a Bruker AVANCE 400 spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^1H and ^{13}C NMR. Infrared and UV-vis spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series-II) and a Shimatzu PC 2100, respectively.

2,7-Di(pyrazol-1-yl)-1,8-naphthyridine (L_a)

A mixture of **2** (500 mg, 2.5 mmol) and pyrazole (410 mg, 6 mmol) in DMF (0.5 mL) was sealed in a glass reactor and heated to 140 °C for 12 h. The reaction mixture was dissolved in THF (100 mL) and re-preciptitated in water to give $\mathbf{L_a}$ as a light yellow solid (460 mg, 69%): IR ($CHCl_3$): 1611, 1575 cm^{-1}; ^1H NMR (400 MHz d_6-acetone): δ 8.86 (d, J = 2.8 Hz, 2 H, Pz), 8.61 (d, J = 8.4 Hz, 2 H, Naph-*H*), 8.29 (d, J = 8.4 Hz, 2 H, Naph–*H*), 7.87 (d, J = 1.2 Hz, 2 H, Pz–*H*), 6.65 (dd, J = 1.2, J = 2.8 Hz, 2 H, Pz-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 143.0, 139.5, 128.0, 119.9, 112.5, 108.7, 94.3. UV-Vis (MeOH): λ_{max} (ε) = 256 (7.1×10^4), 337 (3.7×10^4), 352 (4.9×10^4).

Anal. Calcd. for $C_{14}H_{10}N_6$:C, 64.11; H, 3.84; N, 32.04. Found: C, 63.58; H, 3.41; N, 31.00.

2,7-Bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,8-naphthyridine (L_b)

The preparation of this compound is similar to that of $\mathbf{L_a}$. White solid (62%): IR (CH_2Cl_2): 1610, 1571 cm^{-1}; ^1H NMR (400 MHz d_6-acetone): δ 8.44 (d, J = 8.8 Hz, 2 H, Naph–*H*), 8.19 (d, J = 8.8 Hz, 2 H, Naph–*H*), 6.14 (s, 2 H, Pz–*H*), 2.87 (s, 6 H, Me), 2.26 (s, 6 H, Me); ^{13}C NMR (100 MHz d_6-acetone): δ 155.6, 153.4, 150.4, 142.7, 139.3, 118.5, 114.3, 110.4, 14.9, 13.1. UV-Vis (MeOH): λ_{max} (ε) 256 (4.7×10^4), 338 (2.6×10^4), 352 (3.4×10^4). The spectral data is essentially identical the literature reported.[12]

2,7-Bis(3,5-diphenyl-1*H*-pyrazol-1-yl)-1,8-naphthyridine (L_c)

A mixture of **2** (300 mg, 1.5 mmol), 3,5-diphenyl-1*H*-pyrazole (485 mg, 2.2 mmol), and K_2CO_3 (790 mg, 5.7 mmol) in DMF (6 mL) was placed in a round-bottom flask and was heated at 120 °C for 12 h under a nitrogen atmosphere. Upon cooling to room temperature, pyrrolidine carboxylic acid (60 mg, 0.47 mmol) and CuI (30 mg, 0.14 mmol) was added to the above mixture under inert gas atmosphere. The resulting mixture was heated at 130 °C under microwave irradiation for 3 h. The reaction mixture was extracted with dichloromethane and washed with water. The extracts were combined and chromatographed on silica gel with elution of (ethyl acetate/CH_2Cl_2/hexane = 7 : 1 : 12). Compound $\mathbf{L_c}$ was obtained as a white solid (243 mg, 39%): IR (CH_2Cl_2): 1606, 1551 cm^{-1}; ^1H NMR (400 MHz, d_6-acetone): δ 8.65 (d, J = 8.4 Hz, 2 H, Naph–*H*), 8.19 (d, J = 8.8 Hz, 2 H, Naph–*H*), 8.03 (d, J = 5.2 Hz, 4 H, Ph–*H*), 7.25–7.49 (m, 16 H, Ph–*H*), 7.08 (s, 2 H, Pz–*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 152.8, 152.7, 146.1, 138.4, 132.4, 130.8, 129.0, 128.5, 128.3, 128.2, 127.7, 125.8, 120.1, 117.4, 107.9; ^{13}C NMR (100 MHz, d_6-acetone): δ 155.3, 153.4, 147.0, 140.4, 133.5, 131.8, 129.8, 129.4, 129.1, 129.0, 128.6, 126.6, 121.6, 118.5, 108.4; UV-Vis (MeOH): λ_{max} (ε) = 247 (4.0×10^4), 355 (2.0×10^4); HRMS (ESI): m/z calcd. for $C_{38}H_{27}N_6$ ($[M + H]^+$) = 567.2297, found 567.2287; Anal. Calcd. for $C_{38}H_{26}N_6$:C, 80.54; H, 4.62; N, 14.83. Found: C, 80.16; H, 4.45; N, 14.89.

Complex 3

To a mixture of $\mathbf{L_a}$ (100 mg, 0.38 mmol) and $NiCl_2$ (98.8 mg, 0.76 mmol) was added dry THF (10 mL) and dry MeOH (20 mL). The resulting solution was heated at 50 °C for 48 h under a nitrogen atmosphere. Upon concentration, the residue was re-crystallized in CH_3OH/CH_2Cl_2 to yield **3** as a yellowish green solid (200 mg, 90%): IR (KBr): 1607, 1573 cm^{-1}; UV-Vis (MeOH): λ_{max} (ε) = 257 (3.8×10^4), 352 (3.6×10^4), 360 (3.6×10^4), 672 (7) nm; Anal. Calcd. for $C_{16}H_{18}Cl_4N_6Ni_2O_2$: C, 32.82; H, 3.10; N, 14.35. Found: C, 32.59; H, 2.70; N, 14.60.

Complex 4

The preparation procedure is similar to that of **3**. Green solid (95%): IR (KBr): 1612, 1587 cm^{-1}; UV-Vis (MeOH):λ_{max} (ε) = 254 (7.9×10^4), 352 (5.7×10^4), 371 (2.2×10^4), 668 (6) nm; Anal. Calcd. for $C_{20}H_{26}Cl_4N_6Ni_2O_2$: C, 37.44; H, 4.08; N, 13.10. Found: C, 37.65; H, 3.70; N, 12.84.

Complex 5

The preparation procedure is similar to that of **3**. Dark green solid (96%): IR (KBr): 1609, 1573 cm^{-1}; UV-Vis (MeOH): λ_{max} (ε) = 362 (4.4×10^4), 385 (3.8×10^4) nm; Anal. Calcd. for $C_{40}H_{34}Cl_4N_6Ni_2O_2$: C, 53.98; H, 3.85; N, 9.44. Found: C, 53.23; H, 3.42; N, 9.38.

General procedures for homocoupling reaction

A mixture of acetylene (0.5 mmol), $NaOBu^t$ (1 mmol) and Ni complex (1.25×10^{-3} mmol) in toluene (0.6 mL) was stirred in the air or O_2 atmosphere at room temperature. After reaction for a certain period, the reaction mixture was filtered through celite to remove the metal species. The filtrate was concentrated, chromatographed on silica gel and analyzed by ^1H and ^{13}C NMR spectroscopy. The spectral data of the coupling product were essentially identical to those reported in literature.

Spectral data of products. 1,4-Diphenylbuta-1,3-diyne.[16] Yellowish white powder (93%): ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.6 Hz, 4 H), 7.36–7.31 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 73.8, 81.5, 121.6, 128.3, 129.0, 132.3.

1,4-Di-*p*-tolylbuta-1,3-diyne.[16] Yellowish white powder (91%): ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 8.0 Hz, 4 H), 7.11 (d, J = 7.6 Hz, 4 H), 2.35 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 73.4, 81.5, 118.6, 129.0, 132.2, 139.3.

1,4-Bis(4-*t*-butylphenyl)buta-1,3-diyne.[16] White powder (89%): ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 8.4 Hz, 4 H), 7.34 (d, J = 8.4 Hz, 4 H), 1.35 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 132.1, 125.3, 118.7, 81.5, 73.4, 35.0, 31.2.

1,4-bis(4-methoxyphenyl)buta-1,3-diyne.[16] White powder (86%): ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.2 Hz, 4 H), 6.83 (d, J = 7.2 Hz, 4 H), 3.81 (s, 6 H); ^{13}C NMR(100 MHz $CDCl_3$): δ 55.4, 72.9, 81.2, 113.8, 114, 133.9, 160.0.

1,4-Bis(4-fluorophenyl)buta-1,3-diyne.[16] Yellow powder (72%): ^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (m, 4 H), 7.01 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 161.6, 134.4, 134.3, 117.7, 115.9, 115.7, 80.4, 73.5.

1,4-Dicyclohexenylbuta-1,3-diyne.[17] Yellowish white powder (61%): ^1H NMR (400 MHz $CDCl_3$): δ 6.22 (m, 2 H), 2.11 (m, 8 H), 1.59 (m, 8 H); ^{13}C NMR (100 MHz $CDCl_3$): δ 21.4, 22.2, 26.0, 28.8, 71.6, 82.7, 119.8, 137.9.

2,2,7,7-Tetramethylocta-3,5-diyne.[17] White powder (73%): ^1H NMR (400 MHz, $CDCl_3$): δ 1.23 (s, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.0, 30.7, 63.6, 86.2.

Dodeca-5,7-diyne.[18] Colorless oil (66%): ^1H NMR (400 MHz, $CDCl_3$): δ 2.24 (t, J = 6.8 Hz, 4 H), 1.45–1.52 (m, 4 H), 1.37–1.44 (m, 4 H), 0.89 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 19.0, 22.0, 30.4, 65.2, 77.4

Hexadeca-7,9-diyne.[16] Colorless oil (58%): ^1H NMR (400 MHz $CDCl_3$): δ 2.23 (t, J = 7.2 Hz, 4 H), 1.41–1.53 (m, 4H), 1.32–1.40 (m, 4 H), 1.18–1.31 (m, 8 H), 0.87

(t, J = 6.8 Hz, 6 H); ^{13}C NMR (100 MHz $CDCl_3$): δ 14.1, 19.3, 22.6, 28.4, 28.6, 31.4, 65.2, 77.5.

Icosa-9,11-diyne.[17] Colorless oil (47%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23(t, J = 7.2 Hz, 4 H), 1.46–1.53 (m, 4 H), 1.26–1.40 (m, 20 H), 0.87 (t, J = 6.8 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 19.3, 22.7, 28.4, 28.9, 29.1, 29.2, 31.9, 65.3, 77.6.

Tetracosa-11,13-diyne.[19] Colorless oil (59%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22 (t, J = 6.8 Hz, 4 H), 1.46–1.53 (m, 4 H), 1.24–1.37 (m, 14 H), 0.86 (t, J = 6.8 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 19.6, 23.1, 28.7, 29.2, 29.6, 29.8, 29.9, 30.0, 32.2, 65.3, 77.5.

Crystallography

Crystals suitable for X-ray determination were obtained for **3** and (**4**+**4′**) by recrystallization from methanol/CH_2Cl_2 at room temperature. Cell parameters were determined by a Siemens SMART CCD diffractometer. The structure was solved using the SHELXS-97 program[20] and refined using the SHELXL-97 program[21] by full-matrix least-squares on $F2$ values.

Crystal data for **3**: $C_{18}H_{22}Cl_8N_6Ni_2O_2$, F_w = 755.44, Monoclinic, $P2_1/n$, a = 10.9327(6) Å, b = 16.7419(6) Å, c = 16.6176(9) Å, α = 90, β = 93.925(5)°, γ = 90, V = 3034.5(3) Å^3, Z = 4, D_c = 1.654 Mg m^{-3}, F(000) = 1520, crystal size: 0.25 × 0.20 × 0.10 mm^3, 3.07 to 27.49°, 22170 reflections collected, 6957 reflection [R(int) = 0.0453], Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0592, wR_2 = 0.1764, for all data R_1 = 0.0955, wR_2 = 0.1878, Goodness-of-fit on F^2 = 1.125.

Crystal data for (**4**+**4′**): $C_{68}H_{106}Cl_{16}N_{18}Ni_6O_{12}$, F_w = 2287.17, Trigonal, $P3_221$, a = 14.76480(10) Å, b = 14.76480(10) Å, c = 36.4182(6) Å, α = 90°, β = 90°, γ = 120°, V = 6875.50(13) Å^3, Z = 3, D_c = 1.657 Mg m^{-3}, F(000) = 3528, crystal size: 0.20 × 0.15 × 0.10 mm^3, 2.98 to 27.49°, 42248 reflections collected, 10505 reflections [R(int) = 0.0401], Goodness-of-fit on F^2 = 1.124, Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0541, wR_2 = 0.1542, for all data R_1 = 0.0603, wR_2 = 0.1587.

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