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Reactions of Tris(2-pyridyl)phosphines and Tris(2-pyridyl)phosphine Oxides with Some Electrophiles

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ABSTRACT

Treatment of tris(2-pyridyl)phosphine or tris(2-pyridyl)phosphine oxide with electrophiles such as chlorine, bromine, deuterium chloride, or benzenediazonium chloride gave unusual coupling products, i.e., 5-chloro-, 5-bromo-, 5-deuterio-, or 5-phenylazo-2,2′-bipyridyls, respectively, as a major coupling product in each case. This is considered to be the result of electrophilic substitution on a pyridyl ring in a pentacovalent phosphorane intermediate formed in each reaction. © *1997 John Wiley & Sons, Inc. Heteroatom Chem* **8***: 439–449, 1997*

INTRODUCTION

Earlier, we have shown that tris(2-pyridyl)phosphine (**1a**) or tris(2-pyridyl)phosphine oxide (**2a**) gave a ligand coupling product, 2,2′-bipyridyl, upon treatment with a nucleophile such as 2-pyridyllithium in THF, or with hydrochloric acid in an aqueous medium [1]. These reactions were considered to proceed via a pentacoordinated phosphorus intermediate formed by attack of a suitable nucleophile on the phosphorus atom. We have further extended our study to the reactions of various tris(2-pyridyl)phosphines (**1**) and tris(2-pyridyl)phosphine oxides (**2**) with some electrophiles and found that interesting coupling reactions occurred [2]. This article reports the reactions of **1** and **2** with some electrophiles such as chlorine, bromine, deuterium chloride, and arenediazonium chlorides.

RESULTS AND DISCUSSION

Reactions of Tris(2-pyridyl)phosphines with Halogens

Treatment of tris(2-pyridyl)phosphine (**1a**) with excess chlorine in dichloromethane or acetonitrile at room temperature, followed by the removal of solvent and excess chlorine, gave a crystalline adduct, $Py_3P^+Cl\ Cl^-$ (**3**), which was hygroscopic and sensitive to moisture. The adduct was also obtained by treating **1a** with liquid chlorine. The adduct (**3**) afforded tris(2-pyridyl)phosphine oxide (**2b**) in a 49% yield upon treatment with aqueous sodium hydroxide. In contrast, the reaction with dilute hydrochloric acid led to the formation of 2,2′-bipyridyl (**4a**)

Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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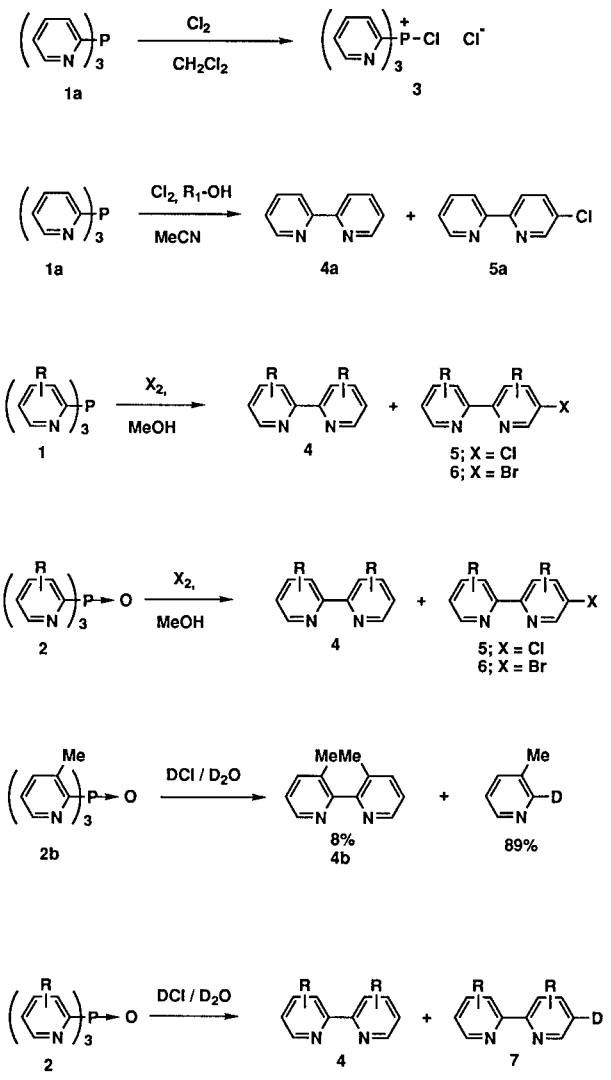
(51%). These results are similar to those previously reported for the reactions of benzyltris(2-pyridyl)phosphonium bromide, in which benzylbis(2-pyridyl)phosphine oxide or **4a** was formed upon treatment with aqueous sodium hydroxide or with dilute hydrochloric acid, respectively [1].

When **1a** was treated with chlorine in acetonitrile and then the resulting adduct was treated with methanol, the coupling product (**4a**) was obtained in a 68% yield together with a trace amount of 5-chloro-2,2′-bipyridyl (**5a**). Interestingly, when the chlorination of **1a** was carried out in acetonitrile in the presence of a small amount of water or alcohols, the yield of **5a** markedly increased. These results are summarized in Table 1.

Reaction of **1a** with chlorine in methanol gave **5a** as the major coupling product, together with a small amount of **4a.** The reactions of some substituted tris(2-pyridyl)phosphines (**1**) with chlorine in acetonitrile in the presence of 10 equivalents of methanol or in methanol solution were carried out and found to afford the corresponding 5-chloro-2,2′-bipyridyls (**5**), except in the reaction with tris(6-bromo-2-pyridyl)phosphine (**1f**). The results are summarized in Table 2. The reaction of **1f** with chlorine in methanol afforded no coupling product, but tris(6-bromo-2-pyridyl)phosphine oxide was obtained in a quantitative yield.

It is known that triphenylphosphine dihalides react with alcohol to afford the corresponding haloalkane and triphenylphosphine oxide by the Arbusov reaction [3]. The poor yields of **4e** and **5e** in the reaction of **1e** may be due to the occurrence of a similar Arbusov reaction.

The reactions between the phosphines and bromine similarly gave the corresponding 5-bromo-2,2′-bipyridyls (**6**) together with 2,2′-bipyridyls (**4**). These results are also summarized in Table 2. In the reaction of **1a** with bromine in methanol, dimethyl 2-



STRUCTURE

TABLE 1 Chlorination of **1** in the Presence of Alcohols or Water in Acetonitrile

R-OH	*R_1-OH/Py_3P*[a]	*Reaction Time (h)*	*Product Yield (%)*[b]	
			4a	***5a***
H_2O	10	4	14	73
MeOH	10	4	7	61
EtOH	10	4	11	75
i-PrOH	10	4	5	85
n-BuOH	10	4	17	72
t-BuOH	10	4	2	84

[a]Mol ratio.
[b]Determined by gas chromatography.

TABLE 2 Reaction of Phosphines (**1**) with Halogen in Methanol

Compd.	*R*	*X_2*	*Product Yield*[a] (%)			
1a	H	Cl_2	**4a**	3	**5a**	77
1b	3-Me	Cl_2	**4b**	2	**5b**	11
1c	4-Me	Cl_2	**4c**	6	**5c**	63
1d	6-Me	Cl_2	**4d**	2	**5d**	73
1e	6-Ph	Cl_2	**4e**	19[c]	**5e**	3[c]
1f	6-Br	Cl_2	**4f**	0	**5f**	0
1a	H	Br_2[b]	**4a**	14	**6a**	76
1c	4-Me	Br_2[b]	**4c**	36	**6c**	48
1d	6-Me	Br_2[b]	**4d**	22	**6d**	69

[a]Determined by gas chromatography.
[b]Three equivalents of bromine were used.
[c]Isolated yield.

pyridylphosphonite was isolated as the phosphorus-containing product of a ligand coupling reaction.

Reaction of Tris(2-pyridyl)phosphine Oxides with Halogens

The reaction of tris(2-pyridyl)phosphine oxide (**2a**) with chlorine or bromine was also examined. The reaction was carried out in acetonitrile in the presence of methanol or in methanol solution at room temperature. As in the reactions of phosphines described above, ligand coupling was found to take place giving the corresponding 5-halo-2,2′-bipyridyls together with 2,2′-bipyridyl.

The reaction of **2a** with chlorine was interrupted after half completion, and then a product analysis was performed. No chlorinated phosphine oxide, (5-chloro-2-pyridyl)bis(2-pyridyl)phosphine oxide, was detected. This result shows that a halo-substituted phosphine oxide is not an intermediate in the formation of the 5-halo-2,2′-bipyridyl. Reactions of methyl-substituted phosphine oxides (**2b–2d**) with chlorine or bromine were also examined. The results are shown in Table 3. Here again, 5-halo-2,2′-bipyridyls, **5** or **6,** respectively, were formed by the reactions with both chlorine and bromine and in good yields, except in the case of **2b.**

Reactions of Tris(2-pyridyl)phosphine Oxides with Deuterium Chloride

The reactions with other electrophiles are also quite interesting. In a previous article, we have reported that **2a** gave **4a** as a ligand coupling product, upon treatment with 2-pyridyllithium in THF, or with hydrochloric acid in aqueous media [1]. These reactions were considered to proceed via a pentacoordinated phosphorus intermediate formed by attack of an appropriate nucleophile on the phosphorus atom. There is, therefore, a limitation on the use of an electrophile, since the electrophile has to maintain its electrophilic character in the presence of the nucleophile that is required to make an attack on the phosphorus atom to give a pentacoordinate intermediate in these types of reactions.

We examined the reaction of **2a** with D^+, as an electrophile. When **2a** was treated with 20% DCl/D_2O at room temperature, a mixture of **4a** and 5-deuterio-2,2′-bipyridyl (**7a**) was obtained in a 50% yield with a ratio of 31:69. The MS spectra of the product showed that no significant dideuterio-2.2′-bipyridyl was formed in the coupling.

The reactions of some substituted tris(2-pyridyl)phosphine oxides (**2b–2h**) were carried out in 20% DCl/D_2O at room temperature. The results are summarized in Table 4. The ratio of **4** to **7** was estimated by H^1 NMR analysis. As shown in Table 4,5-deuteriated bipyridyls (**7**) were formed in the reactions of **2a, 2c, 2d, 2e,** and **2h.** In the reaction of **2b,** a ligand coupling product **4b** was obtained in poor yield (8%), but no detectable amount of the deuteriated coupling product (**7b**) was observed. The major product from **2b** was the ligand exchange product, is 2-deuterio-3-methylpyridine (89%).

The reactions of **2f** and **2g** with 20% DCl/D_2O did not proceed at room temperature but, at 60°C gave the respective ligand coupling products in moderate yields. The phosphine oxide **2d,** bearing pyridine rings that are protected at the 5-position by a methyl group, did not give ipso-substituted or deuteriated 2,2′-bipyridyls, but rather afforded 5,5′-dimethyl-2,2′-bipyridyl in a 74% yield.

We also examined the reaction of tris(2-quinolyl)phosphine oxide with 20% DCl/D_2O at room tem-

TABLE 3 Reactions of Phosphine Oxides (**2**) with Halogene

				Product Yield (%)			
Compd	*R*	X_2	*Solvent*				
2a	H	Cl_2	MeCN/MeOH[c]	**4a**	29	**5a**	69
2a	H	Cl_2	MeOH	**4a**	8	**5a**	62
2b	3-Me	Cl_2	MeCN/MeOH[c]	**4a**	trace	**5b**	6
2c	4-Me	Cl_2	MeCN/MeOH[c]	**4c**	3	**5c**	60
2d	6-Me	Cl_2	MeOH	**4d**	10	**5d**	64
2a	H	Br_2[e]	MeOH	**4a**	15	**6a**	74
2c	4-Me	Br_2[d]	MeCN/CCl_4/MeOH[b]	**4c**	49	**6c**	40
2d	6-Me	Br_2[d]	MeCN/CCl_4/MeOH[b]	**4d**	26	**6d**	64

[a]Determined by gas chromatography.
[b]MeCN: CCl_4: CMeOH = 4:2:1.
[c]Ten equivalents of MeOH in MeCN.
[d]Four equivalents of bromine were used.
[e]Three equivalents of bromine were used.

TABLE 4 Reaction of 2 with DCl/D_2O.

		Yield (%)[a)]	Ratio[b)]
Compd	*R*	*4 + 7*	*4 : 7*
2a	H	50	31 : 69
2b	3-Me	8	100 : 0
2c	4-Me	66	23 : 77
2d	6-Me	74	7 : 93
2e	6-Ph[c)]	63[d)]	56 : 44
2f	6-Br[c)]	50[d)]	100 : 0
2g	5-Me	69	100 : 0
2h	4,6-Me, Me	69	16 : 84

a) Determined by gas chromatography.
b) Estimated by H^1 NMR analysis.
c) Refluxed for 6 h.
d) Isolated yield.

perature and found 2,2′-biquinolyl to be formed in almost quantitative yield. Benzyltris(2-pyridyl)phosphonium bromide also gave only the normal ligand coupling product, **4a,** in good yield, by treatment with DCl/D_2O at room temperature.

Reactions of Tris(2-pyridyl)phosphine Oxides with Arenediazonium Chlorides

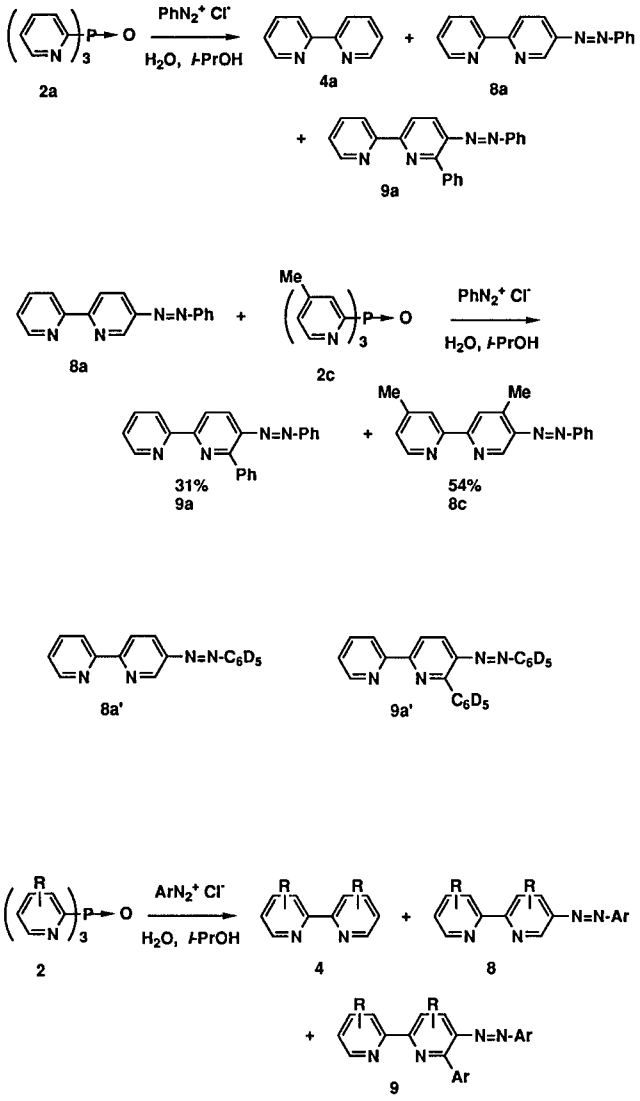
Next, we investigated the reactions of **2** with arenediazonium chlorides in acidic media. The reaction of **2a** with three equivalents of benzenediazonium chloride proceeded smoothly at 0°C in H_2O/i-PrOH (1:1) and was completed within 30 minutes to afford a complex mixture. Diazo coupling products, 5-phenylazo-2,2′-bipyridyl (**8a**) and 6-phenyl-5-phenylazo-2,2′-bipyridyl (**9a**) were isolated from the mixture in 27% and 5% yields, respectively, together with small amounts of **4a** and biphenyl.

The variation of the product yields (as determined by HPLC) with reaction time is shown in Figure 1. It is to be noted that the maximum yield of **8a** was attained after 30 minutes, and, after that, the yield decreased somewhat. When the reaction was carried out with 10 equivalents of the diazonium salt, the yield of **8a** was decreased to 15%. These results suggest that **8a** may undergo further attack by the diazonium salt to afford secondary products.

We therefore, examined the reaction of **8a** with benzenediazonium chloride. When **8a** was treated with three equivalents of benzenediazonium chloride at 0°C for 4 hours, the starting material was completely recovered. When the reaction was carried out, however, in the presence of one equivalent of tris(4-methyl-2-pyridyl)]phosphine oxide (**2c**), the phenylated products (**9a**) and **8c** were obtained in 31% and 54% yields, respectively, and 50% of **8a** was recovered.

In the reaction of **2a** with benzenediazonium chloride, a small amount of biphenyl was found to be formed by a detailed product analysis of the reaction mixture. Formation of biphenyl indicates that reduction of benzenediazonium ion with formation of a phenyl radical and subsequent radical coupling occur during the reaction. The phenyl radical would probably have been formed by reduction of a benzenediazonium ion by a trivalent phosphorus species formed by ligand coupling of a pentacovarant intermediate. The phenylated product (**9a**) would then be formed by the reaction of **8a** with a phenyl radical.

Table 5 shows the results of the reactions of some phosphine oxides (**2**) with benzenediazonium chloride and of **2a** with some diazonium ions. The structures of **8a** and **9a** were assigned on the basis of spec-



STRUCTURE

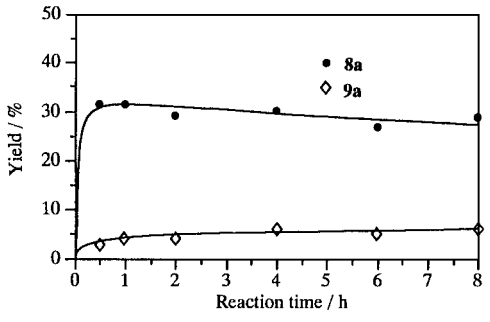


FIGURE 1 Variation of yields of **8a** and **9a** with reaction time in the reaction of **2a** with benzenediazonium chloride.

tral data and elemental analysis. In the ^{1}H NMR spectrum of **9a,** the proton signals of the pyridine rings overlap with those of the benzene rings. However, the structures of **8a** and **9a** could easily be assigned by the ^{1}H NMR spectrum of the products, **8a′** and **9′**, which were obtained from the reaction of **2a** with deuteriated benzenediazonium chloride.

Mechanism

In the previous articles [1], we proposed the mechanism of ligand coupling for tris(2-pyridyl)phosphine oxide or benzyltris(2-pyridyl)phosphonium bromide. The mechanism involves formation of the pentacoordinated phosphorus intermediate by attack of a nucleophile on the phosphorus atom, followed by coupling of an axial ligand with an equatorial ligand within the trigonal bipyramidyl intermediate.

We have also postulated a mechanism for the formation of **5a** in the reaction of tris(2-pyridyl)phosphine or tris(2-pyridyl)phosphine oxide with chlorine [2]. The mechanism involves chlorination of the axial pyridyl group of a pentacoordinated phosphorus intermediate. The mechanism is based on the following theory.

The axial bonds to phosphorus in phosphorus(V) compounds are three-center four-electron bonds formed primarily from *p*-orbitals [4]. The phosphorus atom of a pentacoordinated phosphorus intermediate such as that shown in structure **10** would behave as an electron-donating group to the axial pyridine ring because of the electron-rich axial bond. Consequently, the axial pyridine ring would readily undergo electrophilic attack at the 5 position, as shown in Scheme 1.

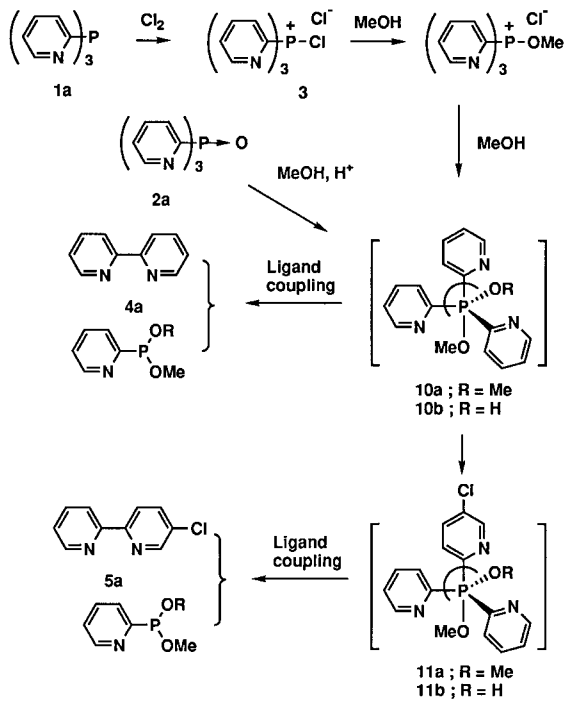
The complete postulated mechanism for the formation of 5-chloro-2,2-bipyridyl in the chlorination of **1a** or **2a** in methanol is shown in Scheme 1. In the chlorination, **1a** or **2a** reacts with chlorine in methanol to yield pentacoordinated intermediates **10a** or **10b,** respectively. Those intermediates would be expected to undergo ligand coupling to afford **4a** or chlorination of the pyridine ring to yield chlorinated intermediates **11a** or **11b.** Subsequent ligand coupling within the trigonal bipyramidyl intermediates as shown in **11** results in formation of **5a.**

An alternative possible mechanism for the formation of the 5-substituted 2,2′-bipyridyl from **10** remains to be considered. The mechanism involves an electrophilic attack on the equatorial pyridine ring of the intermediate (**10**). The electrophilic attack could promote migration of the axial pyridyl ligand from the phosphorus atom to the pyridine carbon atom, giving intermediate **12,** as shown in Scheme 2. Elimination of the proton and the triva-

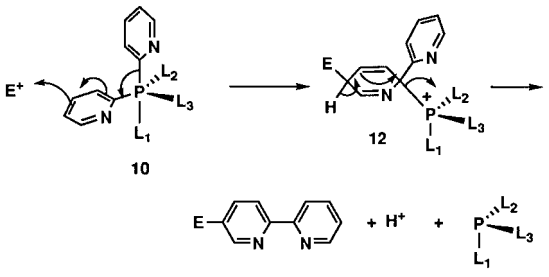
TABLE 5 Reactions of phosphine oxides (2) with arenediazonium chlorides

			Product Yield					
Compd	*R*	*Ar*	%					
2a	H	Ph	**4a**	2	**8a**	36	**9a**	6
2a	H	p-ClC_6H_4	**4a**	4	**8i**	60[c]	**9i**	5[c]
2a	H	p-$EtO_2CC_6H_4$	**4a**	4	**8j**	55[c]	**9j**	4[c]
2c	4-Me	Ph	**4c**	1	**8c**	37	**9c**	[d]
2d	6-Me	Ph	**4d**	15	**8c**	77	**9d**	[d]
2f	4,6-Me	Ph	**4f**	15	**8f**	38	**9f**	[d]

a) Determined by gas chromatography.
b) Determined by HPLC.
c) Isolated yield.
d) Not determined.



SCHEME 1



SCHEME 2

lent phosphorus species as shown lead to formation of the 5-substituted 2,2′-bipyridyl.

It should be noted that both **2a** and benzyltris(2-pyridyl)phosphonium bromide gave **4a** in good yields by treatment with dilute hydrochloric acid, but the latter compound did not give any deuteriated 2,2′-bipyridyl, as mentioned previously. This could conceivably be attributed to the short life of the pentacoverant intermediate formed by nucleophilic attack on the phosphorus atom as depicted in Scheme 1. The intermediates derived from **2a** are relatively stable phosphorus intermediates with two electronegative oxygen ligands and three carbon ligands; i.e., relatively longer life intermediates would be formed in the reactions of **2a.** On the other hand, in the case of the phosphonium bromide, the intermediate has one electronegative oxygen ligand and four carbon ligands. A ligand coupling reaction might be expected to take place within such a relatively destabilized intermediate to lead to the formation of **4** prior to occurrence of an electrophilic substitution. Thus, we favor the interpretation depicted in Scheme 1.

The reason why the 3-methyl substituted phosphine (**1b**) and the phosphine oxide (**2b**) gave a rather poor yield of the coupling product may be attributed to steric hindrance imposed by the 3-methyl groups in the pentacoordinated intermediate. When both the axial and equatorial pyridine rings are perpendicular to each other, the interaction between the two pyridine ligands would be at a maximum. The pyridine rings are thus hardly in a position to attain the favorable arrangement for coupling due to the steric hindrance of the 3-methyl groups. Thus, ligand coupling is inhibited, and preferential ligand exchange would be expected to take place.

EXPERIMENTAL

General

All the melting points are uncorrected. Gas chromatographic analyses were carried out by using a Shimadzu GC12A gas chromatograph on a 3m packed column with Thermon 1000 + KOH(10 + 3%) supported on Chromosorb W, and the peaks on the chromatograms were integrated with a Shimadzu C-R6A Chromatopac. High-performance liquid chromatography (HPLC) was performed on a Shimadzu LC-6A instrument. Mass spectra were recorded on a JEOL JMS-AX505W spectrometer at 70 eV. NMR spectra were recorded on a Varian Unity-300 NMR spectrometer in $CDCl_3$ solution using tetramethylsilane as an internal standard.

Phosphines

Tris(2-pyridyl)phosphine (**1a**) and substituted tris(2-pyridyl)phosphines (**1c**) and (**1d**) were prepared by the reaction of each corresponding lithium compound with phosphorus trichloride according to the procedure reported previously [1b].

*Preparation of Tris(3-methyl-2-pyridyl)]phosphine (**1b**)*

To a solution of butyllithium prepared from lithium (1.82 g, 0.262 g-atom) and 1-bromobutane (20.5 g, 0.150 mol) in ether (150 mL) was added a solution of 2-bromo-3-methylpyridine (22.6 g, 0.131 mol) at −40°C with stirring under an argon atmosphere. The reaction mixture was then stirred for 2 hours at −60°C. To the reaction mixture was added a solution of phosphorus trichloride (5.7 g, 0.041 mol) in ether (60 mL). After having been stirred for 1 hour, the mixture was allowed to warm to room temperature. The reaction mixture was extracted with sulfuric acid (0.75 M, 200 mL). The acid layer was separated and made alkaline with NaOH. The separated crystals were collected by filtration and washed with water and petroleum ether, and then recrystallized from acetone to give **1b** in a 50% yield. Mp 161.5–162.5°C. MS *m/z* (rel. intensity); 307 (M^+, 10), 216 (16), 215 (100), 213 (14), 200 (25), 183 (26). Anal. calcd for $C_{18}H_{18}N_3P$: C, 70.35; H, 5.90; N, 13.67. Found: C, 70.36; H, 5.95; N, 13.46.

*Preparation of Tris(6-phenyl-2-pyridyl)phosphine (**1e**)*

To a solution of butyllithium prepared from lithium (1.83 g, 0.264 g-atom) and 1-bromobutane (20.0 g, 0.146 mol) in ether (70 mL) was added a solution of 2-bromo-6-phenylpyridine (30.8 g, 0.132 mol) in ether (100 mL) at −40°C with stirring under an argon atmosphere. The reaction mixture was then stirred for 2 hours at −60°C. The reaction mixture was added to a solution of phosphorus trichloride (5.8 g, 0.042 mol) in ether (60 mL). After having been stirred for 1 hour, the mixture was allowed to warm to room temperature. To the reaction mixture was added water (50 mL), and the separated crystals were collected by filtration. The crystals were washed with water and petroleum ether and then recrystallized from dichloromethane ether to give **1e** in a 32% yield. Mp 185.5–186.5°C [6].

*Preparation of Tris(6-bromo-2-pyridyl)]phosphine (**1f**)*

To a solution of 2,6-dibromopyridine (32.9 g, 0.139 mol) in ether (200 mL) was added an ethereal solu-

tion of butyllithium (1.60 M, 87 mL 0.139 mol) (100 mL) at −30°C with stirring under an argon atmosphere. The reaction mixture was then stirred for 2 hours at −15°C. The reaction mixture was added to a solution of phosphorus trichloride (6.13 g, 0.045 mol) in ether (150 mL) at −60°C. After having been stirred for 1 hour, the mixture was allowed to warm to room temperature. To the reaction mixture was added water (100 mL), and the separated crystals were collected by filtration. The crystals were washed with water and petroleum ether and then recrystallized from toluene to give **1f** in a 57% yield. Mp 228–229°C [6].

Tris(5-methyl-2-pyridyl)]phosphine (**1g**) and tris[(4,6-dimethyl-2-pyridyl)phosphine (**1h**) were prepared in a similar manner to the preparation of **1b** in 48% and 62% yields, respectively.

Tris(5-methyl-2-pyridyl)]phosphine. Mp 96.5–98.0°C. MS *m/z* (rel. intensity); 307 (M^+, 7), 216 (20), 215 (100), 214 (17), 200 (19).

Tris-(4,6-dimethyl-2-pyridyl)]phosphine. Mp 113.5–114.5°C. MS *m/z* (rel. intensity); 349 (M^+, 11), 259 (10), 244 (16), 243 (100), 228 (16). ^{1}H NMR ($CDCl_3$) δ = 2.200 (3H, s), 2.407 (3H, s), 6.875 (2H, s,). Anal. calcd for $C_{21}H_{24}N_3P$: C, 72.19; H, 6.92; N, 12.03. Found: C, 72.29; H, 6.96; N, 11.91.

Phosphine Oxides

Tris(2-pyridyl)phosphine oxide (**2a**) was prepared by oxidation of the corresponding phosphine with hydrogen peroxide in acetone according to the procedure reported previously [1b].

*Preparation of Phosphine Oxides (**2b**)*

A typical procedure for the preparation of phosphine oxides is as follows: To a solution of tris(3-methyl-2-pyridyl)phosphine (**1b**) (2.5 g, 0.008 mol) in acetone was added hydrogen peroxide (17%, 3.0 g, 0.015 mol) under cooling at 10°C. Separated crystals were collected by filtration and recrystallized from ethanol to give **2b** in a 60% yield. Mp 219.0–220.0°C. MS *m/z* (rel. intensity); 324 [$(M + 1)^+$, 21], 323 (M^+, 100), 308 (76), 231 (66), 213 (44), 184 (19), 183 (44), 169 (16), 93 (21), 92 (25).

*Tris(4-methyl-2-pyridyl)phosphine Oxide (**2c**).* Mp 147.0–148.0°C. MS *m/z* (rel. intensity); 323 (M+, 47), 322 (18), 231 (100). Anal. calcd for $C_{18}H_{18}N_3OP$: C, 66.87; H, 5.61; N, 13.00. Found: C, 66.88; H, 5.66; N, 12.83.

*Tris(6-methyl-2-pyridyl)phosphine Oxide (**2d**).* Mp 193.0–194.0°C. MS *m/z* (rel. intensity); 324 [$(M + 1)^+$, 11], 323 (M^+, 49), 308 (14), 232 (15), 231 (100), 184 (14), 92 (13). Anal. calcd for $C_{18}H_{18}N_3OP$: C, 66.87; H, 5.61; N, 13.00. Found: C, 66.94; H, 5.65; N, 12.83.

*Tris(6-phenyl-2-pyridyl)phosphine Oxide (**2e**).* Mp 222.5–223.5°C. MS *m/z* (rel. intensity); 509 (M^+, 24), 508 (63), 355 (26), 354 (100), 254 (12), 199 (11), 154 (13), 138 (11), 127 (13). Anal. calcd for $C_{33}H_{24}N_3OP$: C, 77.79; H, 4.75; N, 8.25. Found: C, 77.78; H, 4.85; N, 8.15.

*Tris(6-bromo-2-pyridyl)phosphine Oxide (**2f**).* Mp 210.5–211.5°C. MS *m/z* (rel. intensity); 520 [$(M + 5)^+$, 4], 518 [$(M + 3)^+$, 11], 517 [$(M + 2)^+$, 5], 516 [$(M + 1)^+$, 10], 514 (4), 439 (41), 437 (100), 435 (48), 362 (22), 360 (46), 358 (24), 235 (18), 233 (22), 158 (22), 156 (20), 82 (27), 80 (28). Anal. calcd for $C_{15}H_9Br_3N_3OP$: C, 34.79; H, 1.75; N, 8.11. Found: C, 34.95; H, 1.83; N, 8.03.

*Tris(5-methyl-2-pyridyl)phosphine Oxide (**2g**).* Mp 160.5–161.5°C. MS *m/z* (rel. intensity); 323 (M^+, 46), 232 (14), 231 (100), 183 (10). Anal. calcd for $C_{18}H_{18}N_3OP$: C, 66.87; H, 5.61; N, 13.00. Found: C, 66.78; H, 5.56; N, 12.77.

*Tris(4,6-dimethyl-2-pyridyl)phosphine Oxide (**2h**).* Mp 150.0–151.0°C. MS *m/z* (rel. intensity); 366 [$(M + 1)^+$, 9] 364 (32), 349 (27), 260 (18), 259 (100), 212 (17), 211 (15). Anal. calcd for $C_{21}H_{24}N_3OP$: C, 69.35; H, 6.62; N, 11.50. Found: C, 68.93; H, 6.70; N, 11.35.

*Preparation of Tris(2-pyridyl)phosphine Dichloride (**3**)*

Dry chlorine gas was bubbled into the solution of **1a** (265 mg, 1 mmol) in dry dichloromethane (10 mL) until the solution became yellow. The solvent was removed in vacuo to afford pale yellow crystals **3.** Anal. calcd for $C_{15}H_{12}N_3PCl_2$: C, 53.59; H, 3.60; N, 12.50. Found: C, 52.97; H, 4.11; N, 12.06.

A low carbon analysis value is inevitable for this compound because it is extreme hygroscopic and sensitive to moisture.

*Reaction of Tris(2-pyridyl)phosphine Dichloride (**3**) with Aqueous Sodium Hydroxide*

Dry chlorine gas was bubbled into the solution of **1a** (265 mg, 1 mmol) in dry dichloromethane (10 mL)

until the solution became yellow. The solvent was evaporated and then aqueous sodium hydroxide (1 M/l, 10 mL) was added to the residue and stirred for 10 minutes. The resulting reaction mixture was extracted with dichloromethane. The organic layer was dried over Na_2SO_4, and the solvent was evaporated in vacuo to afford **2a** in a 49% yield.

*Reaction of Tris(2-pyridyl)phosphine Dichloride (**3**) with Hydrochloric Acid*

Dry chlorine gas was bubbled into the solution of **1a** (265 mg, 1 mmol) in dry dichloromethane (10 mL) until the solution became yellow. The solvent was evaporated and then hydrochloric acid (2 M, 10 mL) was added to the residue and stirred for 4 hours. The resulting reaction mixture was made alkaline with NaOH and then extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and concentrated. The residue was chromatographed on silica gel using chloroform as an eluent to give **4a** in a 51% yield.

*Reaction of Tris(2-pyridyl)phosphines (**1**) with Chlorine in Methanol*

A typical procedure for the reaction of **1** with chlorine in methanol is as follows. Into a solution of **1a** (265 mg, 1 mmol) in methanol (10 mL) was bubbled chlorine gas at room temperature until the solution became yellow. After the solution had been kept for 4 hours, the solvent and chlorine were removed under reduced pressure, The residue was made slightly alkaline with NaOH aqueous solution and m-dinitrobenzene (100 mg) was added as an internal standard, and then the whole mixture was extracted with dichloromethane (30 mL). The organic layer was dried over Na_2SO_4 and subjected to GC analysis.

In order to isolate the reaction product, the above solution was concentrated and then chromatographed on silica gel using chloroform as an eluent to give **5a.** Mp 71.0–72.0°C. MS *m/z* (rel. intensity); 192 [$(M + 2)^+$, 30], 190 (M^+, 93), 155 (51), 128 (100), 78 (43). ^{1}H NMR ($CDCl_3$) δ = 7.337 7.794 (1H, dd, J = 7.5, 4.5), 7.794 (1H, dd, J = 8.4, 2.4), 7.838 (1H, ddd, J = 7.8, 7.5, 1.8), 8.381 (1H, d, J = 8.4), 8.402 (1H, d, J = 7.8), 8.624 (1H, d, J = 2.4), 8.679 (1H, d, J = 4.5). Anal. calcd for $C_{10}H_7N_2Cl$: C, 63.01; H, 3.70; N, 14.70. Found: C, 62.83; H, 3.41; N, 14.55.

*5-Chloro-3,3′-dimethyl-2,2′-bipyridyl (**5b**).* Mp 50.0–51.0°C. MS *m/z* (rel. intensity); 220 [$(M + 2)^+$, 8], 218 (M^+, 19), 203 (35), 92 (52), 74 (100). ^{1}H NMR ($CDCl_3$) δ = 2.165 (3H, s), 2.171 (3H, s), 7.255 (1H, dd, J = 7.8, 4.5), 7.633 (1H, ddd, J = 7.8, 2.4, 0.6), 7.639 (1H, dd, J = 2.4, 0.6), 8.480 (1H, d, J = 2.4), 8.516 (1H, d, J = 4.5).

*5-Chloro-4,4′-dimethyl-2,2′-bipyridyl (**5c**).* Mp 147.0–148.0°C. MS *m/z* (rel. intensity); 220 [$(M + 2)^+$, 32], 218 (M^+, 100), 184 (14), 156 (12). ^{1}H NMR ($CDCl_3$) δ = 2.433 (3H, s), 2.466 (3H, s), 7.133 (1H, d, J = 5.1), 8.189 (1H, s), 8.280 (1H, s), 8.517 (1H, d, J = 5.1), 8.542 (1H, s). Anal. calcd for $C_{12}H_{11}N_2Cl$: C, 65.91; H, 5.07; N, 12.81. Found: C, 65.94; H, 5.08; N, 12.62.

*5-Chloro-6,6′-dimethyl-2,2′-bipyridyl (**5d**).* Mp 99.0–100.0°C. MS *m/z* (rel. intensity); 220 [$(M + 2)^+$, 32], 218 (M^+, 100), 203 (21), 183 (17), 153 (9), 142 (47), 92 (19), 65 (42). ^{1}H NMR ($CDCl_3$) δ = 2.617 (3H, s), 2.692 (3H, s), 7.153 (1H, d, J = 7.8), 7.680 (1H, t, J = 7.8), 7.709 (1H, d, J = 7.8), 8.175 (1H, d, J = 7.8), 8.203 (1H, d, J = 7.8). Anal. calcd for $C_{12}H_{11}N_2Cl$: C, 65.91; H, 5.07; N, 12.81. Found: C, 65.77; H, 5.35; N, 12.62.

*5-Chloro-6,6′-diphenyl-2,2′-bipyridyl (**5e**).* Mp 161.0–162.0°C. MS *m/z* (rel. intensity); 344 [$(M + 2)^+$, 25], 342 (M^+, 67), 307 (48), 152 (54), 127 (80), 77 (100). ^{1}H NMR ($CDCl_3$) δ = 7.37–7.58 (6H, m), 7.759 (1H, dd J = 7.8, 1.2), 7.834 (1H, t, J = 7.8), 7.874 (2H, dd, J = 7.5, 1.5), 7.902 (1H, d, J = 8.4), 8.145 (2H, ddd, J = 7.5, 2.1, 1.5), 8.434 (1H, dd, J = 7.8, 1.2), 8.558 (1H, d, J = 8.4).

*Reaction of Tris(2-pyridyl)phosphines (**1**) with Bromine in Methanol*

A typical procedure for the reaction of **1** with bromine in methanol is as follows. To a solution of **1a** (265 mg, 1 mmol) in methanol (5 mL) was added a solution of bromine (480 mg, 3 mmol) in methanol (5 mL) at room temperature. After the solution had been kept for 4 hours, the solvent was removed under reduced pressure. The product yields were estimated by GC analysis by a procedure similar to the foregoing procedure.

After the usual workup, the products were chromatographed on silica gel using chloroform as an eluent to give **6a.** Mp 75.0–76.0°C. MS *m/z* (rel. intensity); 236 [$(M + 2)^+$, 100], 234 (M^+, 99), 155 (43), 128 (42). ^{1}H NMR ($CDCl_3$) δ = 7.322 (1H, dd, J = 7.5, 4.5), 7.814 (1H, ddd, J = 7.8, 7.5, 1.5), 7.935 (1H, dd, J = 8.4, 2.4), 8.314 (1H, d, J = 8.4), 8.368 (1H, d, J = 7.8), 8.667 (1H, d, J = 4.5), 8.719 (1H, d, J = 2.4). Anal. calcd for $C_{10}H_7N_2Br$: C, 51.09; H, 3.00; N, 11.92. Found: C, 51.24; H, 3.06; N, 11.77.

*5-Bromo-4,4′-dimethyl-2,2′-bipyridyl (**6c**).* Mp

150.0–151.0°C. MS *m/z* (rel. intensity); 264 [(M + 2)$^+$, 95], 262 (M$^+$, 100), 183 (32), 138 (60), 77 (38). ^{1}H NMR ($CDCl_3$) δ = 2.434 (3H, s), 2.478 (3H, s), 7.140 (1H, d, J = 5.1), 8.195 (1H, s), 8.279 (1H, s), 8.517 (1H, d, J = 5.1), 8.674 (1H, s). Anal. calcd for $C_{12}H_{11}N_2Br$: C, 54.77; H, 4.21; N, 10.65. Found: C, 54.93; H, 3.98; N, 10.71.

*5-Bromo-6,6′-dimethyl-2,2′-bipyridyl (***6d***)*. Mp 95.0–95.5°C. MS *m/z* (rel. intensity); 264 [(M + 2)$^+$, 96], 262 (M$^+$, 100), 183 (27), 142 (20). ^{1}H NMR ($CDCl_3$) δ = 2.619 (3H, s), 2.733 (3H, s), 7.164 (1H, d, J = 7.8), 7.682 (1H, t, J = 7.8), 7.890 (1H, d, J = 8.4), 8.114 (1H, d, J = 8.4), 8.184 (1H, d, J = 7.8). Anal. calcd for $C_{12}H_{11}N_2Br$: C, 54.77; H, 4.21; N, 10.65. Found: C, 54.49; H, 4.32; N, 10.74.

Reaction of Tris(2-pyridyl)phosphine Oxides (2) with Chlorine

A typical procedure is as follows. Into a solution of **2a** (281 mg, 1 mmol) in acetonitrile (10 mL) and methanol (320 mg, 10 mmol) was bubbled chlorine gas at room temperature until the solution became yellow. After the solution had been kept overnight, the solvent and chlorine were removed under reduced pressure. The residue was made slightly alkaline with NaOH aqueous solution, and m-dinitrobenzene (100 mg) was added as an internal standard, and then the whole mixture was extracted with dichloromethane (30 mL). The organic layer was dried over Na_2SO_4 and subjected to GC analysis.

*Reaction of Tris(2-pyridyl)phosphine Oxides (***2***) with Bromine*

A typical procedure is as follows. To a solution of **2a** (281 mg, 1 mmol) in acetonitrile (8 mL) and methanol (2 mL) was added a solution of bromine (480 mg, 4 mmol) in carbon tetrachloride (4 mL) at room temperature. After the solution had been kept overnight, the solvent was removed under reduced pressure. The residue was made slightly alkaline with NaOH aqueous solution, and acenaphthene (50 mg) was added as an internal standard, and then the whole mixture was extracted with dichloromethane (20 mL). The organic layer was dried over Na_2SO_4 and subjected to GC analysis.

*Reaction of Tris(2-pyridyl)phosphine Oxides (***2***) with Deuterium Chloride in D_2O*

A typical procedure is as follows. A mixture of **2a** (0.281 g, 1 mmol) and 20% DCl/D_2O (1.875 g, 10 mmol) was allowed to stand overnight at room temperature. The reaction mixture was made slightly alkaline with NaOH aqueous solution, and m-dinitrobenzene (100 mg) was added as an internal standard, and then the whole mixture was extracted with chloroform (100 mL). The organic layer was dried over Na_2SO_4 and subjected to GC analysis.

Concentration of the chloroform solution followed by chromatographic separation afforded a mixture of **4a** and **7a** (**4a**:**7a** = 31:69) in a 50% yield. The **4a**/**7a** ratio was estimated by ^{1}H NMR analysis.

*Reaction of Tris(2-pyridyl)phosphine Oxides (***2***) with Arenediazonium Chloride*

A typical procedure is as follows. To a solution of benzenediazonium chloride that was prepared from aniline (0.279 g, 3 mmol), conc. HCl (2.2 mL), water (13 mL), and sodium nitrite (0.207 g, 3 mmol) were added **2a** (0.281 g, 1 mmol) and 2-propanol (10 mL) with stirring below 3°C, and then the mixture was allowed to stand overnight in a refrigerator. The reaction mixture was made slightly alkaline with NaOH aqueous solution and extracted with chloroform (100 mL). The organic layer was dried over Na_2SO_4 and subjected to HPLC and GC analyses. Concentration of the chloroform solution followed by chromatographic separation afforded **8a** and **9a,** which were recrystallized from methanol.

*5-Phenylazo-2,2′-bipyridyl (***8a***)*. Mp 144.0–145.0°C. MS *m/z* (rel. intensity); 260 (M$^+$, 100), 155 (79), 128 (16), 77 (77). ^{1}H NMR ($CDCl_3$) δ = 7.343 (1H, dd, J = 7.5, 4.5), 7.48–7.58 (3H, m), 7.847 (1H, td, J = 7.8, 1.8), 7.95–8.00 (2H, m), 8.265 (1H, dd, J = 8.4, 2.1), 8.505 (1H, d, J = 7.8), 8.574 (1H, d, J = 8.4), 8.716 (1H, d, J = 4.5), 8.679 (1H, d, J = 2.1). Anal. calcd for $C_{16}H_{12}N_4$: C, 73.83; H, 4.65; N, 21.52 Found: C, 73.99; H, 4.73; N, 21.38.

*6-Phenyl-5-phenylazo-2,2′-bipyridyl (***9a***)*. Mp 149.0–150.0°C. MS *m/z* (rel. intensity); 336 (M$^+$, 100), 335 (99), 247 (29), 246 (41), 231 (42), 78 (40), 77 (44). ^{1}H NMR ($CDCl_3$) δ = 7.355 (1H, ddd, J = 7.5, 4.8, 1.2), 7.45–7.56 (6H, m), 7.856 (1H, ddd, J = 8.4, 7.5, 0.9), 7.915 (4H, ddd, J = 8.1, 2.4, 1.8), 8.200 (1H, d, J = 8.7), 8.545 (1H, d, J = 8.7), 8.685 (1H, d, J = 8.4), 8.726 (1H, dd, J = 4.8, 0.9). Anal. calcd for $C_{22}H_{16}N_4$: C, 78.55; H, 4.79; N, 16.66. Found: C, 78.00; H, 4.90; N, 15.89.

*Preparation of 5-Phenylazo-2,2′-bipyridyl-d_5(***8a′***)*

To a solution of benzenediazonium chloride that was prepared from aniline-d_7 (2.00 g, 20.4 mmol), conc.

HCl (16 mL), water (80 mL), and sodium nitrite (1.404 g, 21.0 mmol) were added **2a** (2.248 g, 8.0 mmol) and 2-propanol (10 mL) with stirring below 3°C, and then the mixture was allowed to stand overnight in a refrigerator. The reaction mixture was made slightly alkaline with NaOH aqueous solution and extracted with chloroform (300 mL). The organic layer was dried over Na_2SO_4. Concentration of the chloroform solution followed by chromatographic separation afforded **8a′** (1.045g) and **9a** (0.270g), which were recrystallized from methanol.

*5-Phenylazo-2,2′-bipyridyl-d_5 (**8a′**).* Mp 143.0–143.5°C. MS *m/z* (rel. intensity); 266 [$(M + 1)^+$, 17], 265 (M^+, 70), 155 (100), 128 (18), 110 (27), 82 (80), 78 (32). ^{1}H NMR ($CDCl_3$) δ = 7.358 (1H, ddd, J = 7.5, 4.5, 0.9), 7.862 (1H, td, J = 7.5, 1.8), 8.277 (1H, dd, J = 8.7, 2.4), 8.512 (1H, d, J = 8.1), 8.579 (1H, d, J = 8.7), 8.723 (1H, dd, J = 4.8, 1.8), 9.264 (1H, d, J = 2.4). Anal. calcd for $C_{16}H_7D_5N_4$: C, 72.43; HD, 2.66; N, 21.12 Found: C, 72.65; HD, 2.75; N, 21.07.

*6-Phenyl-5-phenylazo-2,2′-bipyridyl-d_{10} (**9a′**).* Mp 149.0–150.0°C. MS *m/z* (rel. intensity); 347 [$(M + 1)^+$, 29], 346 (M^+, 100), 345 (39), 344 (88), 343 (13), 264 (13), 252 (15), 241 (14), 250 (16), 249 (13), 237 (16), 236 (71), 209 (16), 82 (59), 79 (13), 78 (46). ^{1}H NMR ($CDCl_3$) δ = 7.354 (1H, ddd, J = 7.8, 4.8, 1.2), 7.858 (1H, ddd, J = 8.1, 7.8, 0.9), 8.201 (1H, dd, J = 8.4, 0.9), 8.545 (1H, d, J = 8.4), 8.687 (1H, dd, J = 8.1, 1.2), 8.727 (1H, ddd, J = 4.8, 1.2, 0.9). Anal. calcd for $C_{22}H_6D_{10}N_4$: C, 76.27; HD, 1.75; N, 15.96. Found: C, 76.41; HD 1.83; N, 15.96.

*4,4′-Dimethyl-5-phenylazo-2,2′-bipyridyl (**8c**).* Mp 99.0–100.0°C. MS *m/z* (rel. intensity); 289 [$(M + 1)^+$, 17], 288 (M^+, 71), 184 (20), 183 (100), 156 (16), 105 (16), 77 (43). ^{1}H NMR ($CDCl_3$) δ = 2.440 (3H, s), 2.780 (3H, s), 7.155 (1H, d, J = 5.1), 7.49–7.58 3H, m), 7.956 (2H, dd, J = 8.1, 2.1), 8.282 (1H, s), 8.402 (1H, s), 8.550 (1H, d, J = 5.1), 8.809 (1H, s). Anal. calcd for $C_{18}H_{16}N_4$: C, 74.98; H, 5.59; N, 19.43. Found: C, 75.06; H, 5.67; N, 19.33.

*6,6′-Dimethyl-5-phenylazo-2,2′-bipyridyl (**8d**).* Mp 116.0–116.5°C. MS *m/z* (rel. intensity); 288 (M^+, 85), 183 (100), 77 (42). ^{1}H NMR ($CDCl_3$) δ = 2.646 (3H, s), 3.033 (3H, s), 7.195 (1H, d, J = 7.8), 7.46–7.58 (3H, m), 7.724 (2H, dd, J = 7.8, 7.5), 7.966 (2H, dd, J = 8.1, 1.8), 8.408 (1H, d, J = 8.4), 8.319 (1H, d, J = 7.8), 8.374 (1H, d, J = 8.4). Anal. calcd for $C_{18}H_{16}N_4$: C, 74.98; H, 5.59; N, 19.43. Found: C, 74.91; H, 5.66; N, 19.28.

*5-(p-Chlorohenylazo)-2,2′-bipyridyl (**8i**).* Mp 179.0–180.0°C. MS *m/z* (rel. intensity); 296 [$(M + 2)^+$ 5], 295 [$(M + 1)^+$ 25], 294 (M^+, 15), 293 (77), 171 (29), 155 (100), 139 (35), 128 (19), 113 (19), 111 (55), 91 (27), 78 (31). ^{1}H NMR ($CDCl_3$) δ = 7.358 (1H, ddd, J = 7.8, 4.8, 1.2), 7.512 (2H, d, J = 9.0), 7.858 (1H, ddd, J = 8.1, 7.8, 1.8), 7.922 (2H, d, J = 9.0), 8.253 (1H, dd, J = 8.4, 2.1), 8.506 (1H, dd, J = 8.1, 1.2), 8.575 (1H, d, J = 8.4), 8.720 (1H, dd, J = 4.8, 1.9), 9.244 (1H, d, J = 2.1). Anal. calcd for $C_{16}H_{11}ClN_4$: C, 65.20; H, 3.78; N, 19.01. Found: C, 65.34; H, 3.85; N, 18.97.

*6-(p-Chlorophenyl)-5-(p-chlorophenylazo)-2,2′-bipyridyl (**9i**).* Mp 181.5–183.0°C. MS *m/z* (rel. intensity); 407 [$(M + 3)^+$, 13], 406 [$(M + 2)^+$, 25], 405 [$(M + 1)^+$, 77], 404 (M^+, 74), 403 (100), 402 (74), 368 (27), 265 (31), 230 (27), 229 (35), 111 (40). ^{1}H NMR ($CDCl_3$) δ = 7.375 (1H, ddd, J = 7.5, 4.8, 1.2), 7.490 (2H, dd, J = 9.0, 0.9), 7.502 (2H, dd, J = 8.4, 0.9), 7.854 (2H, d, J = 8.4), 7.870 (2H, dd, J = 9.0, 0.9), 7.8–7.0 (1H, ddd, J = 8.1, 7.5, 1.8), 8.205 (1H, d, J = 8.4), 8.557 (1H, d, J = 8.4), 8.649 (1H, dd, J = 8.1, 1.2), 8.732 (1H, dd J = 4.8, 1.8).

*5-(p-Ethoxycarbonylphenylazo)-2,2′-bipyridyl (**8i**).* Mp 178.0–178.5°C. MS *m/z* (rel. intensity); 333 [$(M + 1)^+$, 14], 332 (M^+, 60), 156 (15), 155 (100), 149 (39), 128 (17), 103 (18), 78 (32). ^{1}H NMR ($CDCl_3$) δ = 1.438 (3H, t, J = 7.2), 4.431 (2H, q, J = 7.2), 7.366 (1H, ddd, J = 7.5, 4.8, 0.9), 7.866 (1H, ddd, J = 8.1, 7.5, 1.8), 8.006 (2H, ddd, J = 8.7, 2.1, 1.8), 8.223 (2H, ddd, J = 8.7, 2.1, 1.8), 8.288 (1H, dd, J = 8.4, 2.4), 8.521 (1H, ddd, J = 8.1, 0.9, 0.9), 8.598 (1H, dd, J = 8.4, 0.6), 8.727 (1H, ddd, J = 4.8, 1.8, 0.9), 9.291 (1H, dd, J = 2.4, 0.6). Anal. calcd for $C_{19}H_{16}N_4O_2$: C, 68.66; H, 4.85; N, 16.86. Found: C, 68.72; H, 4.94; N, 16.82.

*6-(p-Ethoxycarbonylphenylphenyl)-5-(p-ethoxycarbonylphenylazo)-2,2′-bipyridyl (**9j**).* Mp 204.0–205.0°C. MS *m/z* (rel. intensity); 481 [$(M + 1)^+$, 17], 480 (M^+, 51), 479 (29), 452 (31), 451 (100), 407 (41), 319 (20), 231 (22), 230 (32), 229 (45), 155 (17), 149 (55), 103 (29), 78 (37). ^{1}H NMR ($CDCl_3$) δ = 1.427 (3H, t, J = 7.2), 1.452 (3H, t, J = 7.2), 4.419 (2H, q, J = 7.2), 4.447 (2H, q, J = 7.2), 7.377 (1H, ddd, J = 7.5, 4.8, 0.9), 7.874 (1H, ddd, J = 8.1, 7.5, 1.8), 7.899 (2H, d, J = 8.7), 7.983 (2H, d, J = 8.1), 8.196 (H, d, J = 8.7), 8.196 (H, d, J = 8.1), 8.243 (1H, d, J = 8.4), 8.594 (1H, d, J = 8.4), 8.663 (1H, dd, J = 8.1, 0.9), 8.773 (1H, dd, J = 4.8, 1.8).

REFERENCES

[1] (a) Y. Uchida, H. Kozawa, S. Oae, *Tetrahedron Lett., 30,* 1989, 6365; (b) Y. Uchida, K. Onoue, N. Tada, F. Nagao, H. Kozawa, S. Oae, *Heteroatom Chem., 1,* 1990, 295.
[2] Y. Uchida, R. Kajita, R. Kawasaki, S. Oae, *Tetrahedron Lett., 36,* 1995, 4077.
[3] L. Horner, H. Oediger, H. Hoffmann, *Ann. Chim., 626,* 1969, 26.
[4] R. E. Rundle, *J. Am. Chem. Soc., 85,* 1963, 112.
[5] S. Oae, *Heteroatom Chem., 1,* 1988, 304.
[6] Y. Uchida, N. Echigawa, S. Oae, *Heteroatom Chem., 5,* 1994, 409.