Structure and Reactivity of Aryl(bromo)nickel Complexes Relevant to Nickel(0) Complex-promoted Dehalogenative Polycondensation of Organic Dihalides†

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Reactions of 4-bromobiphenyl, 1,4-dibromobenzene, and 9,10-dibromoanthracene with $[Ni(cod)_2]$ (cod = cycloocta-1,5-diene) in the presence of PEt_3 gave arylnickel complexes, *trans*-$[NiBr(C_6H_4C_6H_5)(PEt_3)_2]$ **1**, *trans*-$[NiBr(C_6H_4Br\text{-}p)(PEt_3)_2]$ **2**, and *trans*-$[NiBr(C_{14}H_8Br)(PEt_3)_2]$ **3**, respectively. 4,4'-Dibromobiphenyl reacted with a $[Ni(cod)_2]$–PEt_3 mixture to give *trans, trans*-$[(Et_3P)_2BrNi(C_6H_4C_6H_4)NiBr(PEt_3)_2]$ **4**. The structures of complexes **1–4** with *trans* configuration around square-planar nickel centres have been determined by X-ray crystallography. The NMR (^1H, ^{13}C, and ^{31}P) spectra of the complexes are consistent with the *trans* structures. Complexes **2** and *trans*-$[NiBr(Ph)(PEt_3)_2]$ **5** did not undergo any thermal reaction at 60 °C in dimethylformamide. Complex **2** reacted with MeI at room temperature to give a mixture of *p*-bromotoluene (17%) and 4,4'-dibromobiphenyl (8%), while similar reaction of **5** gave a mixture of toluene (15%) and biphenyl (78%). Reaction of complex **4** with MeI gave 4-methylbiphenyl and quaterphenyl.

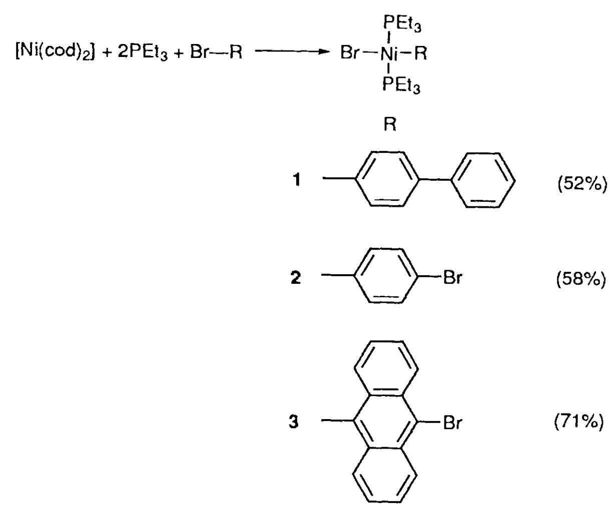
Nickel(0) complex-promoted dehalogenative coupling of aryl halides giving biaryls[1–7] provides a useful tool for synthesis of several organic molecules.[8,9] Recently dehalogenative polycondensation of arylene dibromides by nickel(0) complexes has been developed to give various π-conjugated polymers such as poly(*p*-phenylene), poly(thiophene-2,5-diyl), poly(pyridine-2,5-diyl), poly(2,2'-bipyridine-5,5'-diyl), their alkyl substituted derivatives, and their copolymers (Scheme 1).[10]

Since arylnickel complexes are believed to play important roles as intermediates both in the preparation of biaryls and of π-conjugated polymers, it seems to be significant to study the detailed structures and properties of the complexes. Kochi and his co-workers[11] established the pathway of the reaction of *trans*-$[NiBr(R)(PEt_3)_4]$[12] (R = aryl) with aryl bromide to give biaryls through nickel-(I) and -(III) intermediates. Recently we reported that coupling of RBr by $[Ni(cod)_2]$–bipy in dimethylformamide (dmf) proceeds through formation of [NiBr(R)(bipy)] followed by its disproportionation to give $[NiBr_2(bipy)]$ and $[NiR_2(bipy)]$ the latter of which is responsible for formation of R–R.[13] The pathway using bipy as ligand is highly dependent on the solvent used, and similar reaction in toluene proceeds through nickel-(I) or -(III) radical intermediates rather than through disproportionation of the [NiBr(R)(bipy)] intermediate.

In the polycondensation of arylene dibromides, arylnickel complexes with bromo substituents on the aryl ligand are involved as intermediates. There have been only a few reports on the preparation and properties of the complexes. Previously we have prepared *trans*-$[NiX(C_{14}H_8X)(PPh_3)_2]$ (X = Cl or Br; $C_{14}H_8X$ = 10-halogeno-9-anthryl) in order to study their structure and reactivity and to compare the possible reaction pathways for dehalogenative polycondensation of arylene dibromides.[14] However, the low crystallinity and poor reactivity of the complexes prevent us from obtaining details of their structure and reactivity. Here we report the preparation of bromo(bromoaryl)nickel complexes with PEt_3 ligands, *trans*-$[NiBr(YBr)(PEt_3)_2]$ (Y = arylene), their crystal structures and results of their reactions with organic halides.

$$\text{Br–Y–Br} + [Ni(cod)_2] + 2L \xrightarrow{-2\,\text{cod}} \frac{1}{n}\,\text{Br}\left(\text{Y}\right)_n\text{Br} + [NiBr_2L_2]$$

Scheme 1 Y = *p*-Phenylene, thiophene-2,5-diyl, pyridine-2,5-diyl, *etc.*; L = PPh_3 or 2,2'-bipyridine (bipy), cod = cycloocta-1,5-diene

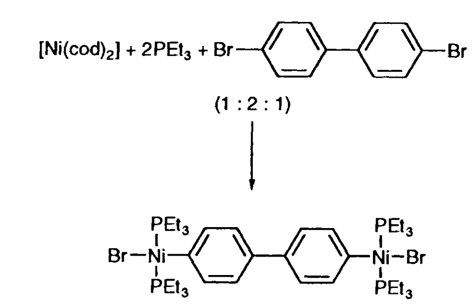


Scheme 2

Results and Discussion

Aromatic halides such as 4-bromobiphenyl, 1,4-dibromobenzene, and 9,10-dibromoanthracene react with $[Ni(cod)_2]$ in the presence of PEt_3 to give monoarylnickel complexes formulated as $[NiBr(R)(PEt_3)_2]$ (R = $C_6H_4C_6H_5$ **1**, $C_6H_4Br\text{-}p$ **2**, $C_{14}H_8Br$ **3**), respectively, through oxidative addition of a C–Br bond to the nickel centre (Scheme 2). The last two

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



4 (10% based on dibromide)

Scheme 3

reactions do not give a dinuclear nickel complex with a bridging arylene ligand which would be formed by oxidative addition of the remaining C–Br bond to another nickel(0) centre. Reaction of 9,10-dichloroanthracene with a $[Ni(cod)_2]$–PPh_3 mixture was also reported to give *trans*-$[NiCl(C_{14}H_8Cl)(PPh_3)_2]$ exclusively.[14]

Reaction of 4,4′-dibromobiphenyl with a $[Ni(cod)_2]$–PEt_3 mixture in tetrahydrofuran (thf) causes oxidative addition of both C–Br bonds in the substrate to two nickel(0) centres to give the dinuclear nickel complex *trans,trans*-$[(Et_3P)_2BrNi(C_6H_4C_6H_4)NiBr(PEt_3)_2]$ **4** with a bridging biphenylene ligand (Scheme 3). Reaction of $[Ni(cod)_2]$ and 4,4′-dibromobiphenyl in a 1:1 ratio gives **4** in 10% yield based on the substrate. The reaction in a 2:1 ratio also gives **4** in poor yield (9%, based on dibromide). Although the isolated yields of the product are not high, another possible by-product with mononuclear structure, $[NiBr(C_6H_4C_6H_4Br)(PEt_3)_2]$, from oxidative addition of a C–Br bond to the nickel(0) centre, is not observed in the reaction products. A major nickel-containing by-product in the 1:1 reaction is a green and air-sensitive compound the ^1H NMR spectrum of which shows the presence of a cyclooctadiene or cyclooctadienyl, PEt_3, and aryl or arylene ligands although full characterization is not feasible due to its high air-sensitivity and to broadening of the NMR peaks probably caused by contamination with a small amount of paramagnetic impurities. Reaction of 4,4′-dibromobiphenyl with $[Ni(cod)_2]$–PEt_3 at 60 °C in dmf also gives complex **4**. Dehalogenative polycondensation which would give poly(*p*-phenylene) does not occur although 1,4-dibromobenzene undergoes polycondensation in the presence of $[Ni(cod)_2]$–PPh_3 at 60 °C in dmf to give poly(*p*-phenylene).[10e,f]

Figs. 1–4 show the molecular structures of complexes **1**–**4** as determined by X-ray crystallography.[15] Tables 1 and 2 summarize the crystallographic data and selected bond distances and angles, respectively. Molecule **2** has a crystallographic mirror plane including six phenyl carbon atoms, the nickel centre, and two bromine atoms, while **3** has a crystallographic C_2 axis along the line including atoms Br(1), Ni, C(1), C(8) and Br(2). The Ni–Br bond distances are almost the same in the complexes. The Ni–C bond distances in **2**–**4** are in the range 1.86–1.89 Å, while that in **1** [1.924(7) Å] is somewhat longer. They are similar to those for *trans* monoarylnickel complexes with two phosphine ligands such as *trans*-$[NiBr(C_6F_5)(PMe_2Ph)_2]$ [1.880(4) Å][16] and $[Ni\{OC(Ph)CHPPh_2\}Ph(PPh_3)]$ [1.899(15) Å][17] and seem to be shorter than that of the corresponding bond in alkylnickel complexes. Previously this structural characteristic of arylnickel complexes was attributed to lowering of the energy of the highest occupied molecular orbital (HOMO) of Ni by double bonding of the aryl group.[12] The C–Br bond distances in **2** [1.986(15) Å] and **3** [1.908(4) Å] are similar to sum of the covalent radii of carbon and bromine or somewhat longer.[18] No significant shortening of the C–Br bond distances is observed in the crystal structure although hyperconjugation along the bonds seems to exist.

The NMR spectra of complexes **1**–**4** are consistent with the

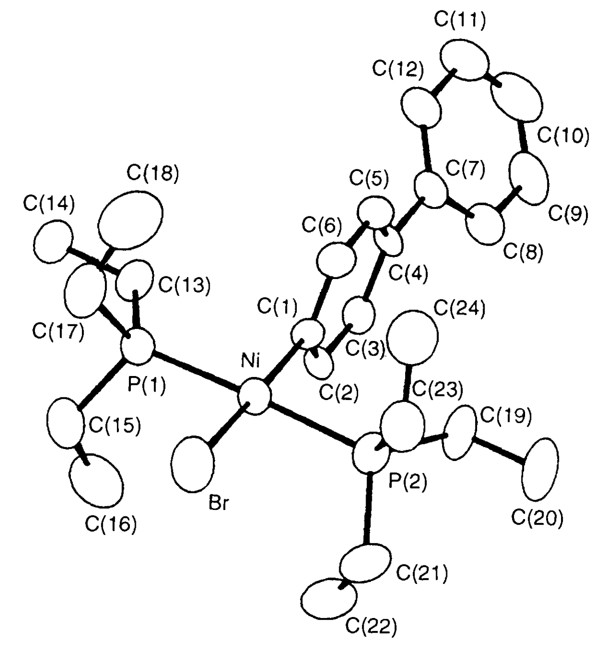


Fig. 1 An ORTEP drawing of *trans*-$[NiBr(C_6H_4C_6H_5)(PEt_3)_2]$ **1** showing thermal ellipsoids at 50% probability

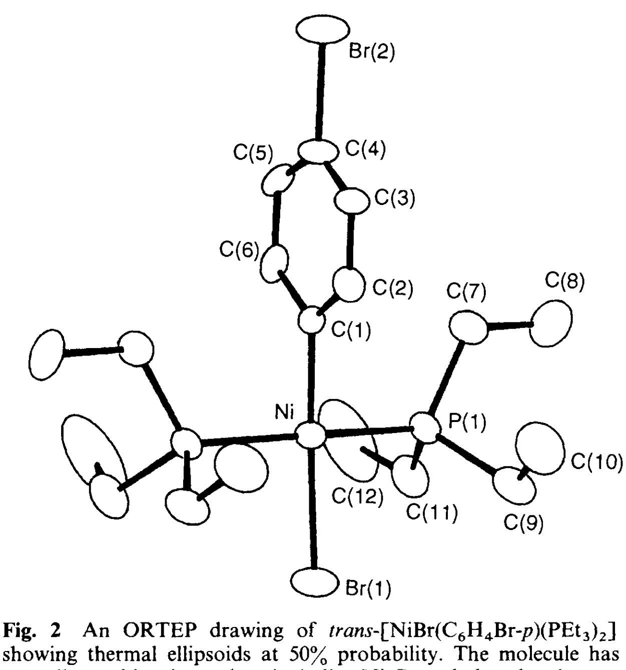


Fig. 2 An ORTEP drawing of *trans*-$[NiBr(C_6H_4Br\text{-}p)(PEt_3)_2]$ **2** showing thermal ellipsoids at 50% probability. The molecule has a crystallographic mirror plane including Ni, Br and phenyl carbons

trans structure. The ^1H NMR spectra show the methyl hydrogens of the PEt_3 ligands as apparent quintets due to virtual coupling of two phosphine ligands at mutually *trans* positions,[19] in addition to H–H coupling with the CH_2 hydrogens. The CH_3 and CH_2 signals of **3** appear at significantly higher magnetic field positions than the corresponding peaks of the other complexes, possibly due to the magnetic anisotropic effect of the π electrons of the anthryl ligand which is close to two ethyl groups in the crystal structure.

Heating *trans*-$[NiBr(Ph)(PEt_3)_2]$ **5** at 60 °C for 1 h in $DCON(CD_3)_2$ does not cause a change in the ^1H NMR spectrum, while [NiBr(Ph)(bipy)] was reported to liberate biphenyl on dissolution in dmf at room temperature through disproportionation to give $[NiPh_2(bipy)]$ followed by reductive elimination of the product. Heating complex **2** at 60 °C in

Table 1 Crystal data and details of structure refinement of complexes **1**–**4**

Complex	**1**	**2**	**3**	**4**
Formula	$C_{24}H_{39}BrNiP_2$	$C_{18}H_{34}Br_2NiP_2$	$C_{26}H_{38}Br_2NiP_2$	$C_{36}H_{68}Br_2Ni_2P_4$
M	527.79	530.53	630.72	901.46
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca* (no. 61)	*Cmc*2$_1$ (no. 36)	*C*2/*c* (no. 15)	*P*2$_1$/*c* (no. 14)
a/Å	15.399(8)	12.726(3)	19.221(5)	9.071(2)
b/Å	25.235(7)	13.219(3)	12.374(3)	18.314(5)
c/Å	13.943(5)	14.160(3)	14.444(5)	14.342(3)
β/°	—	—	127.76(2)	108.06(1)
U/Å^3	5409.9	2382.1	2716.3	2265.4
Z	8	4	4	2
μ/cm^{-1}	23.07	42.73	37.60	27.43
F(000)	2208	1080	1288	940
D_c/g cm^{-3}	1.301	1.480	1.543	1.322
Crystal size/mm	0.40 × 0.45 × 0.80	0.40 × 0.50 × 0.55	0.30 × 0.45 × 0.55	0.20 × 0.40 × 0.45
2θ range/°	3.0–45.0	3.0–50.0	3.0–55.0	3.0–45.0
Scan rate/° min^{-1}	4	4	4	4
Scan range	$+h, +k, +l$	$+h, +k, +l$	$\pm h, +k, +l$	$\pm h, +k, +l$
Unique reflections	3530	1197	3050	2987
Used reflections [$F_o \geqslant 3\sigma(F_o)$]	2531	1023	2071	1877
R	0.068	0.043	0.040	0.045
R'	0.066	0.067	0.035	0.047
Weighting scheme	$\{[\sigma(F_o)]^2 + [0.020(F_o)]^2\}^{-1}$	$[\sigma(F_o)^2]^{-1}$	$\{[\sigma(F_o)]^2 + [0.024(F_o)]^2\}^{-1}$	$[\sigma(F_o)^2]^{-1}$

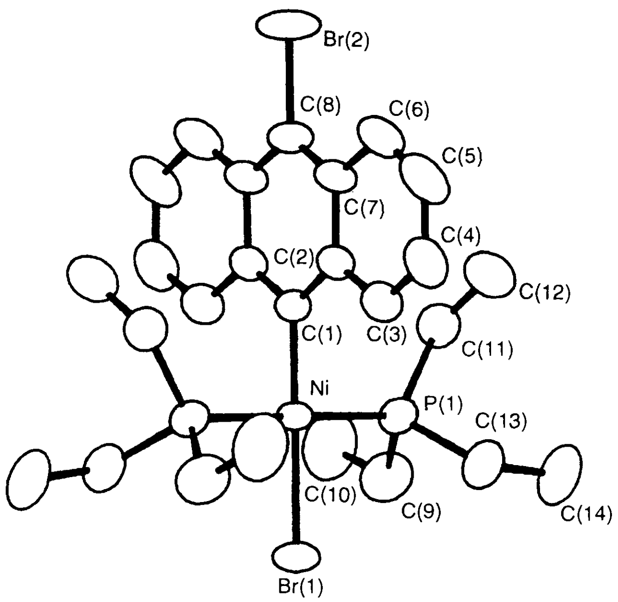


Fig. 3 An ORTEP drawing of *trans*-[NiBr($C_{14}H_8Br$)(PEt_3)$_2$] **3** showing thermal ellipsoids at 50% probability. The molecule has a crystallographic C_2 axis along Br(1)–Ni–C(1)–C(8)–Br(2)

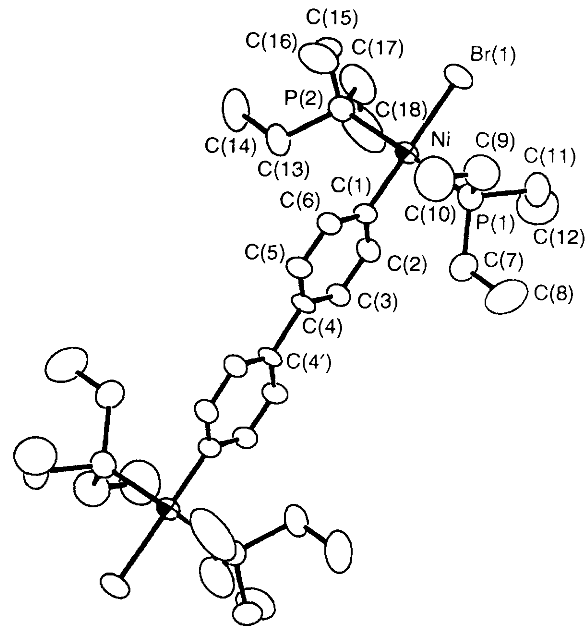


Fig. 4 An ORTEP drawing of *trans,trans*-[(Et_3P)$_2$BrNi($C_6H_4C_6H_4$)-NiBr(PEt_3)$_2$] **4** showing thermal ellipsoids at 50% probability. The molecule has a symmetry centre at the midpoint of the C(4)–C(4') bond

$DCON(CD_3)_2$ also results in complete recovery of the complex. The results indicate that the PEt_3-co-ordinated arylnickel complexes are too stable to undergo disproportionation under these conditions. Closely related is the observation that the reaction of 4,4'-dibromobiphenyl with a [Ni(cod)$_2$]–PEt_3 mixture at 60 °C in dmf does not give a polycondensation product but complex **4** which does not undergo further reaction under the conditions.

Complexes **1** and **2** as well as **5** react with MeI at room temperature to give C–C bond-formation products: **2** gives a mixture of *p*-bromotoluene (17%) and 4,4'-dibromobiphenyl (8%), while **5** gives a mixture of toluene (15%) and biphenyl (78%). Reaction of complex **4** with MeI gives 4-methylbiphenyl (12%) and quaterphenyl. Formation of the latter compound was confirmed by TLC of the reaction mixture (silica gel, hexane eluent), but the yield was not determined by GC or NMR spectroscopy due to the poor solubility in organic solvents. These C–C bond-forming reactions seem to proceed through nickel-(I) and -(III) intermediates similarly to the reactions of *trans*-[NiBr(R)(PEt_3)$_2$] with aryl bromides[11] because the coupling products both from two aryl groups and from methyl and aryl groups are observed in these reactions.

Conclusion

Nickel complexes with bromo-substituted aryl ligands are prepared by oxidative addition of a C–Br bond of arylene dibromide to [Ni(cod)$_2$] in the presence of PEt_3. Reaction of 4,4'-dibromobiphenyl with the nickel(0) complexes gives dinuclear complexes through oxidative addition of two C–Br bonds to the different nickel centres. The bond distances and

Table 2 Selected bond distances (Å) and angles (°) of complexes **1–4**

	1	**2**	**3**	**4**
Ni–Br(1)	2.358(1)	2.353(2)	2.365(1)	2.366(1)
Ni–P(1)	2.197(2)	2.202(2)	2.235(1)	2.198(2)
Ni–P(2)	2.208(2)			2.193(3)
Ni–C(1)	1.924(7)	1.864(12)	1.885(4)	1.890(6)
C(4)–C(7) [or C(4′)]	1.471(10)			1.48(1)
C[4(8)]–Br(2)		1.986(15)	1.908(4)	
Br(1)–Ni–P(1)	89.73(6)	89.53(9)	89.44(3)	90.69(7)
Br(1)–Ni–P(2)	90.10(7)			90.17(7)
P(1)–Ni–C(1)	90.6(2)	90.70(9)	90.56(3)	89.6(2)
P(2)–Ni–C(1)	89.9(2)			89.5(2)
Br(1)–Ni–C(1)	174.9(2)	175.6(4)	179.94(4)	179.5(2)
P(1)–Ni–P(2) [or P(1′)]	176.8(9)		178.9(5)	176.8(1)
Ni–C(1)–C(2)	120.9(5)	121.8(1.0)	120.9(2)	122.6(5)
Ni–C(1)–C(6)	119.7(5)	123.1(1.2)		121.1(5)
Br(2)–C(4)–C(3)		118.9(1.5)		
Br(2)–C(4)–C(5)		118.8(1.3)		
Br(2)–C(8)–C(7)			118.5(2)	

angles around the nickel centres are similar to those found in other arylnickel complexes with tertiary phosphine ligands. The complexes are stable at elevated temperature in dmf and do not give C–C coupling products under these conditions. The arylnickel complexes with PEt_3 ligands react easily with MeI to give C–C bond-formation products probably through nickel-(I) and -(III) radical intermediates. These reactions of the monoarylnickel complexes with PEt_3 ligands are in contrast with our previous observations that monoarylnickel complexes with bipy or PPh_3 ligands undergo disproportionation and ensuing reductive elimination of biaryls in dmf and react with organic halides to cause C–C bond formation through radical intermediates.

Experimental

General Procedure, Materials and Measurements.—All the manipulations of the complexes were carried out under nitrogen or argon using Schlenk techniques. Solvents were dried in the usual manners, distilled and stored under a nitrogen atmosphere. The compounds $[Ni(cod)_2]$,[20] PEt_3,[21] and *trans*-$[NiBr(Ph)(PEt_3)_2]$[11,12] were prepared according to the literature methods. 1,4-Dibromobenzene, 4-bromobiphenyl, 4,4′-dibromobiphenyl and 9,10-dibromoanthracene were obtained from Tokyo Kasei Co. and purified by recrystallization. The NMR spectra (^1H, ^{13}C and ^{31}P) were recorded on JEOL FX-100, GX-270 and GX-500 spectrometers. Elemental analyses were carried out by a Yanagimoto type MT-2 CHN autocorder and a Yazawa halogen and sulfur analyzer. Gas chromatography was performed on a Shimadzu GC-8A instrument with a 2 m silicone OV-1 packed column.

Preparations.—*trans*-$[NiBr(C_6H_4C_6H_5)(PEt_3)_2]$ **1**. To an Et_2O solution of $[Ni(cod)_2]$ (460 mg, 1.7 mmol) were added PEt_3 (400 mg, 3.4 mmol) and 4-bromobiphenyl (390 mg, 1.7 mmol) in that order at room temperature. The orange reaction mixture soon turned red. After stirring for 24 h the solvent was removed by evaporation to afford a yellow solid which was recrystallized from Et_2O to give *trans*-$[NiBr(C_6H_4C_6H_5)(PEt_3)_2]$ **1** as red-brown crystals (460 mg, 52%) (Found: C, 54.3; H, 7.5. $C_{24}H_{39}BrNiP_2$ requires C, 54.6; H, 7.4%); δ_H(270 MHz, in CD_2Cl_2) 1.15 (18 H, apparent qnt due to virtual coupling, CH_3), 1.45 (12 H, br, CH_2), 7.22 (3 H, m), 7.49 (4 H, m) and 7.58 (2 H, m); δ_C(68.5 MHz, in CD_2Cl_2) 8.4 (CH_3), 14.8 (apparent t due to virtual coupling, CH_2), 124.9 (CH), 126.4 (CH), 126.6 (CH), 129.0 (CH), 133.9 (quaternary), 137.6 [t, *J*(PC) 3 Hz, quaternary], 141.9 (quaternary), and 156.0 [t, *J*(PC) 34 Hz, NiC]; δ(^{31}P-{^1H}) (from external 85% H_3PO_4 at 40 MHz in CD_2Cl_2) 10.1 (s).

trans-$[NiBr(C_6H_4Br\text{-}p)(PEt_3)_2]$ **2**. To a mixture of $[Ni(cod)_2]$ (840 mg, 3.0 mmol) and 1,4-dibromobenzene (720 mg, 3.0 mmol) in hexane (15 cm^3) was added PEt_3 (710 mg, 6.1 mmol) at room temperature. Stirring for 3 h resulted in precipitation of a yellow solid. After cooling the reaction mixture for 12 h at −20 °C the yellow solid was filtered off, washed with hexane and recrystallized from hot hexane to give *trans*-$[NiBr(C_6H_4Br\text{-}p)(PEt_3)_2]$ **2** as orange prisms (920 mg, 58%) (Found: C, 40.9; H, 6.5. $C_{18}H_{34}Br_2NiP_2$ requires C, 40.7; H, 6.5%); δ_H(500 MHz, in CD_2Cl_2) 1.13 (18 H, apparent qnt due to virtual coupling, CH_3), 1.41 (12 H, br, CH_2), 7.01 [2 H, d, *J*(HH) 7 Hz, CH] and 7.17 (2 H, d); δ_C(125 MHz in CD_2Cl_2) 8.3 (CH_3), 14.8 (apparent t due to virtual coupling, CH_2), 115.6 (CBr), 129.4 [t, *J*(PC) 2 Hz, CH], 138.5 [t, CH, *J*(PC) 2 Hz] and 155.4 [t, *J*(PC) 34 Hz, NiC]; δ(^{31}P-{^1H}) (from external 85% H_3PO_4 at 40 MHz in CD_2Cl_2) 10.4 (s).

trans-$[NiBr(C_{14}H_8Br)(PEt_3)_2]$ **3**. To a mixture of $[Ni(cod)_2]$ (880 mg, 3.2 mmol) and 9,10-dibromoanthracene (1.1 g, 3.2 mmol) in Et_2O (30 cm^3) was added PEt_3 (730 mg, 6.4 mmol) at room temperature. An orange-brown solid soon separated. It was filtered off and recrystallized from thf–hexane (1 : 1) to give *trans*-$[NiBr(C_{14}H_8Br\text{-}10)(PEt_3)_2]$ **3** as red blocks (1.43 g, 71%) (Found: C, 49.6; H, 6.2. $C_{26}H_{38}Br_2NiP_2$ requires C, 49.5; H, 6.1%); δ_H(500 MHz, in CD_2Cl_2) 0.89 (18 H, apparent qnt due to virtual coupling, CH_3), 1.16 (12 H, m, CH_2), 7.52 (4 H, m, CH), 8.34 [2 H, d, *J*(HH) 8 Hz, CH] and 9.63 (2 H, d, CH); δ_C(125 MHz in CD_2Cl_2) 8.3 (CH_3), 15.5 (apparent t due to virtual coupling, CH_2), 117.2 [t, *J*(PC) 4, CBr], 127.2 (CH), 128.1 (CH), 129.6 [t, *J*(PC) 4, quaternary], 134.5 (CH), 139.0 [t, *J*(PC) 3, quaternary] and 166.1 [t, *J*(PC) 34 Hz, NiC]; δ(^{31}P-{^1H}) (from external 85% H_3PO_4 at 40 MHz in CD_2Cl_2) 10.2 (s).

trans,trans-$[(Et_3P)_2BrNi(C_6H_4C_6H_4)NiBr(PEt_3)_2]$ **4**. To an Et_2O (8 cm^3) solution of $[Ni(cod)_2]$ (320 mg, 1.2 mmol) were added PEt_3 (280 mg, 2.4 mmol) and 4,4′-dibromobiphenyl (360 mg, 1.2 mmol) at room temperature. Stirring the mixture at room temperature resulted in dissolution of 4,4′-dibromobiphenyl to give a yellow solution followed by gradual deposition of a pale green solid. After 20 h the Et_2O insoluble product was filtered off. Cooling the resulting orange filtrate at −30 °C gave an orange solid which was filtered off and recrystallized from Et_2O (110 mg, 10% based on 4,4′-dibromobiphenyl) (Found: C, 47.2; H, 7.9. $C_{36}H_{68}Br_2Ni_2P_4$ requires C, 47.9; H, 7.5%); δ_H(500 MHz, in CD_2Cl_2) 1.15 (36 H, apparent qnt due to virtual coupling, CH_3), 1.43 (24 H, br,

CH_2), 7.15 [2 H, d, J(HH) 8 Hz] and 7.28 (2 H, d); δ_C(125 MHz in CD_2Cl_2) 8.3 (CH_3), 14.8 (apparent t due to virtual coupling, CH_2), 121.1 [t, J(PC) 2, quaternary], 126.8 [t, J(PC) 2, quaternary] 137.3 [t, J(PC) 4, CH] and 155.5 [t, J(PC) = 34 Hz, NiC]; $\delta(^{31}P-\{^1H\})$ (from external 85% H_3PO_4 at 40 MHz in CD_2Cl_2) 10.1 (s).

Complex **4** was also obtained from a similar reaction at elevated temperature in dmf as follows. To a dmf (10 cm^3) solution of [$Ni(cod)_2$] (390 mg, 1.4 mmol) were added PEt_3 (330 mg, 2.8 mmol) and 4,4'-dibromobiphenyl (400 mg, 1.3 mmol) at room temperature. Heating the resulting red solution at 60 °C for 40 h followed by cooling at −40 °C resulted in formation of an orange solid which was filtered off and recrystallized from Et_2O to give **4** (110 mg, 9%).

Crystal Structure Determinations.—Crystals of complexes **1**–**4** were mounted in glass capillary tubes under argon. The unit-cell parameters were obtained by least-squares refinement of 2θ values of 25 reflections with 19 ≤ 2θ ≤ 22°. Intensities were collected on Rigaku AFC-5 or AFC-5R automated four-circle diffractometers by using Mo-Kα radiation (λ = 0.710 69 Å) and the ω–2θ method.

Calculations were carried out by using the TEXSAN program package[22] on a DEC Micro VAXII computer or the SAPI85 program package[23] on a FACOM A-70 computer. Full-matrix least-squares refinements were used for non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located from calculation by assuming ideal positions [d(C–H) = 0.95 Å] and included in the structure calculation without further refinement of the parameters. An empirical absorption correction (ψ-scan method or Gaussian integration) of the collected data was applied. Three reflections (022), (021) and (102) for complex **1** were omitted in the structure calculation because the calculation including these reflections showed much weaker F_o values than the corresponding F_c value, probably due to extinction. Atomic coordinates of the non-hydrogen atoms are listed in Tables 3–6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 3 Atomic coordinates of *trans*-[$NiBr(C_6H_4C_6H_5)(PEt_3)_2$] **1**

Atom	x	y	z
Ni	0.839 41(6)	0.155 60(2)	0.663 47(6)
Br	0.938 84(6)	0.178 69(3)	0.785 06(6)
P(1)	0.868 62(13)	0.071 43(7)	0.687 72(14)
P(2)	0.816 24(14)	0.240 36(7)	0.633 5(2)
C(1)	0.705 3(4)	0.136 9(2)	0.572 9(5)
C(2)	0.768 9(4)	0.131 0(3)	0.478 0(5)
C(3)	0.701 7(5)	0.117 4(2)	0.412 5(5)
C(4)	0.616 5(4)	0.111 0(2)	0.443 2(5)
C(5)	0.600 7(4)	0.117 2(3)	0.540 9(5)
C(6)	0.667 1(5)	0.130 2(3)	0.603 6(5)
C(7)	0.545 5(4)	0.097 8(3)	0.376 8(5)
C(8)	0.541 5(5)	0.120 5(3)	0.285 1(6)
C(9)	0.473 6(7)	0.110 0(4)	0.220 8(7)
C(10)	0.410 2(7)	0.075 6(5)	0.248 3(9)
C(11)	0.410 0(6)	0.053 1(4)	0.340 2(9)
C(12)	0.479 3(5)	0.063 6(3)	0.402 1(7)
C(13)	0.812 0(5)	0.022 6(3)	0.614 1(6)
C(14)	0.829 1(6)	−0.035 6(3)	0.636 8(7)
C(15)	0.982 0(6)	0.056 4(4)	0.666 6(8)
C(16)	1.013 1(7)	0.074 2(5)	0.571 4(9)
C(17)	0.851 8(7)	0.048 3(4)	0.808 4(7)
C(18)	0.761 4(9)	0.054 1(4)	0.845 0(7)
C(19)	0.741 6(6)	0.258 8(3)	0.535 2(5)
C(20)	0.723 9(7)	0.318 1(3)	0.522 7(7)
C(21)	0.916 2(7)	0.275 8(3)	0.606 6(8)
C(22)	0.970 1(7)	0.249 7(4)	0.529 7(8)
C(23)	0.772 4(7)	0.274 8(3)	0.739 0(6)
C(24)	0.687 7(7)	0.251 2(4)	0.770 6(7)

Reaction of Methyl Iodide with the Complexes.—To a thf (3 cm^3) solution of complex **5** (89 mg, 0.20 mmol) was added MeI (140 mg, 0.99 mmol) at room temperature. Stirring resulted in a change from pale to dark brown accompanied by deposition

Table 4 Atomic coordinates of *trans*-[$NiBr(C_6H_4Br)(PEt_3)_2$] **2**

Atom	x	y	z
Ni	0.50	0.373 3(1)	0.902 5(2)
Br(1)	0.50	0.517 5(2)	1.00
Br(2)	0.50	0.004 4(2)	0.587 0(3)
P(1)	0.032 72(2)	0.369 2(2)	0.910 0(3)
C(1)	0.50	0.265 8(9)	0.817 4(9)
C(2)	0.50	0.281 3(13)	0.721 2(11)
C(3)	0.50	0.206 5(12)	0.654 8(10)
C(4)	0.50	0.114 2(13)	0.683(2)
C(5)	0.50	0.088 1(10)	0.778(2)
C(6)	0.50	0.162 4(10)	0.846 0(13)
C(7)	0.259 2(8)	0.272 0(8)	0.846 0(9)
C(8)	0.137 6(10)	0.269 6(11)	0.851 6(14)
C(9)	0.263 8(10)	0.486 0(8)	0.868 4(9)
C(10)	0.284(2)	0.503 3(13)	0.765 8(11)
C(11)	0.282 7(11)	0.355 5(11)	1.032 5(9)
C(12)	0.318(2)	0.269(2)	1.079(2)

Table 5 Atomic coordinates of *trans*-[$NiBr(C_{14}H_8Br)(PEt_3)_2$] **3**

Atom	x	y	z
Ni	0	0.234 70(3)	0.25
Br(1)	0	0.043 61(3)	0.25
Br(2)	0	0.770 15(3)	0.25
P(1)	0.036 74(6)	0.232 97(6)	0.130 11(7)
C(5)	0	0.387 1(3)	0.25
C(6)	0.077 1(2)	0.445 9(2)	0.334 5(3)
C(7)	0.157 3(3)	0.391 0(3)	0.420 6(3)
C(8)	0.233 6(2)	0.444 4(4)	0.500 7(3)
C(9)	0.233 4(3)	0.557 6(4)	0.500 8(4)
C(10)	0.159 3(3)	0.615 2(3)	0.421 8(4)
C(11)	0.078 2(2)	0.562 1(2)	0.335 1(3)
C(12)	0	0.615 9(3)	0.25
C(13)	−0.035 1(3)	0.150 4(3)	−0.001 6(3)
C(14)	−0.125 4(3)	0.193 2(4)	−0.088 7(4)
C(15)	0.044 9(3)	0.356 9(3)	0.068 2(3)
C(16)	0.126 8(3)	0.426 7(3)	0.148 3(4)
C(17)	0.143 7(2)	0.166 4(3)	0.201 9(3)
C(18)	0.176 9(3)	0.151 3(4)	0.130 6(4)

Table 6 Atomic coordinates of *trans,trans*-[$(Et_3P)_2BrNi(C_6H_4C_6H_4)NiBr(PEt_3)_2$] **4**

Atom	x	y	z
Ni	0.282 3(1)	0.160 42(5)	0.753 77(6)
Br(1)	0.188 3(1)	0.229 24(5)	0.862 99(7)
P(1)	0.120 1(3)	0.071 5(1)	0.754 5(2)
P(2)	0.435 9(3)	0.250 8(1)	0.744 8(2)
C(1)	0.359 2(8)	0.105 6(4)	0.667 2(5)
C(2)	0.474 8(8)	0.054 3(4)	0.699 4(5)
C(3)	0.529 4(7)	0.013 4(3)	0.635 5(5)
C(4)	0.471 1(7)	0.022 3(4)	0.533 6(5)
C(5)	0.357 4(9)	0.074 6(4)	0.502 6(5)
C(6)	0.300 4(8)	0.115 5(4)	0.565 9(5)
C(7)	0.138 5(10)	−0.015 0(5)	0.695 5(7)
C(8)	0.028 1(11)	−0.074 3(5)	0.694 8(9)
C(9)	−0.078 0(10)	0.100 3(6)	0.698 9(9)
C(10)	−0.117 6(13)	0.120 5(7)	0.591 1(9)
C(11)	0.119 0(14)	0.042 7(5)	0.877 1(7)
C(12)	0.278(2)	0.018 1(7)	0.941 3(8)
C(13)	0.544 3(12)	0.245 6(5)	0.656 0(7)
C(14)	0.659(2)	0.306 9(8)	0.658 1(11)
C(15)	0.331(2)	0.338 5(5)	0.716 3(9)
C(16)	0.193(3)	0.334 3(8)	0.627 4(10)
C(17)	0.579(2)	0.268 2(8)	0.862 7(10)
C(18)	0.694(2)	0.209 2(11)	0.891 1(10)

of a pale brown solid. After reaction for 72 h, GC analysis of the solution showed formation of toluene (2.8 mg, 15%) and biphenyl (12 mg, 78% based on the phenyl ligand in **5**). Reactions with complexes **1**, **2** and **4** were carried out analogously.

Acknowledgements

The authors are grateful to Drs. Yoshiyuki Nakamura and Masako Tanaka for their help in the NMR measurement and the crystallographic study, respectively. This work was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan. Y.-J. K. thanks the Department of Chemistry, Kangnung National University, Kangnung, Kangwondo, Korea for leave.

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Received 23rd September 1993; *Paper* 3/05753D