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NICKEL-COMPLEX-CATALYZED CROSS-COUPLING OF GRIGNARD REAGENTS WITH 2-HALOGENOBENZOTHIAZOLES

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Abstract—2-Halogenobenzothiazoles undergo C–C cross-coupling reaction with Grignard reagents in the presence of Ni(II)–phosphine complexes. The reaction is considerably influenced by the nature of the phosphine bonded to Ni(II) and the halogen in the halogenobenzothiazole. Particularly efficient catalysts are 2-chlorobenzothiazole coordinated nickel-complexes, $NiBr_2(H_2O)(2\text{-}Cl\text{-}BT)$, $NiBr_2(2\text{-}Cl\text{-}BT)PMe_3$, $NiBr_2(2\text{-}Cl\text{-}BT)PCy_3$ and complex $NiBr_2(DMSO)PMe_3$, which all are here reported for the first time. A possible mechanism for the catalytic activity exhibited by the nickel-complexes in the C–C cross-coupling of 2-halogenobenzothiazoles with Grignards is also reported.

The cross-coupling reaction of organometallics with organic halides is now well recognised to be one of the most efficient methods for the C–C bond formation. Many organometallics have been tested to this end and among them the Ni–phosphine complex activated-Grignard reagents have been found to be particularly useful in synthesis.

The cross-coupling reaction of alkenyl, allyl or aryl halides[1-4] with a variety of such a type of Grignard reagents has been quite deeply investigated but little attention has so far been paid to heterocyclic halides.[5a-d] Specifically, cross-coupling of 2-halogenobenzothiazoles and Grignard reagents has not been investigated at all.

We have recently reported[6] that 2-halogenobenzothiazoles react with lithium dialkyl and diaryl cuprates giving substantially metal halogen exchange. Pursuing our interest in the mechanistic and synthetic aspects of heteroaromatics with organometallics,[6,7] we have undertaken a study of the reaction between 2-halogenobenzothiazoles and Grignard reagents activated by Ni-phosphine complexes.

RESULTS AND DISCUSSION

Reaction of 2-halogenobenzothiazoles and Grignard reagents. We have investigated the reaction of 2-X-benzothiazoles (2-X-BT, X = F, Cl, I) with MeMgI in diethyl ether at room temperature (~ 25°). 2-Fluoro- and 2-chloro-benzothiazole turned out to be unreactive and were recovered practically unchanged even after long reaction times. In contrast, 2-iodobenzothiazole reacted rapidly with MeMgI leading to the reduction product, i.e. the unsubstituted benzothiazole, in high yield, as in the case of the reaction with dialkyl and diaryl lithium cuprates.[6] Dehalogenation also occurred with other Grignard reagents.

Reaction of 2-halogenobenzothiazoles with activated Grignard reagents. The behavior of 2-X-benzothiazoles (X = F, Cl, I) with a number of Grignard reagents in the presence of Ni–phosphine complexes [$NiCl_2(PPh_3)_2$, $NiCl_2(PPh_2Et)_2$, $NiCl_2(PPhEt_2)_2$, $NiCl_2(PEt_3)_2$, $NiCl_2dppe$ (dppee = $Ph_2PCH_2CH_2PPh_2$) and $NiCl_2dppp$ (dppp = $Ph_2PCH_2CH_2CH_2PPh_2$)] has been investigated. Thus, 2-fluoro- and 2-chloro-benzothiazole have been found to react with both alkyl or aryl Grignards in the presence of catalytic amount (about 3% mole) of Ni(II)) complexes in diethyl ether or THF or benzene providing, in all cases, 2-alkyl- and 2-aryl-benzothiazole respectively, in satisfactory yields (Table 1). Under similar conditions, the catalytic activity of the Ni(II) complexes turned out to be markedly dependent upon the nature of the phosphorous ligands, thus clearly indicating that catalytically active species contain ligand(s) on Ni. Moreover, when bidentate phosphines are coordinated to Ni(II) the catalyst exhibits much lower activity than when unidentate phosphines are used as ligands. This trend is just opposite the order of catalytic activity reported for Ni(II) phosphine complexes in the reaction of aryl and alkenyl halides with Grignard reagents.[2] As for unidentate phosphine complexes, all the complexes we used were active in promoting the cross-coupling and the less basic the phosphine the more efficient the catalyst. In contrast, in the reaction of aromatic halides with Grignard reagents it has been reported that only $NiCl_2(PPh_3)_2$ was an efficient catalyst.[2] Of the bidentate phosphine complexes, $NiCl_2(dppp)$ showed a catalytic activity higher than $NiCl_2(dppe)$, according to the Kumada's[2] suggestion that catalytic activity depends on the length of methylene bridge between the two diphenyl–phosphino groups.

2-Fluorobenzothiazole has been found to be very prone to undergo cross-coupling reaction with activated Grignard reagents and to be twice more reactive than 2-chloroderivative (as proved by a competitive reaction). This result contrasts with the reactivity order of the organic halides ($Cl \gg F$)[2] in the cross-coupling process with organometallics. It is noteworthy to emphasize the remarkable reactivity of

Table 1. Reaction of 2-X-benzothiazoles (1 mole) with Grignard reagents (2 mole) in THF at RT

2-X-BT	RMgX	Catalyst	Reaction product (%)[c]	Reduction product %[c]	Reaction time
2-F-BT	MeMgI	-	-	-	16h[d]
"	"	NiCl$_2$(PPh$_3$)$_2$[a]	2-Me-BT(75)	-	10'
"	"	NiCl$_2$(dppe)	" (74)	-	3h
2-Cl-BT	"	-	-	-	16h[d]
"	"	NiCl$_2$(PEt$_3$)$_2$	" (71)	-	1h30'
"	"	NiCl$_2$(PEt$_2$Ph)$_2$	" (68)	-	44'
"	"	NiCl$_2$(PEtPh$_2$)$_2$	" (76)	-	22'
"	"	NiCl$_2$(PPh$_3$)$_2$	" (75)	-	20'
"	"	NiCl$_2$(dppe)	" (61)	-	9h
"	"	NiCl$_2$(dppp)	" (62)	-	1h45'
"	EtMgBr	NiCl$_2$(PPh$_3$)$_2$	2-Et-BT(60)	-	1h
"	*n*-BuMgBr	"	2-*n*-Bu-BT(50)	-	1h30'
"	*i*-PrMgBr	"	2-*i*-Pr-BT(40)	-	9h
"	PhMgBr	"	2-Ph-BT(70)	-	2h
2-I-BT	MeMgI	-	-	80	10'
"	"	NiCl$_2$(PPh$_3$)$_2$	-	70	15'
"	"	"[b]	2-Me-BT(50)	-	15'
2-Cl-BT	"	NiBr$_2$(DMSO)PMe$_3$[e]	2-Me-BT(>95)	-	10'
"	*i*-PrMgBr	"	2-*i*-Pr-BT(>95)	-	3h
"	MeMgI	NiBr$_2$(DMSO)PCy$_3$[e]	2-Me-BT(85)	-	1h
"	*i*-PrMgBr	"	2-*i*-Pr-BT(25)[f]	-	3h

[a] Unless indicated molar ratio of catalyst/RMgX was 0.03. [b] The catalyst was present in stoichiometric amount with respect to RMgX. [c] Yields are for isolated products. [d] Reaction carried out at reflux. [e] The catalyst was present in a molar ratio 0.02 with respect to 2-Cl-BT. [f] The yield in 2-*i*-Pr-BT did not increase at longer reaction times.

2-fluorobenzothiazole in view of the extremely low reactivity commonly reported for organofluoro compounds in the organometallic induced cross-coupling.[7,8]

A quite different behavior has been shown by 2-iodobenzothiazole which yet afforded the reduction product when treated with MeMgI in the presence of catalytic (3%) or substoichiometric amount of $NiCl_2(PPh_3)_2$. Good yield of the cross-coupled product, i.e. 2-methylbenzothiazole, could be obtained only by using at least equimolecular amounts of catalyst and Grignard reagent.

The formation of the reduction product in the reaction of 2-iodobenzothiazole with Grignard reagents as such or activated with catalytic amount of the Ni-complex, might reasonably be accounted for by assuming nucleophilic attack of the organometallic reagent, which is present in large excess with respect to the catalyst, on the halogen,[9] followed by the release of the benzothiazole moiety as anion, the protonation of which would lead to the benzothiazole.

Reaction of 2-chlorobenzothiazole and MeMgI activated by $NiCl_2(PPh_3)_2$ proceeded faster than those with EtMgBr, n-BuMgBr and i-PrMgBr in the order. Besides, particularly low was the yield of the cross-coupled product in the case of i-PrMgBr; this result was not completely unexpected, since β-elimination in alkyl Grignard reagents has previously been reported using $NiCl_2(PPh_3)_2$ as catalyst.[5b,6]

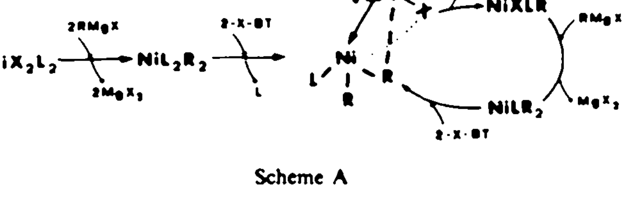
Reactions tend to proceed considerably faster in diethyl ether and benzene than in THF. That a more basic solvent (THF > ether, benzene) interacts more tightly with the reactants to prevent the Ni(II)-complex, the halide and the Grignard reagent to come close to each other so that the reaction can take place, might be a likely explanation.

The foregoing results allow us to propose for the cross-coupling reaction of 2-halogenbenzothiazoles with Ni-phosphine-complex activated Grignard reagents a mechanism of the kind illustrated in the Scheme A. According to this mechanism the complex $NiR_2L(2\text{-}X\text{-}BT)$, derived from NiL_2R_2 by replacement of ligand L with 2-X-BT, would represent the catalytically active species, which leads to the cross-coupled product 2-R BT upon release of the complex NiLXR. Subsequent reaction of the last complex first with RMgX and then with 2-X-BT would regenerate the catalyst. This mechanism is consistent, in our view, with the observed reactivity order of 2-halogenobenzothiazoles (F > Cl > I) in the cross-coupling with Grignards. Indeed, 2-F-BT reacts faster possibly because it would better coordinate on the Ni as a consequence of the smaller volume and higher affinity of fluorine for the metal with respect to other halogens.[10] Moreover, that metal complexes with unidentate phosphines are better catalysts than those with the bidentate ones might tentatively be explained by assuming that replacement of L by 2-X-BT on the Ni complex is a process more difficult with bidentate phosphine because of the higher stability of the ring system $\overline{Ni\text{-}P\text{-}P}$ with respect to NiP_2. In addition this explanation is in agreement with the relation activity-length of methylene bridge. $NiCl_2(dppe)$ has been found to be less efficient than $NiCl_2(dppp)$ in promoting cross-coupling of 2-halogenobenzothiazoles presumably due to the fact that the 5-membered ring $Ni\text{-}PCH_2CH_2P$ opens less easily than 6-membered ring $\overline{Ni\ PCH_2CH_2CH_2P}$.[11] As for unidentate phosphine-complexes, the effect of the basicity of the phosphine is appreciable. The catalytic activity is in the order: $NiCl_2(PPh_3))_2 > NiCl_2(PPh_2Et)_2 > NiCl_2(PPhEt_2)_2 > NiCl_2(PEt_3)_2$. This trend can be rationalized by assuming that the ease of replacement of the ligand phosphine in NiL_2R_2 by 2-X-BT to form the catalytically active species $NiLR_2(2\text{-}X\text{-}BT)$parallels the order of decreasing basicity.

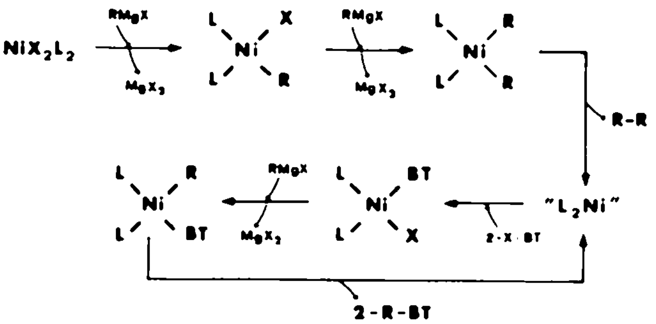
As alternative, one could propose a catalytic cycle of the type depicted in Scheme B, in which a Ni(O) complex is involved as the catalytically active species, the interaction of which with 2-X-BT would lead to the complex NiL_2BTX. Subsequent reaction with RMgX would provide complex $NiL_2(BT)R$; then the release of the cross-coupled product 2-R-BT regenerates Ni(O) complex NiL_2. However, although the addition of 2-X BT to Ni(O) has been established,[12] this is a process much slower than that experimentally observed for the cross-coupling reaction. Moreover, according to Scheme B, the nature of the bonded phosphine would not sensibly affect the reaction rate, as instead by us observed.

In order to ascertain if coordination of 2-X BT to Ni is essential for the C C cross-coupling process of 2-halobenzothiazoles and whether or not the coordinative unsaturation of Ni plays an important role in the catalytic cycle and with a view to evidentiate the role of the phosphorous ligand, we have synthesized Ni(II)-complexes having: (i) 2-halogenobenzothiazole as ligand; (ii) only one phosphine coordinated to Ni.

Although 2-X-benzothiazoles ($X = NH_2$, Me) bind strongly to Ni(II) and other transition metals,[13] 2-halogenobenzothiazoles do not coordinate easily to Ni(II).[14] Indeed, we have found that neither $NiCl_2$ or $NiCl_2 \cdot 2H_2O$ react with 2-X-benzothiazoles (X = Cl, Br, I) even under rather severe conditions ($NiCl_2$ and 2-X BT did not react at 120° in a Carius tube in the absence of solvent for X = Cl, Br or in xylene for X = I). Conversely, $NiBr_2 \cdot 2H_2O$ reacts with



Scheme A



Scheme B

2-Cl benzothiazole in boiling acetone to give the yellow diamagnetic, square planar complex NiBr$_2$(H$_2$O)(2-Cl-BT) I, which is the second neutral complex of 2-halogenobenzothiazole coordinated to Ni(II) to be described. We have checked the effect of complex I in the cross-coupling reaction of 2-Cl-BT with Grignards either in the absence or in the presence of phosphines. As shown in Fig. 1, complex I catalyzes the cross-coupling reaction of 2-Cl-BT and MeMgI. 50% Conversion of 2-Me-BT occurs after about 1 hr. Addition of PMe$_3$ clearly enhances the catalytic activity of the complex I, the best results being obtained when P/Ni (phosphine/Ni) ratio is close to 1. Under these conditions the conversion of 2-Cl-BT into 2-Me-BT is > 90% in a 10 min time. At higher P/Ni ratios a decrease of the catalyzing ability is observed; for P/Ni = 100 the complex becomes nearly inactive. The dependence of the catalytic activity on the added phosphine is also illustrated in Fig. 2, where the % conversion at a given time (10 min) is diagrammed against the P/Ni ratio.

The evidence that the catalyst exhibits its best catalytic activity at a P/Ni = 1 ratio seems to indicate that actually the coordination of 2-X-BT to Ni is a relevant step in the cross-coupling process† and that the coordination of the phosphine is an important factor too. In order to further support this idea we have synthesized a complex of formula NiBr$_2$(L)(PMe$_3$) where L is a ligand (not a phosphorous ligand) that could be replaced by 2-Cl-BT. Thus, we have prepared the complex NiBr$_2$(DMSO)(PMe$_3$) II, that, as expected, reacts with an excess of 2-Cl-BT to afford the complex NiBr$_2$(2-Cl-BT)(PMe$_3$) III.‡ The last complex has been found to be an active catalyst for the C–C coupling reaction of 2-Cl-BT with MeMgI. Under these conditions 2-Me-BT forms in almost quantitative yield.[15] The activity is higher than that of the

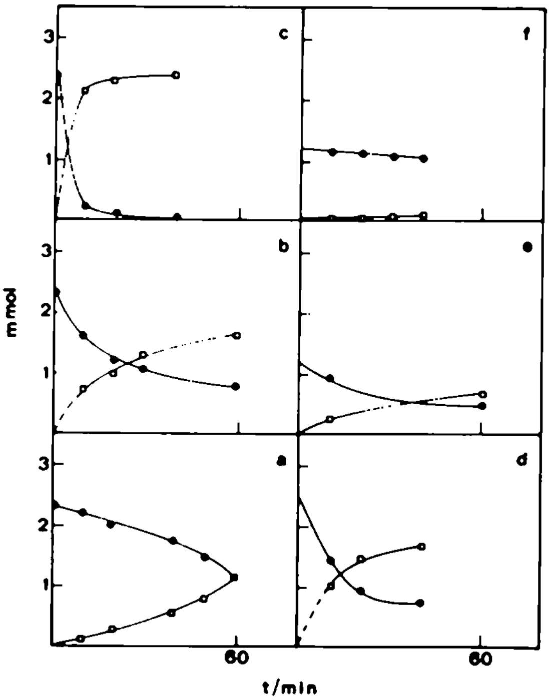


Fig. 1. Conversion of 2-Cl-BT (○) to 2-Me-BT (□) in the presence of: (a) 2% NiBr$_2$(H$_2$O)(2-Cl-BT); (b) 2% NiBr$_2$(H$_2$O)(2-Cl-BT) + PMe$_3$ (P/Ni = 0.07); (c) as in (b) but with P/Ni = 1; (d) as in (b) with P/Ni = 2; (e) as in (b) with P/Ni = 4; (f) as in (b) with P/Ni = 100.

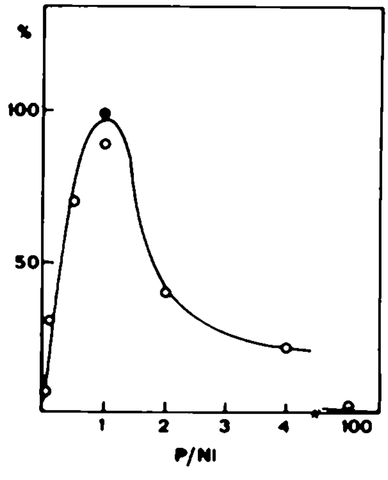


Fig. 2. % Conversion of 2-Cl-BT into 2-Me-BT in the presence of NiBr$_2$(H$_2$O)(2-Cl-BT) and PMe$_3$ in dependence of the PMe$_3$/Ni ratio. ⊙ represents the catalytic activity of the complex NiBr$_2$(DMSO)(PMe$_3$) in the presence of 2-Cl-BT in excess. The evaluation of the conversion was performed 10 min after mixing the reagents.

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†It is worth mentioning that coordination of the benzothiazole moiety on Ni can occur either by the double bond (N C) or by the N atom.[14a] Moreover, coordination on the metal by means of the sulfur atom must not be ruled out, since are known complexes which coordinate on the metal via S rather than via N.[14b]

‡Complex III could not be isolated very pure.

catalytic system obtained by using I and PMe_3 in a 1:1 molar ratio (Fig. 2). The different activity can be explained by assuming that less than 100% of the complex I is converted into III by treating I with PMe_3.†

Complex I promoted cross-coupling also in the reaction of 2-Cl BT and i-PrMgBr and yet the addition of the phosphine PMe_3 caused a change of the catalytic activity, the trend being analogous to that encountered in the reaction with MeMgI. The best catalytic activity was shown at a molar ratio P/Ni close to 1. Also in this case the preformed Ni–PMe_3 catalyst III was more active than that formed *in situ* from I and PMe_3. Also these data seem to suggest that coordination of 2-Cl–BT to Ni plays an important role in the synthesis of 2-R–BT from 2-Cl BT and Grignard reagents.

It is worth noting at this point that catalysts of the kind I + PMe_3 (P/Ni = 1) or III present an activity considerably higher than that exhibited by complexes of formula $NiX_2L_2(L = PR_3)$ (see Table 1) in the C–C coupling reaction of 2-Cl–BT and this becomes particularly relevant with sterically hindered alkyl Grignard reagents. This can be ascribed, according to Scheme A, to an easier interaction of 2-Cl–BT and i-PrMgBr with the Ni–phosphine complex having only one phosphorous ligand bonded to Ni with respect to complexes bearing two of such phosphino groups. The importance of the steric factors is also supported by the results obtained using the catalyst $NiBr_2(DMSO)(PCy_3)$ [PCy_3 = tricyclohexylphosphine] in the coupling reaction of 2-Cl–BT with i-PrMgBr. As shown in Fig. 3, replacement of PMe_3 (cone angle ~ 130°) with the bulky PCy_3 ligand (cone angle ~ 180°)[16] causes a noticeable decrease of the catalytic activity of Ni. In our opinion, such a decrease must be ascribed very likely to a steric effect as the basicity of PMe_3 is very close to that of PCy_3.

Conclusively, Ni(II)–phosphine complexes of formula NiX_2L_2 [L = PEt_3, PEt_2Ph, $PEtPh_2$, PPh_3; $L_2 = Ph_2PCH_2CH_2PPh_2$(dppe), $Ph_2PCH_2CH_2$–CH_2PPh_2(dppp)] are active catalysts in the C–C coupling reaction of 2-halogenobenzothiazoles and Grignard reagents. The unusual order of reactivity observed for C–C heterocoupling of 2-X–BT (F > Cl > I) can be explained taking into account, according to the proposed mechanism (Scheme A), the coordination of 2-X–BT to Ni(II) with displacement of one of the phosphorous ligands. Complexes having only one monodentate phosphorous ligand coordinated to Ni, such as I + PMe_3, II, III are catalysts more active than complexes having two phosphines bonded to Ni. Moreover, complexes having bidentate phosphorous ligands are less active than those having monodentate ligands and, among the bidentate ligands, the longer the methylene bridge between the P donor-atoms the higher the catalytic activity. This is still in agreement with a dissociative mechanism that envisages the replacement of one phosphorous ligand with 2-X–BT as a fundamental step in the cross-coupling reaction. Complexes of Ni(II) having 2-Cl–BT as ligand act as catalysts also in the absence of phosphines but the activity is not too high. Addition of phosphines up to a P/Ni = 1 ratio enhances the activity of the catalyst. The phosphines, therefore, seem to be indispensable in order to stabilize the alkyl complexes of Ni that, reasonably, are intermediates in the C–C cross-coupling process.

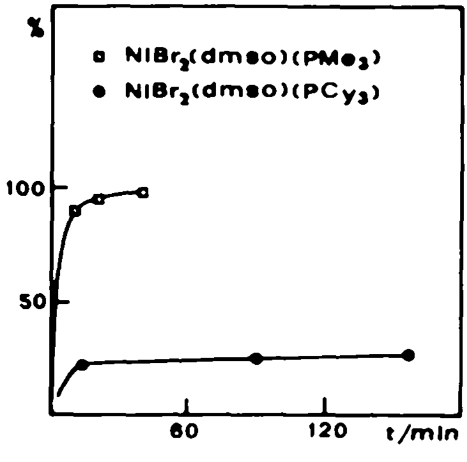

Fig. 3. % Conversion of 2-Cl–BT into 2-i-Pr–BT evaluated at different times. Both complexes were present in a 2% mole ratio with respect to 2-Cl–BT.

Finally, we wish to stress that our procedure to 2-alkyl-, 2-aryl-benzothiazoles from commercially available 2-halogenobenzothiazoles is more convenient than that, recently reported by Takei,[17] starting from 2-thioalkoxybenzothiazoles, which are usually made from 2-halogenobenzothiazoles.[18]

EXPERIMENTAL

^{1}HNMR spectra were recorded on a Varian EM 360A spectrometer in $CDCl_3$ and chemical shifts are reported in ppm (δ) from internal Me_4Si. Microanalyses, performed on a Hewlett-Packard C,H,N analyser, were in satisfactory agreement with the calculated values ($\pm$ 0.3%). GC data obtained on a Hewlett-Packard 5700A chromatograph. M.ps, taken on electrothermal apparatus, were uncorrected.

Materials. Diethyl ether, THF and benzene from commercial sources (RS Carlo Erba) were purified by distillation (twice) from Na wire under N_2. 2-Chlorobenzothiazole was a good commercial quality product, further purified by distillation. 2-Fluoro-,[19] 2-bromo-,[20] and 2-iodobenzothiazole[19] were prepared according to the reported procedures. Grignard reagents were made following the reported procedure.[21] Phosphine–Ni(II) complexes were prepared by known methods. In the following list, the refs given after the compounds are to the method of preparation: $NiCl_2(PPh_3)_2$,[22] $NiCl_2(PEt_3)_2$,[23] $NiCl_2(PPhEt_2)_2$,[24] $NiCl_2(PPh_2Et)_2$,[24] $NiCl_2$(dppe),[25] $NiCl_2$(dppp).[25]

*Dibromo-bis(dimethylsulphoxide)*Ni(II), $NiBr_2(DMSO)_2$. 5.0 g of $NiBr_2$ were suspended in DMSO (100 mL) and the slurry heated to obtain a green soln. Upon cooling to room temp and addition of benzene (50 mL) green crystals separated, which were filtered by vacuum-line technique, washed with benzene and dried *in vacuo* at room temp, yield 90%. M.p.: 83° (dec with loss of DMSO). IR: (Nujol) bands at 1030(vs, br), 955(vs, br), 455(vs, br) cm^{-1} assigned to the coordinated DMSO. (Found: Br, 18.38; Ni, 6.90. Calc for $C_{16}H_{48}Br_2NiO_8S_8$: Br, 18.48; Ni, 6.88%).

4.00 g of $NiBr_2(DMSO)_8$, prepared as above, were heated *in vacuo* with stirring in a round bottomed flask in a oil bath and the DMSO liberated was trapped at 10°. The light blue compound obtained shows in its IR spectrum bands at 1050(s), 1040(s), 1020(s), 1000(s), 950(s), 455(s, br) cm^{-1} due to the coordinated DMSO, m.p.: loses DMSO from 140° *in vacuo*. (Found: Br, 23.03; Ni, 8.77. Calc for $C_{12}H_{36}Br_2NiO_6S_6$: Br, 23.3; Ni, 8.5%).

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†The reaction of $NiBr_2(H_2O)(2\text{-Cl-BT})$ with PMe_3 afforded III which was contaminated by $NiBr_2(PMe_3)_2$.

3.00 g of $NiBr_2(DMSO)_6$ were heated *in vacuo* with stirring in a flask at 150° in an oil bath for 10 h until a pink salmon compound was obtained, m.p.: the complex loses DMSO from 245° *in vacuo*. IR (Nujol): bands at 1230(s, sharp), 1210(m, sharp), 1045(s, sharp), 940(s), 730(m), 480(s, br) cm^{-1} attributed to the coordinated DMSO. (Found: Br, 43.0; Ni, 15.60. Calc for $C_4H_{12}Br_2NiO_2S_2$: Br, 42.96; Ni, 15.50%).

*Aquo - dibromo - (2 - chlorobenzothiazole)*Ni(II), $NiBr_2(H_2O)$ (2-Cl–BT). 2.5 g of $NiBr_2 2H_2O$ (9.8 mmole) were suspended in acetone (40 mL) in a 10 mL flask with stirring and 2.73 mL of 2-Cl–BT (20.8 mmole) added. The suspension was heated at reflux for 90 min and the resulting green soln, upon cooling to room temp, deposited a yellow solid which was filtered off, washed with benzene and dried *in vacuo*, yield 25%, m.p.: loses 2-Cl–BT from 138° *in vacuo*. IR (Nujol): bands at 3460(s, br, H_2O), 3320(s, br, H_2O), 1610(s, br, H_2O), 1312(m, sharp), 1242(m), 1082(m), 1025(m), 1012(s), 982(s), 780(m), 742(m), 665(s, br, H_2O), 460(m) cm^{-1}. (Found: Br, 40.6; Cl, 8.8; Ni, 15.0. Calc for $C_7H_6Br_2ClNNiOS$: Br, 39.41; Cl, 8.74; Ni, 14.5%).

Dibromo - dimethylsulphoxide - trimethylphosphine - Ni(II), $NiBr_2(DMSO)(PMe_3)$. To 0.25 g of $NiBr_2(DMSO)_2$ (0.67 mmole) dissolved in MeCN (60 mL), PMe_3 (0.050 mL, 0.66 mmole) in toluene (10 mL) was added and the soln stirred for 7 hr. The blue resulting soln was concentrated *in vacuo* to 10 mL and, upon addition of toluene, deposited a brown product which was filtered off and discharged. To the blue toluene soln pentane was added and, upon cooling to −30°, nice blue needles were formed which were filtered *in vacuo*, washed with pentane and dried *in vacuo*, yield 50%. IR (Nujol): bands at 1290(m, PCH_3), 1280(s, PCH_3), 1270(s, PCH_3), 1150(m, PCH_3), 1060(s, DMSO), 1010 (s, DMSO), 960(s, DMSO), 820(s, PCH_3), 730(s, DMSO), 720(s, PCH_3), 700(m, PCH_3), 670(m, PCH_3), 450(s, DMSO), 250(s, $NiBr_2$) cm^{-1}. Magnetic moment: 3.3 BM, m.p.: in the range 147–157° with dec *in vacuo*. (Found: Br, 35.63; Ni, 12.47; P, 6.75. Calc for $C_{12}H_{21}Br_2NiO_2PS_2$: Br, 35.47; Ni, 13.02; P, 6.87%).

Reaction of 2-halogenobenzothiazoles and Grignard reagents activated by $NiCl_2L_2$ *complexes* (L = PPh_3, PPh_2Et, $PPhEt_2$, PEt_3, L_2 = dppe, dppp)

Since the procedure used was the same for all the 2-alkyl (aryl) benzothiazoles prepared, only a general procedure will be given. Structures were established by elemental analyses, IR, ^{1}HNMR and comparison with authentic specimen obtained through other reported procedures.

A 50 mL 3-necked flask containing a stirring bar was fitted with N_2 inlet and outlet tubes and then was heated and swept with N_2. After the apparatus cooled, 200 mg (1.18 mmole) 2-chlorobenzothiazole and 49 mg (0.07 mmole) $NiCl_2(PPh_3)_2$ were added along with 20 mL dry ether. Then, MeMgI (2.37 mmole) was added drop by drop under N_2 and the mixture stirred at ambient temp until TLC or GC revealed the complete disappearance of the starting 2-chlorobenzothiazole. The mixture was then poured into 50 mL NH_4Cl aq, the organic layer removed and the aqueous layer extracted several times with ether. The combined and dried (Na_2SO_4) ether layers were concentrated to an oil that was identified as 2-methylbenzothiazole:[26] ^{1}HNMR δ 2.7(s, 3H), 7.1–8.0(m, 4H).

2-*Ethylbenzothiazole*[26] was prepared according to the procedure described above: oil, ^{1}HNMR δ 1.5(t, 3H), 3.1(q, 2H), 7.1–8.0(m, 4H).

2-*i-Propylbenzothiazole*[26] was prepared as described above: oil, ^{1}HNMR δ 1.4(d, 6H), 3.0–3.6(m, 1H), 7.10–7.90(m, 4H).

2-*n-Butylbenzothiazole*[26] was prepared as described above: oil, ^{1}HNMR δ 0.7–2.2(m, 7H), 3.1(t, 2H), 7.1–8.0(m, 4H).

2-*Phenylbenzothiazole*[26] was prepared as described above: m.p. 113–114°; undepressed mixed m.p. with an authentic specimen.

Evaluation of the catalytic activity of the complexes $NiBr_2LL'$ (L = H_2O, DMSO, L′ = PMe_3, 2-Cl–BT, PCy_3)

The following procedure was used for evaluating the catalytic activity of the complexes in the C–C coupling reaction of 2-Cl–BT with RMgX (R = Me, i-Pr). All the reactions were carried out under dry oxygen free N_2 using the vacuum-line technique. The catalyst was used in a 2% molar ratio and the Grignard in a molar ratio equal to 2 with respect to 2-Cl–BT. Complexes were handled out of the contact with air and moisture and stored under N_2:

(a) *Use of* $NiBr_2(H_2O)(2\text{-}Cl\text{–}BT)$ *as catalyst*. The complex was suspended in dry diethyl ether (20 mL) and 2-Cl–BT and the Grignard were added in the order. The soln was stirred and analyses performed as reported below (d).

(b) *Use of* $NiBr_2(H_2O)(2\text{-}Cl\text{–}BT)$ *in the presence of* PMe_3 *or* PCy_3. To a suspension of $NiBr_2(H_2O)(2\text{-}Cl\text{–}BT)$ in ether the phosphine in ether (the required amount of a 10^{-3} M solution) or neat PMe_3 (in the case of P/Ni molar ratio equal 100) was added and the solution stirred for 15 min. 2-Cl–BT and the Grignard were added in the order and the soln worked up as reported below (d).

(c) *Use of* $NiBr_2(DMSO)(PMe_3)$ *or* $NiBr_2(DMSO)(PCy_3)$. To a soln of the complex in dry ether, 2-Cl–BT and, after 15 min stirring, the Grignard were added. The soln was treated as reported in (d).

(d) *Analysis of the solns.* 1.0 mL of the suspension was withdrawn at the given time (every 10 min for the first hour). The organic layer was separated and water extracted with three 1-mL each portions of ether. The organic layers were collected, dried over Na_2SO_4, separated from the exsiccant and diluted to 3 mL. This soln was analysed by gas chromatography using a 2 m 10% SP-2100 on 100/120 Supelcoport (Supelco) column. Standard solns of benzothiazole, 2-chloro-, 2-methyl- and 2-i-propyl-benzothiazole were used as control for quantitative analysis.

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REFERENCES

[1] For a review see: F. Naso and G. Marchese, Modern synthetic uses of organic halides: carbon–carbon bond formation involving transition metal compounds. In *The Chemistry of Functional Groups* (Edited by S. Patai). In press.

[2] K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato and M. Kumada, *Bull. Chem. Soc. Japan* **49**, 1958 (1976).

[3] H. Felkin and G. Swierczewski, *Tetrahedron Report* **31**, 2735 (1975).

[4] J. P. Collman and L. S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry* (Edited by A. Kelly), p. 566. University Science Books, Mill Valley, California (1980).

[5a] E. D. Thorsett and F. R. Stermitz, *J. Heterocyclic Chem.* **10**, 243 (1973); [b]L. N. Pridgen, *Ibid.* **12**, 443 (1975); [c]A. Ohsawa, Y. Abe and H. Igeta, *Chem. Pharm. Bull.* **26**, 2550 (1978); [d]A. Minato, K. Tamao, K. Suzuki and M. Kumada, *Tetrahedron Letters* 4017 (1980).

[6] F. Babudri, L. Di Nunno, S. Florio, G. Marchese and F. Naso, *J. Organometallic Chem.* **166**, 265 (1979).

[7] F. Ciminale, L. Di Nunno and S. Florio, *Tetrahedron Letters* 3001 (1980); F. Babudri, F. Ciminale, L. Di Nunno and S. Florio, *Tetrahedron* **38**, 557 (1982); F. Babudri, L. Di Nunno and S. Florio, *Ibid.* **38**, 3059 (1982).

[8] G. W. Parshall, *J. Am. Chem. Soc.* **96**, 2360 (1974).

[9] G. Bartoli, L. Di Nunno, M. Fiorentino, S. Florio and P. E. Todesco, *J. Chem. Soc.* Perk. II, 1371 (1976) and refs cited.

[10] For a rough comparison we cite the bond energies for Fe–F and Fe–Cl bonds, which are 91 and 50 Kcal/mole respectively. The same trend is observed for Ni–Cl, Ni–Br

and Ni–I bonds. *Bond Energies –Ionization Potentials and Electron Affinities* (Edited by V. I. Vedemeyev). Arnold, London (1966).

[11] This hypothesis is supported by the fact that 6-membered bidentate amine-Pt complexes open more easily than 5-membered ones. G. Annibale, L. Maresca, L. Cattalini and G. Natile, *J. Chem. Soc.* Dalton Trans, 1 (1982) and refs cited.

[12] P. J. Fraser, W. R. Roper and F. G. A. Stone, *Ibid.* Dalton Trans, 102 (1974).

[13a] M. J. M. Campbell, D. W. Card, R. Grzeskowiak and M. Goldstein, *Ibid.* (A), 672 (1970); [b]N. N. Y. Chan, M. Goodgame and M. J. Weeks, *Ibid.* (A), 2499 (1968); [c]P. Powell, *J. Organometallic Chem.* **65**, 89 (1974); [d]M. Aresta, F. Ciminale, *J. Chem. Soc.* Dalton Trans 1520 (1981); [e]N. Dash and R. D. Ramana, *Indian J. Chem.* **11**, 603 (1973).

[14] E. J. Duff, M. N. Hughes and K. J. Rutt, *Inorg. Chem. Acta* **6**, 408 (1972); *J. Chem. Soc.* (A), 2101 (1969).

[15] The reduction product (i.e. benzothiazole) forms only in less than 1% yield. Moroever, no halogen exchange between 2-Cl-BT, NiBr$_2$ and RMgX has been detected.

[16] C. A. Tolman, *J. Am. Chem. Soc.* **92**, 2956 (1970).

[17] H. Takei, M. Miura, H. Sagimura and H. Okamura, *Chem. Lett.* 1447 (1979).

[18] L. Di Nunno, S. Florio and P. E. Todesco, *Boll. Sci. Fac. Chim. Ind. Bologna* **27**, 75 (1969).

[19] P. E. Todesco and P. Vivarelli, *Ibid.* **22**, 16 (1964); *Gazz. Chim. Ital.* **94**, 435 (1964).

[20] Y. Mizuno, K. Adachi and K. Nakamura, *Pharm. Bull. Japan* **1**, 319 (1953).

[21] R. Quelet, P. Bercort and J. d'Angelo, *Bull. Soc. Chim. Fr* **10**, 3258 (1966).

[22] L. M. Venanzi, *J. Chem. Soc.* 719 (1958).

[23] K. A. Jensen, *Z. Anorg. Allg. Chem.* **229**, 265 (1936).

[24] R. G. Hayter and F. S. Humiec, *Inorg. Chem.* **4**, 1701 (1965).

[25] G. R. Van Hecke and W. DeW Horrocks Jr, *Ibid.* **5**, 1968 (1966).

[26] J. Metzger and H. Planck, *Bull. Soc. Chim. Fr* **6**, 1692 (1956).