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DECOMPOSITION OF [NiRR'L_2] COMPLEXES INDUCED BY BROMINE OR ANODIC OXIDATION

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Summary

A study has been made of the decomposition of the compounds t-[NiRR'L_2] (L = PMe_2Ph and PEt_3; R = aryl or vinyl groups) and [Ni(mes)(*o*-tol)bipy] (mes = mesityl) oxidatively induced either by electrochemical means or by bromine. No organometallic compound of Ni^{III} was isolated in the above reactions, but a pentacoordinate intermediate of Ni^{III} is postulated. Breakdown takes place readily after the Ni^{III} intermediate is formed. If the decomposition is induced electrochemically, the intermediate decomposes giving only the coupling product R–R'. When bromine is used as the oxidizing agent, the Ni^{III} intermediate is only formed if coordination to the central atom is allowed by the volume of the ligands. Thus, [$Ni(C_2Cl_3)(mes)(PMe_2Ph)_2$] does not decompose at all, and only [$Ni(C_2Cl_3)(mesBr_2)(PMe_2Ph)_2$] is obtained. The intermediate "$Ni^{III}RR'BrL_2$" undergoes reductive elimination to give R–R', RBr and R'Br. The formation of the products R–R' is increasingly favoured the greater the electronegativity of the organic ligands. The reductive elimination giving RBr takes place more readily the greater the electronegativity of the organic ligand R. The product of the reductive elimination reaction is "Ni^IBr", "Ni^IR", or "Ni^IR'", which in the presence of bromine give Ni^{2+}, [$NiBr(RBr)L_2$], phosphonium salts, RBr, and R'Br.

Introduction

Organometallic compounds of Ni^{III} with σ-metal–carbon bonds have been postulated frequently as intermediates in the mechanisms proposed for several types of reactions [1–3], but only a few compounds of this kind have been prepared, namely [$NiI_2R(PPh_3)_2$] (R = CF_3 or C_3F_7) [4] and [$NiBr_2R(PMe_2Ph)_2$] (R = C_2Cl_3 or C_6Cl_5) [5]. This oxidation state is rarely found for the other metals of the group. The formal platinum(III) state is found in bi- or poly-nuclear complexes containing Pt–Pt bonds. The first mononuclear complex [NBu_4][$Pt(C_6Cl_5)_4$] [6], obtained by oxidation of $(NBu_4)_2[Pt(C_6Cl_5)_4]$ solutions, has been very recently described.

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Diorganonickel(III) compounds are unknown but appear to be intermediates in the oxidatively induced decomposition of diorganonickel(II) complexes [7,8]. The decomposition of $[NiR_2L_2]$ complexes is readily induced by electrochemical or chemical oxidation, but, in accord with the different natures of the two oxidation process, the results may be different. When chemical oxidizing agents are used the products of the reaction also varies widely with the nature of the coordinated ligands and or the nature of the oxidant [9]; thus, n-bromosuccinimide (NBS) brominates the organic ligands in *trans*-$[Ni(C_2Cl_3)((2,6\text{-}MeO)_2C_6H_3)(PMe_2Ph)_2]$ without bringing about decomposition, whereas in most other cases total decomposition is observed [10].

We have examined the decomposition of *trans*-diorganonickel complexes and of [Ni(mes)(*o*-tol)bipy] (mes = mesityl, *o*-tol = *o*-tolyl), oxidatively induced by bromine or electrochemically.

Experimental

All oxidations were carried out under nitrogen but further manipulations were performed in the air. Proton and ^{31}P magnetic resonance spectra were recorded on a Varian XL200 NMR spectrometer with tetramethylsilane or H_3PO_4 as standards. The UV-VIS absorption spectra were recorded on a Beckman UV5230 spectrophotometer. A Hewlett–Packard 5710A gas chromatography with integrator 3390A was used for the analysis or aryl bromides and coupling products. Mass spectra were obtained with a Hewlett–Packard 5930 A instrument.

Materials. The organometallic compounds were made by published methods [11] and recrystallized before use. Commercial reagent grade solvents were purified by standard methods. Diethyl ether or THF were purified by distillation under nitrogen from sodium benzophenone. The aryl bromides were commercial reagents, and the coupling products R–R′ were obtained from electrochemical decomposition of the organometallic as described in this paper. When the pure R–R′ products were not available, the chromatographic quantitative factors were estimated; comparison of estimated and experimentally obtained quantitative factors, when this was possible, showed that the error introduced by using estimated values was lower than the overall experimental errors in the chromatography.

Electrochemical oxidation. Electrolytic oxidations were carried out under nitrogen on a potentiostat Amel 555A and a Coulometer Amel 721 at the working potentials given in Table 1. The three compartment cell included a platinum sheet electrode surrounded by a Pt spiral counterelectrode and a reference electrode of $Hg/Hg_2SO_4/sat.K_2SO_4$. The solvent was deoxygenated acetonitrile, and the supporting electrolyte was 0.05 *M* $LiClO_4$.

Action of bromine on the organometallics

A fresh solution of freshly recrystallized $[NiRR'L_2]$ (0.05 g) in ether (15 ml) was treated with 0.1 *M* Br_2 in ether in 1/2 or/and 1/4 molar ratio and the mixture was stirred at room temperature under nitrogen for 30 min. The solution was then treated with small portions of 5% Na_2CO_3 followed by 1% HCl. The aqueous and diethyl ether solutions were analyzed separatedly. A known amount of biphenyl was added to the ether solution and quantitative chromatographic analysis carried out. The products observed by chromatography were characterized either by using standards or by mass spectrometry. When the ^{31}P NMR spectra of these ether solutions showed the presence of an organometallic species, ethanol (5 ml) was added, the ether evaporated, and the resulting solution cooled to −20°C; this procedure gave the compound $[Ni(C_2Cl_3)(MsBr_2)(PMe_2Ph)_2]$. The aqueous solution was analyzed for free Ni^{II} gravimetrically with dimethyl glyoxime and the resulting nickel-free aqueous solution was used to test for the presence of the corresponding phosphonium salts and to determine their proportions by NMR spectroscopy. The phosphonium salt standards were obtained from the organometallics $[NiClRL_2]$ ($L = PMe_2Ph$ or PEt_3) by the method used by Tsou and Kochi [1]. $[Ni(C_2Cl_3)(MsBr_2)(PMe_2Ph)_2]$, m.p. 161–163°C, δ(P): −2.68 ppm, δ(H)(mes): 2.80 t (J(P–H) 1.5 Hz), 2.39, 2.42 ppm.

Analysis Found (calcd.): C, 43.4 (43.68); H, 4.5 (4.19); total X, 36.6 (35.89)%.

Results

All the $[NiRR'L_2]$ compounds were prepared from the organolithium derivative R'Li and $[NiXRL_2]$. The experimental details have been given previously [11].

The compounds $[NiR_2L_2]$ (L_2 = bipy, R = C_2Cl_3, 2,3-$Cl_2C_6H_3$) were obtained by symmetrization of $[NiClR(PPh_3)_2]$ induced by bipy [12]. $[Ni(C_2Cl_3)_2(PMe_2Ph)_2]$ was prepared by treatment of $[Ni(C_2Cl_3)_2bipy]$ with PMe_2Ph in refluxing benzene. The oxidations were carried out with freshly recrystallized products in order to achieve maximum reproducibility.

Electrochemical oxidation of the bisorganonickel complexes

About 0.1 g of the organometallic was suspended in acetonitrile and process was carried on until no current was passing at the constant potential used. The colourless solution was concentrated and treated with ether and dilute hydrochloric acid to remove the Ni^{II} formed. Only one decomposition product was found in the extracted ether solutions, and this was identified as the coupling product R–R' by gas chromatography and mass spectroscopy. (No polymeric materials were detected, in contrast to the results obtained of Almemark and Akermark [7] with $[Ni(mesityl)_2(PEt_3)_2]$. This difference may be due to the difference in the solvent used.)

The potentials used and the number of electrons exchanged per molecule are given in Table 1. The potentials at which decomposition takes place are 0.68 V (vs. SCE) for the anodic oxidation of $[Ni(aryl)_2(PEt_3)_2]$ in acetone (see ref. 8), and 0.47 V (vs. Ag^+/Ag) for the electrolytic decomposition of $[Ni(o\text{-tol})_2(PEt_3)_2]$ in acetronitrile (see ref. 7). In the present work higher potentials were used in order to ensure that the conversion $Ni^{II} \rightarrow Ni^{III}$ took place.

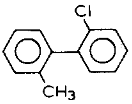
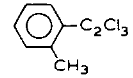
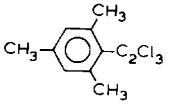
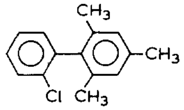
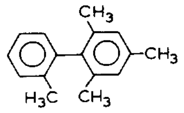
The number of electrons exchanged is higher than two which is the number corresponding to the simple process,

$$Ni^{II}RR' \xrightarrow{-e^-} Ni^{III}RR' \rightarrow Ni^{I} + R\text{–}R' \xrightarrow{-e^-} Ni^{II}$$

The fact that the bipy compound gives a value close to 2 Faradays exchanged per mole may indicate that the phosphine ligands are affected under these conditions, or that the Ni^{III} complex ($Ni^{I} \xrightarrow{-2e^-} Ni^{III}$) is better stabilized by phosphine ligands than by bipy. The process must be regarded as an intramolecular reductive elimination, since no coupling products RR or R'R' were observed.

TABLE 1

ANODIC OXIDATION OF [NiRR'L_2] COMPLEXES IN ACETONITRILE [a]

R	R'	L	*IP* (in V vs. SCE)	[Faraday mol^{-1} Ni]	Decomposition products
o-ClPh	*o*-tol	PEt_3	1.6	3	
C_2Cl_3	*o*-tol	PEt_3	1.4	3.1	
C_2Cl_3	mesityl	PMe_2Ph	1.3	2.8	
o-ClPh	mesityl	PMe_2Ph	1.4	2.4	
mesityl	*o*-tol	1/2 bipy	1.6 1.4	2.15 2.13	

[a] Ionic medium 0.05 *M* $LiClO_4$ in acetonitrile.

Almost no thermal decomposition was observed when the acetonitrile solutions of the organometallics were subjected to the conditions used for the electrolytic oxidation, and so the formation of the coupling products must be due to the presence of a Ni^{III} intermediate. The breakdown of the Ni^{III} species may be accounted for in terms of a mechanism proposed by Tsou and Kochi [8] in which a solvent molecule coordinates to the complex to give a pentacoordinate species, which subsequently gives the coupling product:

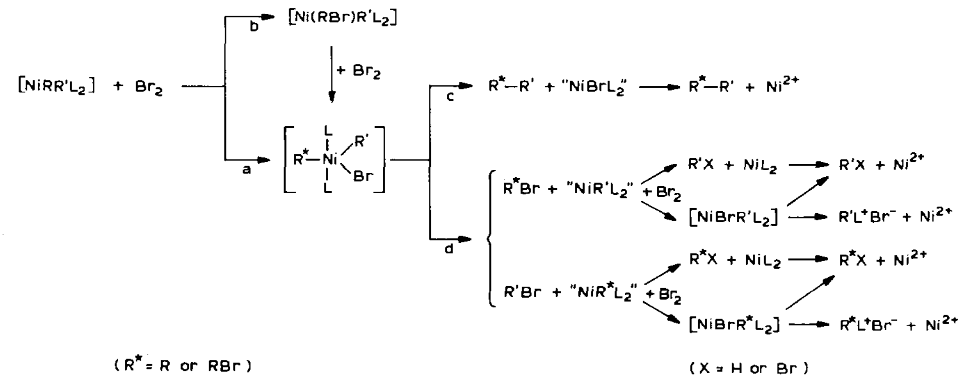
$$\textit{trans}\text{-}[NiRR'L_2] \rightarrow \textit{trans}\text{-}[NiRR'L_2]^+ + S \rightarrow [NiRR'(S)L_2]^+ \rightarrow R\text{-}R'$$

No differences were observed between the products from *cis*-[NiRR'bipy] and those from *trans*-[NiRR'L_2].

Reaction of the organonickel complexes with bromine

The reactions of [NiRR'L_2] with bromine were carried out by mixing ether solutions of both reagents with vigorous stirring. The whole of the bromine solution must be added at once to the solution of the freshly recrystallized organometallic compound. The complex and Br_2 were used in 1/2 and 1/4 mole ratio. The reaction was followed by the analysis of all the products containing R and R'. The products can be accounted for in terms of Scheme 1.

Products. The organometallic compounds react immediately. Some of them decompose completely and others partially (see Table 2 which gives the amount of free Ni^{II} recovered); [$Ni(C_2Cl_3)(mes)(PMe_2Ph)_2$] does not decompose at all. When complete decomposition occurs the solutions obtained are green and become clear



SCHEME 1

on washing with 1% HCl. When decomposition is not complete, the solutions remain orange-yellow even after several washings with HCl. In the case of [Ni(mes)R'(PMe_2Ph)$_2$] (R' = *o*-ClPh, *o*-tol) an organometallic compound formed, but not isolated, was assigned the formula [NiBr(mesBr)(PMe_2Ph)$_2$] on the basis of its ^{31}P and ^1H NMR spectra and of the replacement of Br^- by NCS^-. Proton spectrum was recorded in C_6D_6 after the removal of the ether, it showed three singlets in the methyl region (2.36, 2.49, 2.97 ppm) due to the three non-equivalent

TABLE 2

DECOMPOSITION OF [NiRR'L_2] COMPLEXES INDUCED BY BROMINE

Complex	[Ni]/Br_2 = 1/2			[Ni]/Br_2 = 1/4	
	%Dec. [a]	%R–R' [b]	%R–X [b]	%R–R' [b]	%R–X [b]
[Ni(C_2Cl_3)(*o*-tol)(PEt_3)$_2$]	90	65	35	–	–
[Ni(*o*-ClPh)(*o*-tol)(PEt_3)$_2$]	100	72	28	72	28
[Ni(*o*-tol)(Ph)(PEt_3)$_2$]	100	52	48	47	53
[Ni(*p*-tol)(*o*-tol)(PEt_3)$_2$]	100	56	44	51	49
[Ni(*o*-ClPh)(Ph)(PEt_3)$_2$]	100	74	26	–	–
[Ni(*o*-ClPh)(*p*-tol)(PEt_3)$_2$]	100	80	20	–	–
[Ni(*o*-tol)(mes)(PEt_3)$_2$]	95	95	5	–	–
[Ni(C_2Cl_3)(*o*-tol)(PMe_2Ph)$_2$]	90	75	25	–	–
[Ni(*o*-ClPh)(*o*-tol)(PMe_2Ph)$_2$]	100	77	23	60	40
[Ni(mes)(Ph)(PMe_2Ph)$_2$]	95	36	64	23	77
[Ni(mes)(*o*-tol)(PMe_2Ph)$_2$]	76 [c]	28	72	24	76
[Ni(*o*-ClPh)(mes)(PMe_2Ph)$_2$]	42 [c]	8	92	7	93
[Ni(C_2Cl_3)(mes)(PMe_2Ph)$_2$]	13 [d]	–	–	–	–
[Ni(mes)(*o*-tol)bipy]	100	50	50	46	54

[a] Wt-% of organometallic decomposed (calculated from Ni(DMG)$_2$ obtained from the aqueous solutions used for washing). [b] %R–R' = mole percentage of organometallic which decomposes to give R–R'; %R–X = mole percentage of organometallic which decomposes to give R–X (X = Br, H), as determined by chromatography with respect to the more abundant R–X (R'X). This term does not include amounts estimated as phosphonium salts (see text). The average values for a minimum of three experiments are given. [c] The [NiBr(mesBr)(PMe_2Ph)$_2$] was recovered. [d] The [Ni(C_2Cl_3)(mesBr_2)(PMe_2Ph)$_2$] was recovered.

TABLE 3

DECOMPOSITION PRODUCTS (%) DERIVED FROM R AND R′

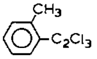
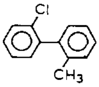
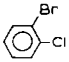
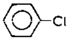
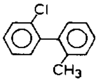
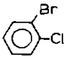
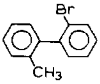
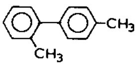
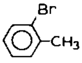
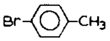
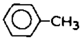
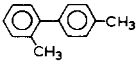
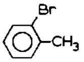
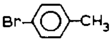
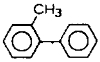
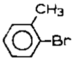
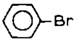
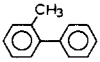
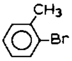
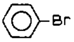
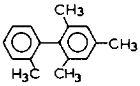
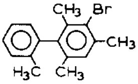
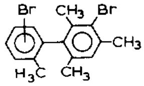
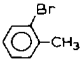
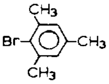
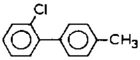
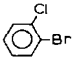
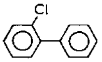
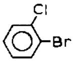
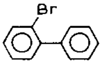
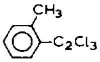
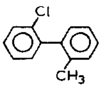
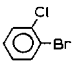
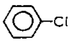
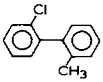
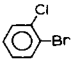
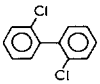
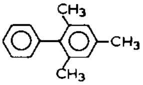
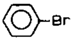
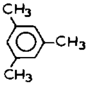
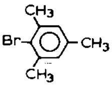
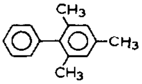
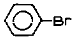
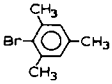
	[Ni]/Br_2	Decomposition products [a,b]		
[Ni(C_2Cl_3)(*o*-tol)(PEt_3)$_2$]	1/2	65 	35 BrC_2Cl_3	* (o-tol)PEt_3^+
	1/2	72 	11 	17 
[Ni(*o*-ClPh)(*o*-tol)(PEt_3)$_2$]	1/4	72 	28 	* 
	1/2	38 	51  + 	11 
[Ni(*o*-tol)(*p*-tol)(PEt_3)$_2$]	1/4	34 	66  + 	
[Ni(*o*-tol)(Ph)(PEt_3)$_2$]	1/2	52 	47 	1 
	1/4	45 	52 	3 
[Ni(mes)(*o*-tol)(PEt_3)$_2$]	1/2	44 	24 	22 
		5 	5 	
[Ni(*o*-ClPh)(*p*-tol)(PEt_3)$_2$]	1/2	80 	20 	
[Ni(*o*-ClPh)(Ph)(PEt_3)$_2$]	1/2	74 	26 	* 
[Ni(C_2Cl_3)(*o*-tol)(PMe_2Ph)$_2$]	1/2	75 	25 BrC_2Cl	
[Ni(*o*-ClPh)(*o*-tol)(PMe_2Ph)$_2$]	1/2	77 	20 	3 
	1/4	60 	40 	* 
[Ni(mes)(Ph)(PMe_2Ph)$_2$]	1/2	30 	53 	5  12 
	1/4	18 	61 	21 

TABLE 3 (continued)

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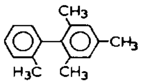
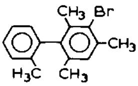
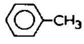
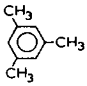
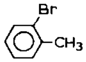
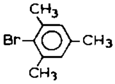
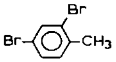
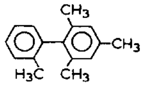
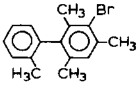
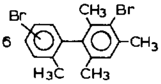
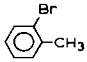
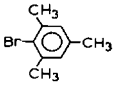
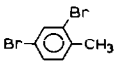
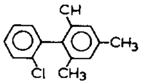
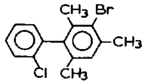
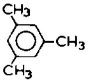
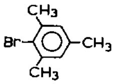
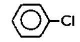
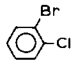
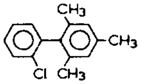
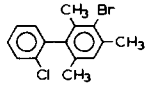
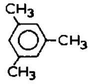
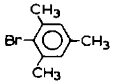
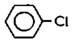
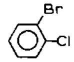
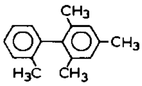
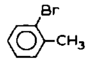
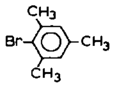
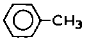
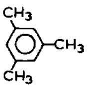
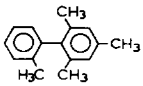
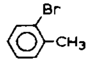
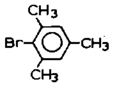
[Ni(mes)(*o*-tol)(PMe$_2$Ph)$_2$]	1/2	19  1  25  8 
		24  14  9 
	1/4	7  5  6 
		28  24  30 
[Ni(*o*-ClPh)(mes)(PMe$_2$Ph)$_2$]	1/2	5  2 
		6  6  55  26 
	1/4	3  3 
		1  11  43  39 
[Ni(mes)(*o*-tol)bipy]	1/2	35  32  30 
		3  5 
	1/4	30  35  35 

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[a] Molar percentage of the products derived from R and R′ which were identified by GLC. Average values for a minimum of three experiments. [b] Starred products detected in small amounts by mass spectrometry.

methyl groups of the bromomesitylene ligand, and another singlet in the aromatic region (6.45 ppm) corresponding to the remaining proton of that same ligand. Addition of bromine to the compound $[Ni(C_2Cl_3)(mes)(PMe_2Ph)_2]$ gave $[Ni(C_2Cl_3)(mesBr_2)(PMe_2Ph)_2]$ almost quantitatively; chemical analyses ^{31}P and ^1H NMR spectroscopy showing that both mesitylene hydrogens had been replaced.

The decomposition products obtained (Table 3) were the mono- and di-brominated aryl derivatives RBr, RBr_2 and R'Br, or the coupling products R–R', (R–R')Br or $(R–R')Br_2$ *. No cross coupling products R–R or R'–R' were detected. The arenes RH and R'H were obtained in some cases when a Ni/Br_2 ratio of 1/2 was used. When the reaction was carried out with an excess of bromine ($Ni/Br_2 = 1/4$), the mono- and di-brominated products were obtained in larger amounts, and the arenes disappeared. Reactions carried out in the dark gave the same results. Different experiments with the same organometallic gave poor reproducibility in terms of the amount of each product ($\pm 5\%$) but, the total amount of coupling products (R–R') or of derivatives RX, R'X, either monobrominated or not, was more constant ($\pm 3\%$). Mesitylene and toluene were the only ligands which gave mono- and/or di-bromoaryl species, in agreement with their greater reactivity towards an electrophilic attack. Thus, both mono- and di-brominated coupling products were formed in the reaction of bromine with $[Ni(mes)(o\text{-tol})(PMe_2Ph)_2]$, and only monobrominated derivatives from $[Ni(mes)(o\text{-ClPh})(PMe_2Ph)_2]$; the amounts of such products (Table 3) indicate that bromination of those groups mainly takes place when the ligands are coordinated [13]. The bromination of the rings takes place preferentially in the compounds with bulkier ligands, where the nickel atom is better protected. Thus, [Ni(mes)(*o*-tol)(bipy], unlike its PMe_2Ph analogue, decomposes before bromination of the organic ligands takes place.

The reaction of $[Ni(C_2Cl_3)_2L_2]$ (L = PMe_2Ph, 1/2 bipy) and [Ni(2,3-$C_6H_3Cl_2$bipy] with bromine under similar conditions was examined in order to determine the effects of the electronegative ligands such as C_2Cl_3 or 2,3-$C_6H_3Cl_2$. Complete decomposition was observed for the compounds containing bipy, and only coupling products were recovered. The complex containing PMe_2Ph, like $[Ni(C_2Cl_3)(mes)(PMe_2Ph)_2]$, was recovered unaltered.

The extent of decomposition of the organometallic was obtained by $Ni(DMG)_2$ gravimetric analyses of the aqueous layer, and the amounts of organometallic decomposed to give coupling or RX (or R'X) (X = Br or H) products were determined by GLC. There were no problems with such analysis provided that all the R and R' ligands went into coupling or R–X and R'X (X = Br or H) products, but a difficulty arose when the amounts of RX and R'X detected by GLC, were not equivalent (see Table 3) due to phosphonium salt formation (by R or R'). In this case the proportion of the organometallic compound converted into RX (R'X) was taken as the larger value for the RX or R'X derivatives as found by GLC this process is strictly valid when only one of the two organic ligands (R, R') forms phosphonium salts, but when both organic groups form phosphonium salts some error is introduced. This error was calculated by taking account of the amount of phosphonium salt found by ^{31}P NMR spectroscopy, and was estimated as being < 5%. The values listed in Table 2 do not include the phosphonium salts either

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* RBr_2 denotes, e.g., $Br_2C_6H_4Me$, and $(R–R')Br_2$, e.g. $BrMeC_6H_3–C_6HBrMe_3$ (see Table 3).

detected in aqueous solution or calculated from the results of the decomposition revealed by chromatography. The approximations involved in the evaluation of the percentage of organometallic decomposed via R–R′ or RX(R′X) are reasonable overall.

Reaction mechanism. Thermal decomposition is negligible while the organometallic was in contact with bromine in ether [11], and so decomposition must occur via a Ni^{III} intermediate. This intermediate seems to be formed by coordination of a bromine atom at the Ni center to give a species similar to $[NiBr_2R(PMe_2Ph)_2]$ [5]. Thus, the stability of $[NiC_2Cl_3mes(PMe_2Ph)_2]$ [11], $[Ni(C_2Cl_3)_2(PMe_2Ph)_2]$ [12], or $[Ni(2,6\text{-}(OMe)_2Ph)_2(PMe_2Ph)_2]$ [14] towards bromine, can be interpreted in terms of the blocking exerted by the phosphines and bulky organic ligands to the coordination of a further ligand. Analogous compounds with smaller ligands, namely $[Ni(C_2Cl_3)_2bipy]$ or $[Ni(C_2Cl_3)(o\text{-tol})(PMe_2Ph)_2]$, decompose completely. The amount of brominated species (R–R′Br, RBr_2) increases as the size of the organic ligand increases. This behaviour may be related to the lower rate of formation of the intermediate, which would facilitate a more extensive bromination of the organic ligands (Scheme 1, steps a, b).

The pentacoordinate intermediate may react via different reductive elimination pathways, depending on the electronic (and possibly steric) properties of the ligands, as well as on the geometry of the intermediate [15] (Scheme 1, steps c and d).

The percentages of organometallic decomposed to give R–R′ via c or via d are given in Table 2. (The values do not include any phosphonium salts arising from R and R′, as indicated above).

The compound $[NiBr(mesBr)(PMe_2Ph)_2]$ was detected, as were the phosphonium salts which must come from the reaction of $[NiXRP_2]$ with Br_2 [1,8]. These salts were not observed when the ratio of RBr and R′Br formed, was about 1/1; on the other hand, when one of the organic ligands is C_2Cl_3, only the phosphonium salt corresponding to the other ligand was observed. These observations indicate that the two most electronegative groups in the intermediate preferentially couple to give RBr or RR′. Thus, the electronegative ligand R never appears as the compound $[NiBrR(PMe_2Ph)_2]$ or in the phosphonium salts. If the group C_2Cl_3 did give rise to $[NiBrC_2Cl_3(PMe_2Ph)_2]$, this could be isolated, since it is stable in the presence of bromine [5] and can be recovered.

The geometry of the pentacoordinate intermediate must be important in the decomposition process, and is probably very sensitive to the size of the various ligands; this is probably an important factor in the behaviour of $[Ni(o\text{-tol})(mes)L_2]$ ($L = PMe_2Ph, PEt_3$) [15,16].

A radical character for the reaction is ruled out by the fact that the molar ratios of decomposition products are independent of the concentration of Br_2, which indicates the presence of an intermediate. The absence of RR or R′R′ species among the decomposition products points to an intramolecular reaction and the ratio of coupling products RR′ to aryl bromides does not seem consistent with radical type disproportionation-combination processes similar to those studied by Stefani [17].

Acknowledgements

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