Nickel atom – ligand reactions: evidence for an unstable η^3-benzylnickel species from mixed-ligand cocondensations with nickel atoms[1]

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Detailed studies of nickel atom – benzyl halide cocondensation reactions, with and without a second organic ligand, have been carried out. Benzyl halides (X = Cl, Br) when cocondensed with nickel atoms at −196°C give no isolable organonickel product but only bibenzyl and nickel(II) halide, indicative of an initial unstable benzylnickel compound. Allyl chloride/benzyl chloride mixtures do not give the stable η^3-allylnickel chloride, but instead a highly-unstable sublimable yellow solid which apparently is the η^3-benzylnickel chloride dimer. All of this work indicates complexities in the initial metal atom interactions with the ligands. A further case is reported in which the presence of aluminosilicate insulating wool drastically changes the products obtained.

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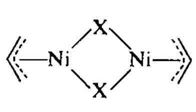
On a étudié en détail les réactions de cocondensation de l'atome de nickel avec l'halogénure benzyle en présence ou en l'absence d'un deuxième ligand organique. La cocondensation des halogénures de benzyle (X = Cl, Br) avec les atomes de nickel à −196°C ne permet pas de d'isoler des produits organonickels mais uniquement du bibenzyle et des halogénures de nickel(II) qui révèlent la formation initiale d'un composé benzylnickel instable. Les mélanges des chlorures d'allyle et de benzyle ne donnent pas le chlorure stable de η^3-allylnickel, mais conduisent de préférence à un solide jaune très instable, qui se sublime, et qui est apparemment un dimère de chlorure de η^3-benzylnickel. Tout ce travail indique la complexité des interactions initiales de l'atome métallique avec les ligands. On rapporte un autre cas où la présence d'une laine isolante alumino-silicate modifie profondément la nature des produits obtenus.

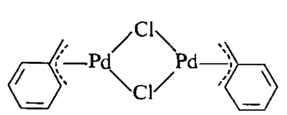
[Traduit par le journal]

Introduction

In the last ten years metal atom – ligand cocondensation reactions have become an important synthetic technique (1–6). In an early study, allyl halides cocondensed with nickel atoms were shown to give the η^3-allylnickel halide dimers **I** (X = Cl, Br) in good yield (7). Palladium analogues of **I** can be prepared similarly (5), and benzyl chloride cocondensed with palladium has been shown to give the η^3-benzylpalladium chloride dimer **II** (8). Conventional synthetic techniques have been used to obtain η^1-benzylnickel chlorides stabilized with a variety of other ligands (9, 10).



I



II

We now report studies of mixed-ligand cocondensations with nickel, carried out with hopes of preparing the nickel analogue of **II** and nickel complexes containing both η^3-allyl and η^3-benzyl ligands. We find that the presence of allyl chloride facilitates formation of a benzylnickel species, not obtainable by cocondensing pure benzyl halide with nickel. We report here our studies of the formation of the highly-unstable benzylnickel species, and of related systems.

Experimental

Metal atom reactions

The metal atom reactor was of a standard type (2, 4, 11), involving generation of metal atoms in an electrically-heated tungsten crucible (Sylvania Emissive Products) and cocondensation with the substrate on the walls of the reaction vessel, cooled with a liquid nitrogen bath. The apparatus is very similar to that of Fig. 3 of ref. 11. A highly detailed description of the procedure is given in ref. 11.

Nickel with allyl bromide (7)

Cocondensation of nickel (1.005 g) with 8.0 mL of allyl bromide at −196°C, followed by pumping off excess allyl bromide and sublimation of the red product at 70°C, gave **I** (X = Br, 1.47 g, 24%). The mass spectrum included clusters at *m/e* 360 (51) $[(C_3H_5)NiBr]_2^+$, 319 (16) $(C_3H_5)Ni_2Br_2^+$, 278 (25) $Ni_2Br_2^+$, 140 (100) $C_6H_{10}Ni^+$, 99 (88) $C_3H_5Ni^+$.

Nickel with allyl chloride (7)

Cocondensation of nickel (1.02 g) with 8.0 mL of allyl chloride at −196°C, followed by pumping off excess allyl chloride and sublimation of the red–brown product at 70°C, gave **I** (X = Cl; 1.12 g, 23.6%). The mass spectrum included clusters at *m/e* 272 $[(C_3H_5)NiCl]_2^+$, 231 $(C_3H_5)Ni_2Cl_2^+$, 190 $Ni_2Cl_2^+$, 99 $NiC_6H_{10}^+$.

Nickel with benzyl chloride

Nickel (0.953 g) was cocondensed with 25 mL of benzyl chloride at −196°C to give a deep red matrix. On warming the matrix colour disappeared. Excess benzyl chloride was pumped off and extraction with chloroform gave 0.52 g of bibenzyl (17.9%). ¹H nmr: δ 2.93 (2H, s), δ 7.25 (5H, s). ¹³C nmr: 141.8,

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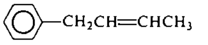
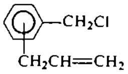
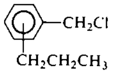
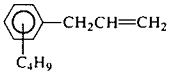
TABLE 1. Minor products from allyl chloride/benzyl chloride/nickel cocondensation, as determined by gas chromatography/mass spectroscopy[a]

Product	Mass spectral data
	132(46), 117(100), 91(61), 77, 65, 51[b]
	168(0.6), 166(1.6), 131(2), 127(12), 125(27), 117(11), 91(100), 77(7), 65(16), 51(11)
	170(1.4), 168(4.7), 133(5), 127(6.7), 125(16), 91(100), 77(6), 65(14), 51(9)
	174(3), 145(4), 131(23), 117(23), 91(100), 77(9), 65(15), 51(8)

[a] GC/MS did not fully resolve all species. As a result all mass abundances are not reported.
[b] Literature values: 132(46), 117(100), 91(55), 77(14), 65(23), 51(26) (ref. 27).

128.5, 128.4, 125.9, and 37.9 ppm. Mass spectrum: *m/e* 182 (16), 104 (3), 91 (100), 65 (11), 51 (5), 39 (7).

Addition of 5 mL Et_3P to the cocondensate at −196°C, followed by warming, gave bibenzyl and a red solid identified as $(Et_3P)_2NiCl_2$ by its mass spectrum: *m/e* 366 (trace) $NiCl_2(PEt_3)_2^+$, 331 (trace) $NiCl(PEt_3)_2^+$, 153 (12) $ClPEt_3^+$, 118 (100) PEt_3^+, 89 (45) PEt_2^+, 60 (31) PEt^+; ^1H nmr: 1.4 (3H, m), 1.7 (2H, m). The ^1H nmr of the crude mixture showed that the products were present in equimolar quantities.

Aggregation or complexation of bibenzyl

Whereas pure bibenzyl (mp 52°C) is easily sublimable under our workup conditions, the matrices obtained from nickel atom cocondensations involving benzyl halides gave a brown involatile solid which did not melt or sublime even at 70°C under high vacuum, and from which we recovered large quantities of bibenzyl by extraction with chloroform. An aggregation or complex of bibenzyl with nickel halide and/or with finely divided metallic nickel is indicated.

Nickel with benzyl bromide

Nickel (0.515 g) was cocondensed with 25 mL of benzyl bromide at −196°C to give a deep red matrix. The colour disappeared on warming. The excess benzyl bromide was pumped off; bibenzyl was recovered and identified by its ^1H nmr and mass spectrum, as above.

Addition of 5 mL Et_3P to the cocondensate at −196°C, followed by warming, gave bibenzyl and a red solid identified as $(Et_3P)_2NiBr_2$ by its mass spectrum: *m/e* 454 (trace) $NiBr_2(PEt_3)_2^+$, 375 (trace) $NiBr(PEt_3)_2^+$, 197 (18.6) $BrPEt_3^+$, 118 (100) PEt_3^+, 89 (42) PEt_2^+, 60 (31) PEt^+. The ^1H nmr of the crude mixture showed that the bibenzyl and $NiBr_2(PEt_3)_2$ were present in equimolar amounts.

Nickel with equimolar allyl chloride/benzyl chloride

Cocondensation of nickel (0.955 g) with 25 mL of an equimolar mixture of allyl chloride and benzyl chloride at −196°C, followed by warming and pumping off the unreacted allyl and benzyl chloride, gave a highly air-sensitive yellow solid which was sublimed to a cold finger at 65°C. This decomposed slowly at ambient temperature to give bibenzyl, nickel chloride, and nickel metal, and could not be obtained in a pure form. (Bibenzyl and nickel(II) chloride do not sublime from our reaction mixtures and hence could only arise as decomposition products.) Repeated attempts to obtain the mass spectrum of the yellow solid under a variety of conditions gave only bibenzyl (parent ion: *m/e* 182). A gas chromatogram of a chloroform solution of the yellow solid on a 3% FE 30 on CHROM W column showed only bibenzyl (calibrated with a known sample). GC/MS analysis of the residue in the reaction vessel after sublimation, using a column with 3% 56 30/CHROM W/SPECIAL GC, showed predominantly bibenzyl and several other organic species which were present in yields of less than 0.5% (Table 1).

Trapping with 5 mL Et_3P at −196°C yielded 0.495 g of bibenzyl and 1.039 g of $(Et_3P)_2NiCl_2$, both of which were identified by ^1H nmr and mass spectra, as above. Trapping with 10 mL triisobutylphosphine at −196°C yielded bibenzyl and red $(i\text{-}Bu_3P)_2NiCl_2$ in equimolar amounts, as determined by comparison of ^1H nmr integrals of the crude mixture. The $(i\text{-}Bu_3P)_2NiCl_2$ (26%) was identified by its ^{13}C nmr: 25.3 ppm (β-C), 25.6 (γ-C), 31.1 (α-C, d of d), and by its uv/visible spectrum (bands at 500, 402, 268, 251 mμ; known sample: 502, 406, 269, 247 mμ).

Nickel with equimolar allyl chloride/benzyl bromide

Cocondensation of nickel (1.33 g) with 25 mL of an equimolar mixture of allyl chloride and benzyl bromide at −196°C, followed by warming and pumping off the unreacted organic substrate, yielded two sublimable products: a yellow solid (subl. 65°C) and a red solid (subl. 70°C). The latter, identified from its mass spectrum as the η^3-allylnickel chloride dimer **I**, had ^{13}C nmr peaks at 56.0 and 105.4 ppm.

Addition of Et_3P to a solution of the yellow solid in chloroform gave, in addition to metallic nickel, bibenzyl and $(Et_3P)_2NiBr_2$ as identified by the mass spectrum (*m/e* 454 (trace), 375 (trace), 197 . . . as above, for the nickel complex; *m/e* 182 (18), 104 (5), 91 (100), 65 (10), and 51 (7) for bibenzyl). The ^1H nmr of the crude mixture showed that the products were present in equimolar quantities.

The yellow solid could not be completely freed of **I** by sublimation; its ^{13}C spectrum showed the 56.0 and 105.4 ppm peaks of **I**, as well as bibenzyl peaks at 37.8, 125.9, 128.3, 128.4, and 141.7 ppm. Peaks assigned to the yellow solid occur at 41.4, 72.0, 126.6, 127.8, 130.6, and 132.2 ppm. These disappear with time as the bibenzyl peaks grow, and all peaks become broad due to the formation of paramagnetic nickel(II) bromide.

Nickel with equimolar allyl bromide/benzyl bromide

Cocondensation of nickel (1.102 g) with 25 mL of an equimolar mixture of allyl bromide and benzyl bromide at −196°C, followed by warming and pumping off the unreacted organic substrate, yielded a red solid (subl. 70°C) identified as the allylnickel bromide dimer, but no sublimable yellow solid. The remainder of the product in the reaction vessel, in addition to nickel metal, was identified as bibenzyl and nickel bromide, in approximately equimolar quantities.

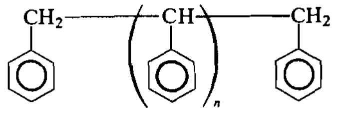
Palladium with equimolar allyl chloride/benzyl chloride

Cocondensation of palladium (0.852 g) with 25 mL of an equimolar mixture of allyl chloride and benzyl chloride at -196°C, followed by pumping off the unreacted organic substrate, yielded 0.184 g (6.3%) of the η^3-allylpalladium chloride dimer **II**, as identified by its mass spectrum (parent ion cluster at *m/e* 368) and ^{1}H nmr (δ 3.03 (2H, d), 4.10 (2H, d), 5.40 (1H, m)). Also observed were very weak clusters at *m/e* 468 (benzylPdCl)$_2^+$ and 377 (benzylPd$_2$Cl$_2$)$^+$ and bibenzyl peaks (*m/e* 182, 91). Thus both η^3-allyl- and η^3-benzylpalladium chloride dimers form, but no peak could be detected at *m/e* 418 which would correspond to the parent ion of an analogous mixed allyl, benzylpalladium chloride compound.

Nickel with benzyl halides, using Kaowool crucible insulation

(i) Nickel with benzyl chloride

Cocondensation of nickel (0.86 g) with 26 g of benzyl chloride at -196°C in the presence of Kaowool crucible insulation gave a matrix which, when allowed to warm to ambient temperature, melted down the sides of the vessel and began to bubble, with evolution of hydrogen chloride (ir bands at 2875 cm^{-1}). After all volatiles were pumped off, 24.3 g of product was collected that was insoluble in all solvents used (pentane, chloroform, acetone, dimethylsulfoxide, acetonitrile). However, the addition of Et$_3$P to the finely ground solid gave 1.42 g of (Et$_3$P)$_2$NiCl$_2$ (26.5% based on nickel; identified by mass spectrum and ^{1}H nmr as above) and 23.8 g of insoluble white solid. This was identified by its mass spectrum as a mixture of polybenzylic species: *m/e* 632 (0.5), 542 (1), 452 (1.4), 362 (3), 272 (8), 181 (23), 179 (38), 91 (100). On slowly heating the mass spectrometer inlet the same peaks were present and also new peaks at higher mass appeared (*m/e* 722, 812, 902, and 992). These became larger as the inlet temperature was increased. These results, together with a fragmentation pattern indicative of a monosubstituted aromatic ring, suggest structures **III** (n = 1–9).



III

Metastable scanning techniques (12, 13) confirm that the polybenzylic mass spectral peaks arise from separate species in the ionization chamber of the mass spectrometer rather than being fragments of a higher-mass parent ion. For a suspected parent ion, a V scan (12) will determine whether it is itself a daughter of some higher-mass ion, while a V^2/E scan (13) will determine its daughter ions. While the results (Table 2) require that the polybenzyls **III** are present in the mass spectrometer source, we cannot exclude the presence of less volatile higher polymers, or that the observed fragments might be formed in the source from the breakdown of a higher polymer.

(ii) Nickel with benzyl bromide

Cocondensation of nickel (0.52 g) with 25 mL of benzyl bromide at -196°C in the presence of Kaowool crucible insulation gave a red matrix. On warming to ambient temperature the red colour disappeared and hydrogen bromide was given off (ir bands at 2560 cm^{-1}). By workup methods similar to those used in the analogous benzyl chloride system, 3.46 g of polybenzylic product were obtained. Mass spectrum: *m/e* 632 (1), 542 (3), 452 (6), 362 (6), 361 (6), 272 (1), 271 (15), 182 (28), 181 (99), 91 (100).

TABLE 2. Metastable scanning techniques applied to suspected parent ions in the mass spectrum of a polybenzyl product

Suspected parent ion *m/e* values	Parent ions (by V scan)	Daughter ions (by V^2/E scan)[a]
632		529, 438, 422, 406, 332, 317
542	635±5	374, 361, 283, 270
452	None	360, 283, 270, 256
362	None	270, 193, 181, 180
272	357±6	193, 180
181	276±5 366±6 459±6 549±6	
179	187±5 195±5 272±4 364±4 455±5	
91	267±7 354±8	

[a] Errors are ±2 *m/e* units.

(iii) Nickel with equimolar allyl bromide/benzyl bromide

Cocondensation of nickel (0.62 g) with 25 mL of an equimolar allyl bromide/benzyl bromide mixture at -196°C in the presence of Kaowool crucible insulation gave an initial red matrix which on warming yielded hydrogen bromide and 2.17 g of a solid. Major peaks of the mass spectrum of the solid (Table 3) show that this is primarily a polybenzyl but that an allyl group or a bromine can become incorporated.

Instrumentation

Mass spectra were obtained on an AEI MS30 double beam spectrometer operating at 70 eV for most compounds, but at 19 eV for some of the less stable compounds. GC/MS runs were performed on a column with 3% 56 30/CHROM W/SPECIAL GC.

V scans and V^2/E scans, the two metastable scanning techniques used in this study, were carried out with the KRATOS metastable scan unit. Both follow decompositions in the field-free region between the ionization chamber and the electrostatic analyser of the MS-30 mass spectrometer. In the V scan, the spectrometer is tuned to a peak of known mass (daughter ion m_2^+). The electrostatic analyser is held constant and the accelerating voltage V is increased linearly. This gives the precursor or parent ions m_1^+ which give rise to that daughter ion (12). In the V^2/E scan, the spectrometer is tuned to a peak of known mass; the electrostatic analyser voltage is then increased linearly while simultaneously V is increased proportionally to the square of the electrostatic analyser voltage. This gives a spectrum which shows the peak the instrument was tuned to, and the daughter ions which arise from it (13).

Nuclear magnetic resonance spectra were recorded on a Bruker WP-60 Fourier Transform nmr spectrometer operating at 60 MHz (^{1}H) and at 15.08 MHz (^{13}C). ^{13}C spectra were obtained using a 3759 Hz sweep width and 1.089 second acquisition time for an 8K FID. Thirty-degree pulses were used, with the Phase Alternating Pulse Sequence, and 5 W of proton noise decoupling were applied. Proton spectra were obtained with a 750 Hz sweep width and a 5.5 s acquisition time.

TABLE 3. Major mass spectral peaks of the polymeric nickel/allyl bromide/benzyl bromide/Kaowool reaction product

	Composition: number of structural units incorporated		
m/e	Benzyl	Allyl	Bromine
182	2	0	0
222	2	1	0
260/262	2	0	1
222	3	0	0
312	3	1	0
362	4	0	0
402	4	1	0

Materials

Nickel pellets (99.95% purity) and palladium sponge (99.5% purity) were obtained from A. D. Mackay Limited. The allyl and benzyl halides (Aldrich) were used without further purification, although purity was checked by GC/MS. Toluene was purified by shaking with cold sulfuric acid, followed by washing with water, drying over phosphorus pentoxide, and distilling, with the first and last cuts being rejected. Chloroform was purified by predrying over calcium chloride and distilling from phosphorus pentoxide, the first and last cuts being rejected, and stored in the dark.

Results and discussion

(i) Single-ligand systems

The cocondensation of benzyl chloride or benzyl bromide with nickel at −196°C gives an initial red matrix, similar to that observed in other arene–metal cocondensations (14) and interpreted as π-arene–metal complex formation, but on warming only bibenzyl and nickel(II) halide can be recovered. The presence of bibenzyl is consistent with the formation of an unstable benzylnickel complex. Trapping experiments, in which triethylphosphine is added to the initial matrix at −196°C in the hope of stabilizing an initially-formed organometallic linkage by incorporation of a phosphine ligand, give only bibenzyl and $(Et_3P)_2NiX_2$ (X = Cl, Br) on warming.

Similar cocondensations of a benzyl halide with nickel, but with the crucible surrounded by aluminosilicate insulating wool (Kaowool, available from Morganite Ceramic Fibers, Neston, England, is a stable high-temperature ceramic fiber with no organic binder, consisting principally of $Al_2O_3 \cdot 2SiO_2$), give on warming a mixture of nickel(II) halide, hydrogen halide, and polybenzyl species containing from three to at least nine benzyl units, as determined by mass spectroscopy. Covering of the insulation by brass foil gives only bibenzyl and nickel(II) halide, as in the absence of insulation. Klabunde and co-workers have recently reported similar major effects of crucible insulation on product distribution and yields in the synthesis of the η^3-benzylpalladium chloride dimer, **II**, and have demonstrated that pyrolysis reactions on the greatly increased surface area, when insulation is present, result in the production of organic free radicals from the substrate (14). Similar free radical processes are implicated here, although the products are different, i.e., polymer rather than the bibenzyl and toluene that were Klabunde's principal products. Hence crucible insulation was dispensed with in the mixed-ligand studies described below, despite the greater thermal losses involved.

The cocondensation of allyl chloride or bromide with nickel, with or without Kaowool insulation, gives the η^3-allylnickel halide dimers **I** in good yield, as reported by Piper and Timms (7).

(ii) Mixed-ligand systems

An equimolar mixture of allyl chloride and benzyl chloride, cocondensed with nickel atoms, does not give **I** but instead a hitherto-unreported yellow sublimable solid that decomposes very readily to bibenzyl, nickel(II) chloride, and nickel. Absence of decomposition products derivable from allyl chloride shows that the allyl group is not incorporated in the sublimable species. Addition of trialkylphosphines (Et_3P, *i*-Bu_3P) to the −196°C matrix yields equimolar amounts of bibenzyl and $(R_3P)_2NiCl_2$ but no other products.

An equimolar mixture of allyl bromide and benzyl bromide, cocondensed with nickel atoms, gives only the products which can be formed in the separate unmixed-ligand experiments, i.e., **I** (X = Br), bibenzyl, and nickel(II) bromide.

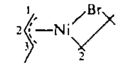
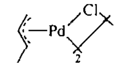
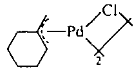
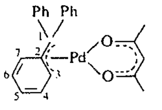
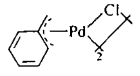
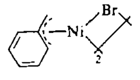
An intermediate mixed-ligand system, allyl chloride and benzyl bromide, when cocondensed with nickel gives two sublimable solids which can be separated by fractional sublimation: red **I** (X = Cl), and a yellow material which decomposes readily to give bibenzyl and nickel(II) bromide, and appears to be the bromine analogue of the sole product of the allyl chloride/benzyl chloride/nickel system. Addition of Et_3P to a solution of this compound gives bibenzyl and $(Et_3P)_2NiBr_2$, identified by its mass spectrum.

Cocondensation of palladium atoms with an equimolar mixture of allyl chloride and benzyl chloride, followed by extraction with toluene, gives a yellow product identified as mainly η^3-allylpalladium chloride dimer from its mass spectrum. The mass spectrum also shows very weak clusters corresponding to the η^3-benzylpalladium chloride dimer **II** but none corresponding to a mixed allyl/benzylnickel chloride dimer.

(iii) Structure of the unstable benzylnickel species

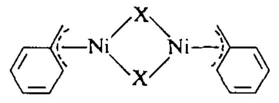
Decomposition of the product of the allyl chloride/benzyl halide/nickel cocondensation reaction,

TABLE 4. ^{13}C chemical shifts of **IV** and some model compounds[a]

Compound	Carbon				Reference
	C-1	C-2	C-3	C-4 to C-7	
	49.6	105.6	71.2		17
	58.3	111.4	81.4		18
	58.2	126.0	68.8		18
	73.3	116.0	102.3[b]	133.1[c], 127.9[d], 102.3[b]	19
	42.1	125–133	107.0	125–133	20
	41.4	126–132	72.0	126–132	This work

[a] ppm to low field of internal tetramethylsilane.
[b] Averaged signal of C-3 and C-7 due to fluxional behaviour.
[c] Averaged signal of C-4 and C-6.
[d] C-5.

to give bibenzyl and nickel(II) halide in a 1:1 molar ratio as well as nickel metal but no other products, suggests structure **IV** (X = Cl, Br) analogous to **I** and **II**. Trapping experiments are consistent with this. However, the volatility of the product, greater than that of the allylnickel chloride dimer is anomalous and suggests that **IV** may vaporize as a monomer. Dissociation to the highly unstable monomer would be consistent with its extreme reactivity.

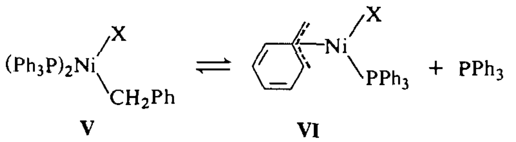


IV

Compound **II**, the palladium analogue of our proposed structure **IV**, also gives bibenzyl as a final product when reacted with Et_3P, but in the palladium case stepwise addition allows the isolation of an η^1-benzylnickel complex (15). An analogous but less stable η^1-benzylnickel complex is a likely intermediate in the reaction of **IV** with phosphines. Palladium species of this type tend to be much more stable than their nickel analogues (16).

Attempts to obtain mass spectra of **IV** showed only the presence of bibenzyl. A ^{13}C nmr spectrum was obtained on a deuterochloroform solution of **IV** (X = Br) but decomposition had already commenced and peaks attributable to bibenzyl were already larger than those of the unstable species. The peaks assigned to the unstable compound diminish on standing at ambient temperature, with corresponding growth of the bibenzyl peaks. The chemical shifts are reasonably consistent with those of other, similar η^3-allylmetal compounds (17–20) (Table 4). A complete assignment is difficult since peaks in the 125–133 ppm region are obscured by additional resonances, including the bibenzyl decomposition product. The peaks at 41.4 and 72.0 ppm are fully consistent with allylic bonding to nickel (21), and are difficult to account for in any other way.

The only previously-reported η^3-benzylnickel compounds appear to be **VI**. Compound **V** (X = Cl, Br) has been prepared by ethylene displacement from $(Ph_3P)_3Ni(C_2H_4)$ by benzyl halides (22). An $\eta^1 \rightleftharpoons \eta^3$ equilibrium in solution, with displacement of Ph_3P, was proposed on the basis of cryoscopic and ^1H nmr studies. These authors obtain decomposition products analogous to ours from their solutions (bibenzyl, Ph_3P, $(Ph_3P)_2NiX_2$, and nickel) but their complexes are considerably more stable. As in our work, no nickel-containing fragments were detected in the mass spectrum.



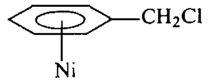
V **VI**

(iv) Rationalization of product distributions

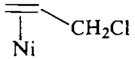
In metal atom – ligand cocondensations the interaction of metal atom and substrate first occurs on the freshly-formed cocondensation surface. The substrate and metal atoms are still mobile and the metal atoms are highly reactive, and in favourable cases a bond can form between metal atom and substrate. The initial organometallic species may then undergo further reactions, either at the cocondensation temperature or during warmup, to give the isolable products. Mobilities within the cocondensation matrix are important, especially when intermolecular reactions such as dimerization must occur, and are greatly affected by changes in attractive forces among the large excess of substrate molecules forming the matrix. Hence products and yields can be greatly changed by minor modifications to the matrix that affect mobility. For example, the use of *n*-hexane as substrate diluent in place of *n*-pentane when trimethylphosphine is cocondensed with iron atoms drastically decreases the yield of $HFe(CH_2PMe_2)(PMe_3)_3$ (1, 23), and the differing internal attraction of *n*-pentane and *n*-hexane, typified by their 35° difference in melting points, can explain this. Recent studies by Ozin and co-workers involving metal atom condensations in polymer matrices at temperatures much higher than −196°C have confirmed the importance of mobility effects (24). Aggregation of metal atoms to form colloidal metal can become predominant when mobility is either too low or too high, leaving a narrow temperature (i.e., mobility) range which favours desired products.

On the assumption that substrate melting points are indicative of mobilities in low-temperature matrices, our pattern of reactivities can be rationalized. The allyl halides have the lowest melting points of our organic substrates (allyl chloride, −134.5°C; allyl bromide, −119.4°C; benzyl chloride, −39°C; benzyl bromide, −3°C; acrylonitrile, −83.5°C). Hence the allyl halides form matrices of the highest mobility, favouring the formation of η^3-allylnickel halide dimers by monomer diffusion. Benzyl halide matrices should be far less mobile, and the intitial monomeric benzylnickel halide probably decomposes before it can diffuse to form the less unstable dimer. Allyl halide/benzyl halide matrices should have intermediate mobilities, and dimerization of benzylnickel halide monomer is more likely to win out over monomer decomposition. Even here, a close balance of the two processes is apparently involved; the absence of **IV** from the allyl bromide/nickel bromide cocondensations might be the result of significantly lower mobility in this matrix, in accord with the higher melting points of the bromides compared to the analogous chlorides.

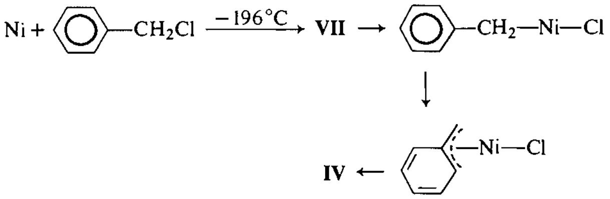
The absence of **I** from the allyl chloride/benzyl chloride cocondensation product might result from preferential formation of **VII** rather than **VIII** in the initial metal atom – ligand interaction. **VIII** is known from the work of Ozin and Powers (25) and is stable up to −153°C. **VII** is the nickel analogue of the initial benzyl chloride – palladium species proposed by Klabunde *et al.* (8, 15). Once **VII** forms in preference to **VIII**, intramolecular rearrangement followed by dimerization would give **IV**, as in the analogous palladium system (8, 15):



VII



VIII



Some **VIII** should form as well at −196°C, and a mixed η^3-allyl-η^3-benzylnickel halide dimer would be expected. No such species has been detected, but GC/MS analysis of the cocondensation residue, after sublimation of the volatile product, does show several organic species in addition to bibenzyl, all of which incorporate both allyl and benzyl fragments (Table 1). All of these products can be rationalized in terms of reactions of ligands in a mixed allylbenzylnickel compound.

A similar effect in inhibiting the formation of **I** has been observed in allyl bromide/acrylonitrile/nickel cocondensations. Neither **I**, nor the polymer obtained in acrylonitrile/nickel cocondensations, is obtained but instead a highly-unstable species which, from its decomposition products, appears to be a nickel complex containing both allyl and acrylonitrile groups (26). Metal atom cocondensation reactions with mixed ligands may hold many surprises even in cases in which the corresponding single-ligand reactions are well known.

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