

## REDUCTIVE ELIMINATION FROM ORGANOMETALS. THERMAL AND INDUCED DECOMPOSITION OF ARYLMETHYLNICKEL(II) COMPLEXES

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### Summary

The thermal decomposition of arylmethylbis(triethylphosphine)nickel(II),  $\text{ArNiMeL}_2$ , is studied in hydrocarbon solutions, both in the presence and absence of aryl halide. The direct thermolysis affords methylarenes without aryl scrambling, by first-order kinetics. The inverse phosphine dependence of the rate is related to a dissociative mechanism proceeding via reductive elimination directly from the coordinatively unsaturated  $\text{ArNiMeL}$  intermediate. In contrast, the reductive elimination of methylarene induced by aryl halide is a radical chain process in which there is extensive scrambling of aryl groups, consistent with paramagnetic nickel(I) and nickel(III) species, and not aryl radicals, as reactive intermediates. The induced reductive elimination is a significantly more facile process than direct thermolysis. However, the relative contributions from these pathways in the reductive elimination of  $\text{ArNiMeL}_2$  can be deliberately manipulated by additives (inhibitors and promoters) which control the induction period relating to the generation of nickel(I, III) intermediates required for chain initiation. The radical chain mechanism for the formation of carbon-carbon bonds by reductive elimination in this system is essentially the same as that previously deduced for aryl coupling to biaryls from arylhalonickel(II) and aryl halides.

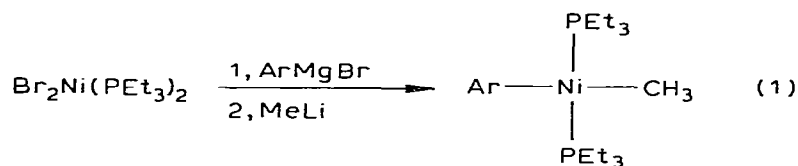
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### Introduction

Organometallic species are important intermediates in a variety of organic reactions catalyzed by transition metal complexes. As such, mechanistic insight into the formation and the decomposition of these organometallic intermediates is crucial to the further development of efficient catalytic processes [1–5]. Nickel complexes are among the most versatile catalysts, and they are also useful for mechanistic studies since many types of organonickel complexes have now been identified [6]. Although reductive elimination of organonickel(II)

intermediates represents an important step in the catalytic function of nickel, there is only limited information available as to how the organic ligands are actually lost.

We have chosen arylnickel(II) derivatives for the study of reductive elimination, since they are isolable in pure crystalline form and readily characterized in solution, particularly by NMR spectroscopy [7,8]. For example, a variety of arylmethylnickel(II) complexes I,  $\text{Ar}(\text{CH}_3)\text{Ni}(\text{PEt}_3)_2$ , are readily synthesized by the successive metathesis of the dibromonickel(II) complexes  $\text{Br}_2\text{Ni}(\text{PEt}_3)_2$  with the appropriate arylmagnesium bromides followed by methyllithium,



(I)

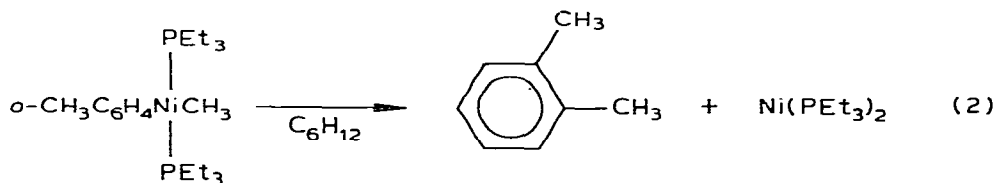
The phenyl, *o*-tolyl and *o*-anisyl derivatives are obtained as yellow crystalline, air-sensitive materials. They are diamagnetic complexes in which the square planar configuration about nickel is *trans*. Thus the  $^1\text{H}$  NMR spectrum in hydrocarbon solutions shows the methyl ligands as 1 : 2 : 1 triplets, and the  $^{31}\text{P}$  NMR spectrum shows only a single sharp resonance for both phosphine ligands [8]. Furthermore, the absence of significant line broadening in either the  $^1\text{H}$  or  $^{31}\text{P}$  NMR spectrum at ambient temperatures (25–60°C) indicates that there is neither rapid exchange with any paramagnetic, tetrahedral intermediates nor facile loss of phosphine ligands under these conditions.

## Results

Reductive elimination of methylarene from the arylmethylnickel(II) complexes I\* were carried out under essentially two reaction conditions. First, the arylmethylnickel(II) complex was thermolyzed alone in either cyclohexane, decalin, or benzene solution. The induced decomposition of the same arylmethylnickel(II) complexes was then examined in the presence of various aryl halides.

### *Direct thermal decomposition of arylmethylnickel(II) complexes*

The thermolysis of *o*-tolylmethylnickel(II),  $o\text{-CH}_3\text{C}_6\text{H}_4\text{NiCH}_3(\text{PEt}_3)_2$ , in either cyclohexane or benzene solution at 75°C afforded good yields (>90%) of *o*-xylene resulting from reductive elimination, i.e.,



\* For clarity, I will be designated hereafter as an arylmethylnickel(II) complex without reference to the bis-triethylphosphine ligands, unless required for the discussion.

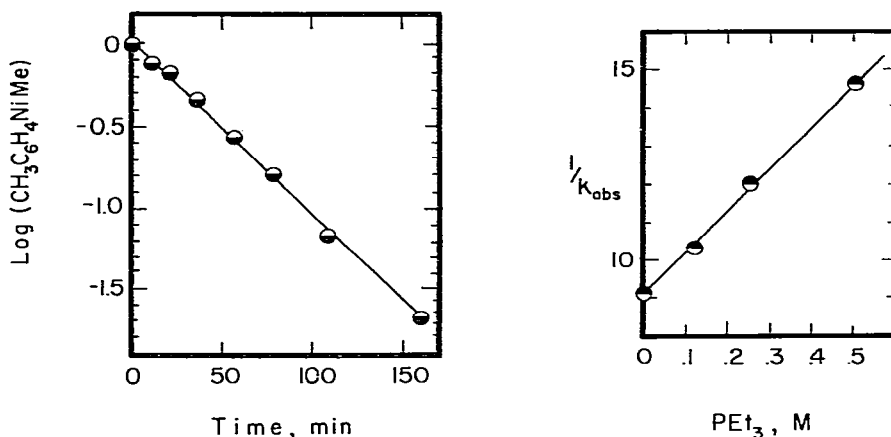
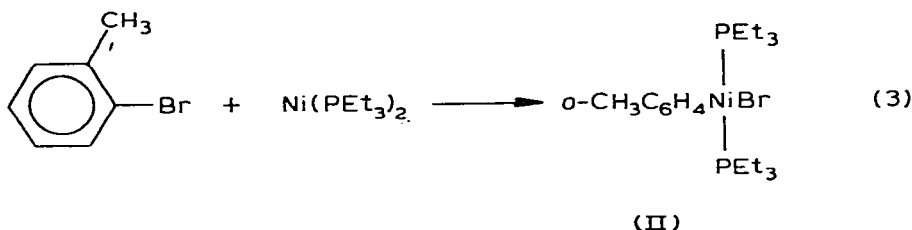


Fig. 1. The first-order disappearance of *o*-tolymethylnickel(II) in 0.50 *M* benzene solution at 80°C.

Fig. 2. Phosphine dependence of the observed first-order rate constant in the thermolysis of *o*-tolymethylnickel(II) in 0.5 *M* benzene solution at 80°C.

The small remainder ( $\sim 10\%$ ) is accounted for as toluene, together with *o*,*o'*-bitolyl. The purple nickel product ( $\lambda_{\max}$  498 nm) was not isolated, but it is presumed to be the reduced nickel(0) species  $\text{Ni}(\text{PEt}_3)_2$ , judging from the stoichiometry (see eq. 2) and the oxidative adduct II obtained upon the addition of *o*-tolyl bromide, i.e.,



The rate of decomposition of *o*-tolymethylnickel(II) follows first-order kinetics in benzene solution to more than two half lives, as shown in Figure 1.

$$-\frac{d[\text{ArNiCH}_3]}{dt} = k_{\text{obs}}[\text{ArNiCH}_3] \quad (4)$$

The observed first-order rate constant  $k_{\text{obs}} = 6.6 \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$  is independent of the *o*-tolymethylnickel(II) concentration between 0.02 and 0.2 *M*. However, added triethylphosphine retarded the decomposition of *o*-tolymethylnickel(II), although the rate still followed first-order kinetics. Quantitatively the inverse phosphine dependence of the observed first-order rate constant is given by eq. 5, as illustrated in Figure 2. The phosphine-independent rate constant  $k$  affords a value for the dissociation constant of  $K = 2 \times 10^{-4} \text{ M}$ , derived from the slope  $1/kK$ .

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k} \left[ 1 + \frac{[\text{PEt}_3]}{K} \right] \quad (5)$$

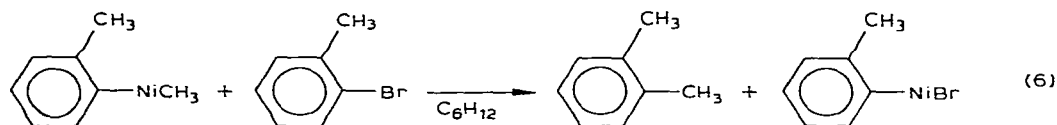
TABLE 1  
INDUCED DECOMPOSITION OF ARYL METHYLNICKEL(II) BY ARYL HALIDES<sup>a</sup>

Ar(CH <sub>3</sub> ) <sub>2</sub> Ni(PEt <sub>3</sub> ) <sub>2</sub>		Ar'X	mmol	Solvent	ArCH <sub>3</sub> mmol (%)	Ar'CH <sub>3</sub> mmol (%)	ArH mmol	Material Balance <sup>b</sup>
Ar	mmol							
C <sub>6</sub> H <sub>5</sub>	0.065	C <sub>6</sub> H <sub>5</sub> Br	0.195	Benzene	0.060(92)			0.92
C <sub>6</sub> H <sub>5</sub>	0.065	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	0.195	Benzene	0.047(72)	0.014(21)		0.93
C <sub>6</sub> H <sub>5</sub>	0.039	<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	0.117	Benzene	0.023(59)	0.013(33)		0.92
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	0.203			Cyclohexane	0.176(87)		0.020	0.97
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	0.218	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	0.218	Cyclohexane	0.192(88)		0.023	0.98
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	0.218	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	1.09	Cyclohexane	0.177(81)		0.021	0.91
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	0.200	<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	0.200	Cyclohexane	0.093(47)	0.079(40)	0.005	0.90
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	0.200	<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	1.00	Cyclohexane	0.060(33)	0.098(49)	0.005	0.85
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	0.159	C <sub>6</sub> H <sub>5</sub> Br	0.477	Benzene	0.062(39)	0.092(58)		0.97
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	0.083	C <sub>6</sub> H <sub>5</sub> Cl	0.249	Benzene	0.045(54)	0.030(36)		0.90
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	0.075	C <sub>6</sub> H <sub>5</sub> I	0.225	Benzene	0.023(31)	0.045(60)		0.91
<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub>	0.168	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	0.504	Benzene	0.137(82)	0.024(15)		0.97
<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub>	0.057	C <sub>6</sub> H <sub>5</sub> Br	0.171	Benzene	0.037(65)	0.014(24)		0.89
<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub>	0.057	<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	0.171	Benzene	0.045(74)		0.005	

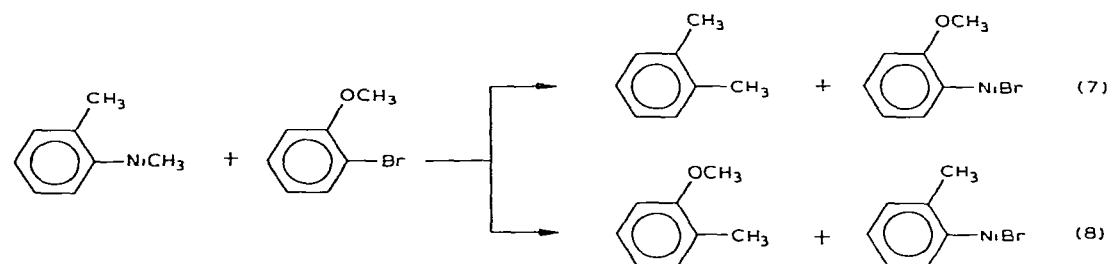
<sup>a</sup> In sealed tubes at 75°C. <sup>b</sup> Includes only ArCH<sub>3</sub>, Ar'CH<sub>3</sub> and ArH as (Σ Ar, Ar')/ArNiCl<sub>2</sub>.

*Induced decomposition of arylmethylnickel(II) by aryl halides*

The thermolysis of *o*-tolylmethylnickel(II) in the presence of *o*-tolyl bromide produces *o*-xylene and *o*-tolylbromonickel(II) according to the stoichiometry:

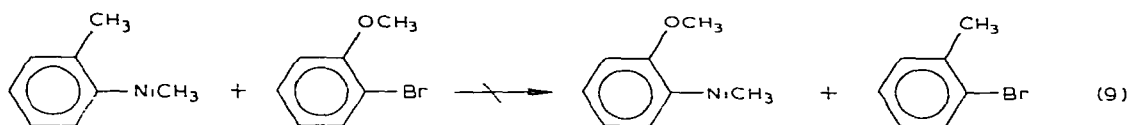


A small amount of toluene is also produced (see Table 1). When bromobenzene is used in place of *o*-tolyl bromide, the yield of *o*-xylene decreased to 40%, and the toluene yield increased correspondingly to 60%. The latter results from the incorporation of the phenyl group from bromobenzene into I during the induced decomposition. Such a scrambling of aryl groups can be clearly differentiated by the use of a methoxy substituent, i.e., *o*-anisyl bromide, and *o*-tolylmethylnickel(II) affords a mixture of *o*-xylene and *o*-methoxytoluene,



The formation of the corresponding amounts of the arylbromonickel(II) products, *o*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>NiBr(PET<sub>3</sub>)<sub>2</sub> and *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NiBr(PET<sub>3</sub>)<sub>2</sub>, can also be readily determined from their characteristic <sup>1</sup>H NMR spectra (see Experimental section). Thus the extent of the scrambling of aryl groups during this induced decomposition is indicated by the competition between eq. 7 and eq. 8.

The scrambling does not take place by the prior exchange of aryl groups between the aryl halide and the arylmethylnickel(II) complex, i.e.,



The occurrence of such a halogen exchange would be readily detected by carrying out the reaction with excess *o*-anisyl bromide to allow *o*-tolyl bromide, if formed, to be diluted sufficiently and survive intact. However, no *o*-tolyl bromide was detected, despite the increased aryl scrambling under these conditions (compare entries 7 and 8 in Table 1). The extensive material balance observed in these systems precludes such a preequilibrium halogen exchange. Furthermore, halogen exchange was not observed with any other aryl group, for the combinations listed in Table 1 (see Experimental section).

The rate of the induced decomposition of *o*-tolylmethylnickel(II) shows biphasic behavior in Figure 3. In the presence of added bromobenzene, the decomposition of I initially follows first-order kinetics for  $\tau = 37$  min, where-

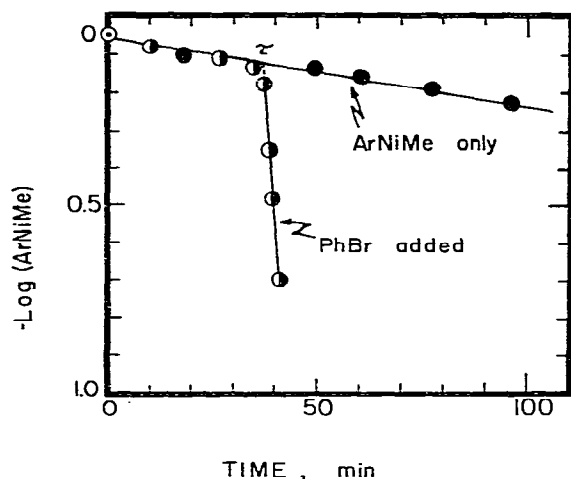


Fig. 3. The rates of reductive elimination of 0.50 M *o*-tolylmethylnickel(II) in the presence  $\circ$  and absence  $\bullet$  of 1.50 M bromobenzene in benzene solution at 75°C.

upon there is an abrupt, marked increase in rate characteristic of an inhibited chain process. The first-order rate constant is essentially the same as that obtained in the absence of bromobenzene (see Figure 1). The kinetic behavior in Figure 3 is not affected by the products, since the deliberate addition of 15% *o*-tolylbromonickel(II) had no noticeable effect on  $\tau$ . However, the induction period was extremely sensitive to the presence of free ligand,  $\tau$  being increased fourfold by 0.10 equivalent of added triethylphosphine (Table 2). More importantly, the deliberate addition of either nickel bromide (heterogeneous) or methyl triflate (homogeneous), drastically decreased or entirely eliminated the induction period as shown in Figure 4.

The dual observations of the aryl scrambling and the induction period in the induced decomposition of *o*-tolylmethylnickel(II) by bromobenzene suggest the occurrence of (1) a radical chain process and (2) aryl radicals as reactive intermediates. Indeed, the participation of chain processes was supported by inhibitor studies. For example, the addition of 0.1 equiv. duroquinone, which is known to be an effective suppressor of chain reactions proceeding via radical-

TABLE 2

CHANGES IN THE INDUCTION PERIOD BY ADDITIVES DURING THE REDUCTIVE ELIMINATION OF *o*-TOLYLMETHYLNICKEL(II)<sup>a</sup>

Additive	Conc. (M)	Induction Period (min)
None	—	37
None	<sup>b</sup>	$\infty$
<i>o</i> -C <sub>6</sub> H <sub>4</sub> NiBr	0.075	41
PEt <sub>3</sub>	0.050	149
CH <sub>3</sub> O <sub>3</sub> SCF <sub>3</sub>	0.12	<0.1
NiBr <sub>2</sub>	0.050 <sup>c</sup>	<0.1
Duroquinone	0.025	150

<sup>a</sup> At 75°C in 0.5 M benzene solution containing 1.50 M bromobenzene, except as indicated. <sup>b</sup> No added bromobenzene. <sup>c</sup> Heterogeneous.

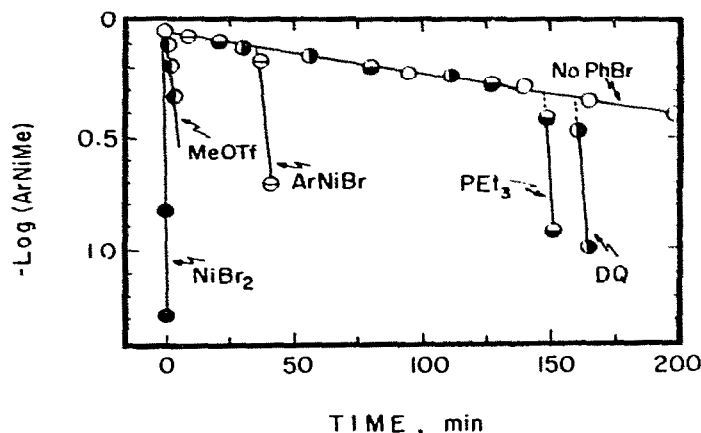


Fig. 4. Effects of additives on the induction period for the induced decomposition of 0.50 *M* *o*-tolylmethylnickel(II) by 1.50 *M* bromobenzene. Additives:  $\text{PEt}_3$  (15%)  $\circ$ ,  $o\text{-CH}_3\text{C}_6\text{H}_4\text{NiBr}_2$  (15%)  $\bullet$ , MeOTf (25%)  $\ominus$ ,  $\text{NiBr}_2$  (0.050 equiv, heterogeneous)  $\bullet$ , duroquinone (7%)  $\circ$ . The direct thermolysis of *o*-tolylmethylnickel(II) in the absence of bromobenzene is indicated by the first-order slope ( $\circ$ ).

anion intermediates [9], increased the induction period fourfold (Table 2). Unfortunately, the effect of *p*-dinitrobenzene, another well-known inhibitor, could not be tested owing to its rapid reaction with I. Secondly, the effect of phenyl radicals as possible intermediates was examined by their independent co-generation in situ from phenylazotriphenylmethane (PATM), i.e. [10],



However, phenyl radicals have no effect on the production of the cross-coupled *o*-methoxytoluene during the induced decomposition of *o*-anisylmethylnickel(II) by *o*-anisyl iodide,

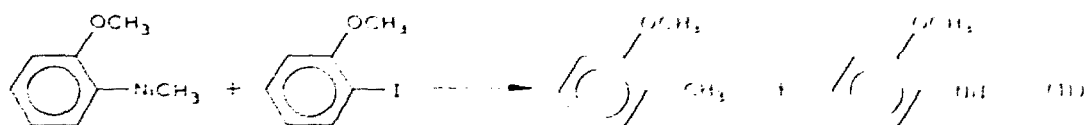



TABLE 3

EFFECT OF PHENYL RADICALS ON THE INDUCED DECOMPOSITION OF *o*-ANISYLMETHYLNICKEL(II) BY IODOBENZENE <sup>a</sup>

PATM <sup>b</sup> mmol	 mmol	<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub> NiMe mmol	PhI mmol	Products (mmol)		
				MeOC <sub>6</sub> H <sub>4</sub>	<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> I
0	0	0.10	1.0	0.008	0.074	0 <sup>c</sup>
0	0.094	0.060	0.60	0.004	0.045	0 <sup>c</sup>
0.125	0.143	0.10	1.0	0.021	0.075	0.014 <sup>c</sup>
0.125	0.143	0.10	1.0 <sup>d</sup>	0.015	0.072	0.011 <sup>c</sup>

<sup>a</sup> In benzene solution at 75°C. <sup>b</sup> Phenylazotriphenylmethane. <sup>c</sup> No toluene (<0.001 mmol) observed. <sup>d</sup> In the presence of 0.085 mmol  $\text{NiBr}_2$  added to remove the induction period.

TABLE 4  
 RATES OF THE INDUCED DECOMPOSITION OF *o*-TOLYLMETHYLNICKEL(II) BY VARIOUS  
 ARYL HALIDES <sup>a</sup>

Aryl Halide	$t_{1/2}$ (sec)	$k_i$ <sup>b</sup> ( $10^3 M^{-1} \text{sec}^{-1}$ )
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> Br	219	0.63
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	227	0.61
C <sub>6</sub> H <sub>5</sub> Br	202	0.69
C <sub>6</sub> H <sub>5</sub> Br <sup>c</sup>	198	0.70
C <sub>6</sub> H <sub>5</sub> Br <sup>d</sup>	193	0.72
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> Br	150	0.93
<i>p</i> -CH <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> Br	94	1.5

<sup>a</sup> At 60°C in 0.25 *M* benzene solutions, containing 5.0 *M* aryl halide and 2.84 equiv. nickel bromide.

<sup>b</sup> Apparent second-order rate constant. <sup>c</sup> 1.42 equiv. NiBr<sub>2</sub>. <sup>d</sup> In the presence of 1.40 equiv MeOTf, NiBr<sub>2</sub> absent.

as shown by a comparison of entry 2 with entries 3 and 4 in Table 3. Moreover, the absence of *o*-anisyl radicals as key intermediates in eq. 11 is indicated by the lack of trapping by 1,4-dihydrobenzene (entry 1) \*. Therefore, free aryl radicals, either from arylmethylnickel(II) or aryl halide, cannot be directly involved in the induced decomposition.

The rate of the induced decomposition of *o*-tolylmethylnickel(II) is shown by the steep portion of Figure 3, following the induction period. The rate decreases with the concentration of bromobenzene, in accord with a second-order dependence, \*\* and it is also dependent on the nature of the aromatic substituents listed in Table 4. The apparent second-order rate constants  $k_i$  were obtained under a standard set of reaction conditions, in which only the aromatic halide was varied (see Experimental section).

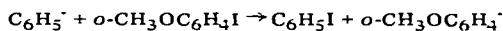
## Discussion

The kinetics as well as the aryl scrambling studies indicate that arylmethylnickel(II) complexes I can undergo reductive elimination of methylarenes by at least two principal pathways. The first involves an intramolecular loss of the aryl and methyl groups in a unimolecular step. The inverse dependence of the rate on the phosphine concentration supports a dissociative loss of this ligand from I, prior to reductive elimination. Scheme 1 represents the simplest formulation of the mechanism which accords with the results (L = triethylphosphine).

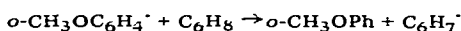
### SCHEME 1



\* The formation of iodobenzene in Table 3 arises via the facile transfer of iodine from anisyl iodide to phenyl radical [11].



The resulting anisyl radical eventually leads to enhanced yields of anisole by hydrogen abstraction from 1,4-dihydrobenzene.



\*\* The detailed kinetics have not been carried out.

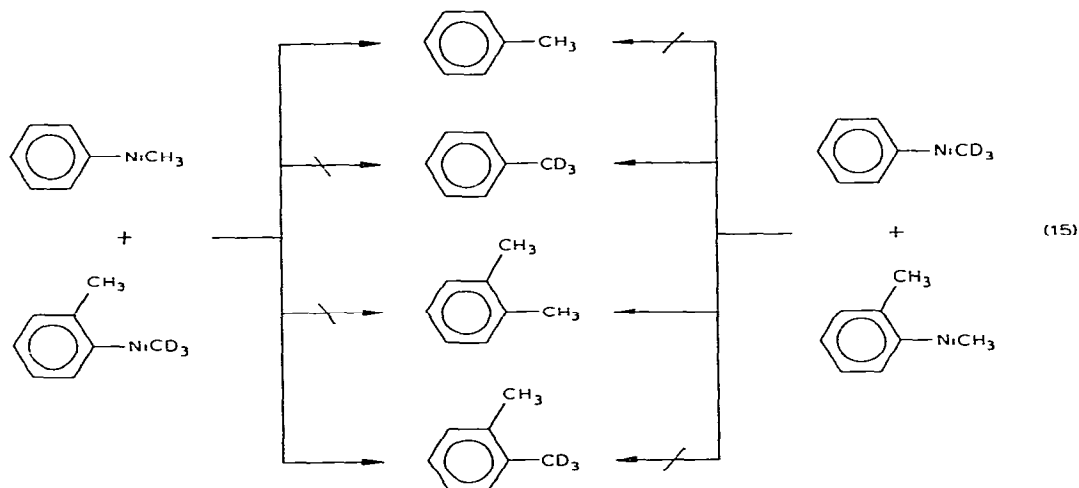


According to Scheme 1, the kinetics for reductive elimination is given by the rate expression:

$$-\frac{d[\text{ArNiMeL}_2]}{dt} = \frac{k_1 K_1}{K_1 + [\text{L}]} [\text{ArNiMeL}_2] \quad (14)$$

in which the inverse phosphine dependence derives from the mass law effect in eq. 12. Indeed, the pseudo first-order rate constant defined by  $k_1 k_1 / (K_1 + [\text{L}])$  in eq. 14 is identical to the experimentally observed rate constant  $k_{\text{obs}}$  in eq. 5, with  $k_1 = k$  and  $K_1 = K$ .

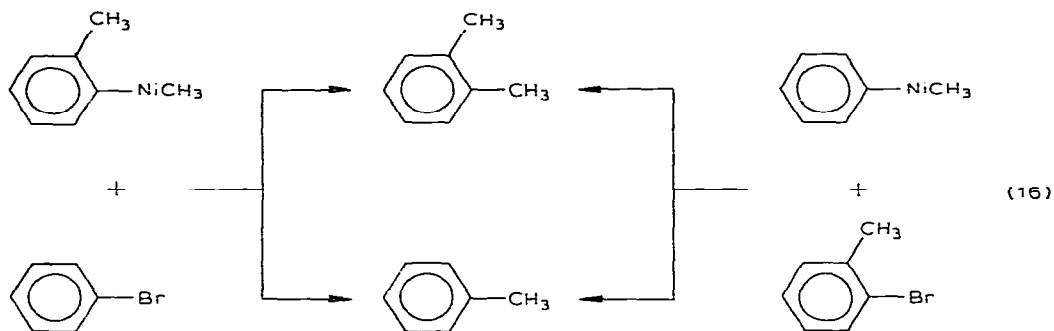
The dissociative mechanism in Scheme 1 relates the reductive elimination from  $\text{ArNiMeL}_2$  directly to the coordinatively unsaturated intermediate  $\text{ArNiMeL}$ . As such, it is analogous to other dissociative mechanisms for reductive eliminations previously examined with a variety of organogold(III) and platinum(IV) complexes [12]. Such a relatively straightforward process, however, is in striking contrast to the second route for the reductive elimination of arylmethylnickel(II), namely that induced by aryl halides. Although the stoichiometries of both reactions are the same (i.e., reductive elimination in eq. 2 followed by oxidative addition in eq. 3 is equivalent to the induced decomposition in eq. 6), they must proceed via entirely different pathways. Kinetically, the induced decomposition proceeds much more readily than the straight thermolysis (see Figure 3)\*. More distinctively, the direct thermal reductive elimination involves no scrambling of aryl and methyl groups. Thus isotopic double labelling studies show that the thermal reductive elimination in eq. 2 is an intramolecular process, since no crossover (scrambled) products were formed when an equimolar mixture of deuterium labelled compounds was thermolyzed in decalin solution, i.e., [8]



On the other hand, in the induced decomposition of *o*-tolylmethylnickel(II) by bromobenzene, the *o*-tolyl and methyl ligands are extensively scrambled with

\* A quantitative comparison of first-order and second-order processes is precluded.

the phenyl group, i.e.,



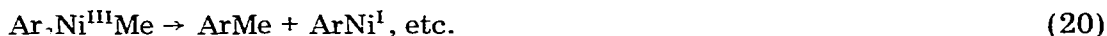
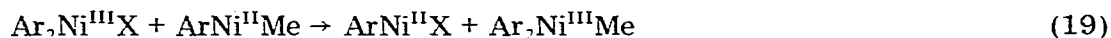
(See also eqs. 7 and 8.) The induced decomposition clearly cannot proceed via an intramolecular elimination (i.e., eq. 2) followed by oxidative addition of bromobenzene (compare eq. 3).

A further, important distinction between these pathways evolves from kinetic studies. Thus, the induced decomposition is a radical chain, as opposed to a molecular process. Indeed the observation of induction periods, the effects of inhibitors (phosphine, quinones) and promoters (nickel bromide, methyl triflate), and the scrambling of aryl groups in the absence of halogen exchange are all earmarks of a radical chain process, the details of which have been carefully delineated in a related study of biaryl formation from arylhalonickel(II) and aryl halides, i.e. [13],



As applied to the reductive elimination from arylmethylnickel(II), the propagation steps for this radical chain mechanism are represented in Scheme 2\*. (The phosphine ligands have been omitted, and the formal oxidation states of nickel are included only to emphasize the redox changes.)

SCHEME 2

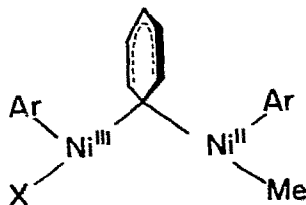


According to this mechanism\*\*, paramagnetic nickel(I) and nickel(III) species are the reactive intermediates leading to the scrambling of aryl groups during reductive elimination. Thus, the aryl halide is introduced into the catalytic cycle by oxidative addition to nickel(I) in eq. 18, and this aryl group is subsequently scrambled by ligand transfer in eq. 19. Such an aryl transfer is tantamount to electron transfer between nickel(II) and nickel(III) centers, and it should be considered in the context of inner-sphere redox processes [14]. Ac-

\* To avoid repetition, the reader is referred to ref. 13 for details of the mechanistic analysis of radical chain processes, based on this type of experimental results.

\*\* See ref. 13 for other mechanisms considered, but rejected on the basis of similar experimental evidence. See also ref. 5, p. 393 ff. The selectivity in the transfer of aryl ligands in eq. 19 is noteworthy.

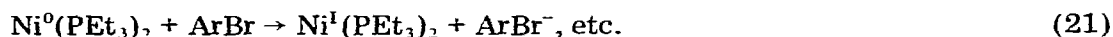
cordingly, the activated complex III draws upon other examples of bridging aryl ligands [15].



(III)

(Aryl radicals could also conceivably induce aryl scrambling, but the results in Table 3 conclusively rule them out as viable intermediates during reductive elimination.) In Scheme 2, the metastable nickel(III) intermediate [16,17] undergoes preferential reductive elimination of methylarene in eq. 19, rather than biaryl\*. The low yields of biaryls may be attributed to such a competition, although this cannot be rigorously differentiated from the further reaction of the product in eq. 17. The lability of various organonickel(III) species to reductive elimination as in eq. 20 has been described in previous studies [16,17,18].

The initiation of the radical chain mechanism for reductive elimination in Scheme 2 is directly related to the formation of either nickel(I) or nickel(III) species. There are several routes by which these paramagnetic species may be generated from diamagnetic precursors. Thus the induction period could be overcome by the partial reductive elimination of arylmethylnickel(II) in eq. 2, followed by the facile oxidation of  $\text{Ni}^0(\text{PEt}_3)_2$  to nickel(I) species by aryl halide, i.e.,



Such an electron transfer process has recently been demonstrated for  $\text{Ni}(\text{PEt}_3)_3$  [19]. Aryl halides are also capable of oxidizing arylmethyl(II) directly to nickel(II) species\*\*. Indeed, the close analogy of I to arylhalonickel(II), described earlier, [13] provides additional routes by which the radical chain process in Scheme 2 can be initiated. Furthermore, the inhibition studies follow similar patterns in both systems, and the interested reader is referred to that study [13] for the detailed discussion of the inhibitory effects of various additives on these radical chain processes.

## Conclusions

Two concurrent pathways have been identified for reductive elimination of methyl-arenes from a variety of square planar arylmethyl-bis(triethylphosphine)-nickel(II) complexes,  $\text{ArNiMeL}_2$ . In the straight thermolysis, the kinetics and aryl scrambling studies support a dissociative mechanism in which the prior loss

\* The selectivity in the reductive elimination of aryl and methyl ligands merits further study.

\*\* Arylmethylnickel(II) should be a significantly better electron donor than the corresponding aryl-bromonickel(II). See ref. 5, chapter 15.

of one of the phosphine (L) ligands is followed by an intramolecular reductive elimination of the aryl and methyl ligands concomitantly from the 3-coordinate arylmethyl-mono-phosphinenickel(II) intermediate. Aryl halides induce a second pathway in which a radical chain process can be identified by its susceptibility to inhibition, and attributed to paramagnetic nickel(I) and nickel(III) species as reactive intermediates. The latter, not aryl radicals, play the key role in aryl exchange leading to extensive scrambling of ligands during the induced reductive elimination. This represents the first instance in which the competition between molecular and radical chain processes has been clearly identified for reductive elimination, important for the formation of carbon-carbon bonds in organometallic systems.

## Experimental section

### Materials

Triethylphosphine was purchased from Pressure Chemical Co. and used without further purification. *trans*-Dibromobis(triethylphosphine)nickel(II) was prepared by the procedure described by Jensen and Nygaard [20]. A solution of methyllithium in ether was obtained from the Foote Chemical Co. and the concentration was determined by double titration and GLC methods. [21] Phenylazotriphenylmethane was prepared according to Wang's procedure [10]. Diphenylmethane and 1,4-dihydrobenzene, obtained from Aldrich Chemical Co., were redistilled before use. Solvents and reagents used in this study were commercial reagent grade materials, repurified by standard methods: Tetrahydrofuran, diethyl ether and hydrocarbon solvents were purified by distillation from sodium benzophenone ketyl under argon prior to use. Acetonitrile was distilled from P<sub>2</sub>O<sub>5</sub>. All reactions and manipulations of air-sensitive nickel complexes were carried out under an argon atmosphere using Schlenk equipment and standard benchtop techniques [22]. Melting points were determined in sealed capillary tubes in vacuo and are uncorrected. Proton magnetic resonance spectra were obtained on a Varian T-60 spectrometer using tetramethylsilane as an internal standard, or otherwise as specified. The <sup>31</sup>P NMR spectra were recorded at 40.4 MHz on a Varian XL-100 NMR spectrometer, employing 85% H<sub>3</sub>PO<sub>4</sub> as an external standard. The ultraviolet-visible absorption and infrared spectra were recorded on Cary 14 and Perkin-Elmer 221 spectrophotometers, respectively. A Beckmann GC-5 gas chromatograph was used for the analysis of arenes.

### Synthesis of arylbromobis(triethylphosphine)nickel(II)

*trans*-*o*-Tolyl-bromo-bis(triethylphosphine)nickel(II). An ethereal solution of *o*-tolylmagnesium bromide was prepared by the entrainment method from 6.7 g *o*-bromotoluene (40 mmol), 4.5 g ethylene bromide (24 mmol) and 4 g magnesium turnings. The solution was cooled in an ice bath and a benzene solution of 12 g (25 mmol) dibromobis(triethylphosphine)nickel(II) added. After 10 min, the reaction was cooled further and an aqueous solution of 10% HBr was added. Extraction with ether, followed by washing, drying and evaporation of the solvent gave a yellow oil which afforded 8.3 g (70% yield) of material

melting at 102–103°C (dec.) after recrystallization from ethanol [23]. The  $^1\text{H}$  NMR spectrum consisted of an *o*-CH<sub>3</sub> singlet ( $\delta$  2.80 ppm, 3 H) and unresolved multiplets for aromatic protons at  $\delta$  6.75 (3 H) and  $\delta$  7.25 ppm (1 H), in addition to the ethyl multiplets between  $\delta$  0.7 and 1.6 ppm. The  $^{31}\text{P}$  NMR spectrum consisted of a sharp singlet,  $\delta$  9.5 ppm. The visible absorption spectrum of *o*-tolylbromonickel(II) has an absorption maximum at 407 nm ( $\epsilon$   $4.67 \times 10^2$ ) in hexane solution.

Anal. Found: C, 48.7; H, 8.1; P, 13.1. Calcd. for C<sub>19</sub>H<sub>37</sub>NiP<sub>2</sub>Br: C, 48.96; H, 8.00; P, 13.29%

*trans-o-Anisylbromobis(triethylphosphine)nickel(II)* was prepared by a similar procedure: to a stirred ethereal solution of 6.0 g (13.2 mmol) *trans*-dibromobis(triethylphosphine)nickel(II) at  $-10^\circ\text{C}$ , was added a solution of *o*-anisylmagnesium bromide prepared from 3.5 g (18.7 mmol) *o*-anisyl bromide, 1.0 g (41 mmol) magnesium and 2.0 g (10.6 mmol) 1,2-dibromoethane in 30 ml ether. After 10 min, the reaction mixture was cooled further and a solution of 5% aqueous HBr added. Extraction, followed by washing, drying and evaporation of the solvent, gave a dark brown solid residue which included some starting material. The product was recrystallized from hot hexane several times, yielding 1.0 g of brown crystals, mp. 108–110°C. The  $^1\text{H}$  NMR spectrum in C<sub>6</sub>D<sub>6</sub> consisted of a singlet ( $\delta$  3.30 ppm 3 H) for the methoxy group and unresolved multiplets ( $\delta$  6.22, 6.81 ppm; 4 H) for the aromatic protons, in addition to multiplets (between  $\delta$  0.65 and 1.65 ppm; 30 H) for the ethyl groups.

Anal. Found: C, 47.6; H, 7.8; P, 12.7. Calcd. for C<sub>19</sub>H<sub>37</sub>OP<sub>2</sub>BrNi: C, 47.34; H, 7.74; P, 12.85%.

*trans-Phenylbromobis(triethylphosphine)nickel(II)*. The procedure was similar to that employed for the *o*-tolyl analog except that anaerobic conditions were maintained throughout all operations. Yield: 85%; mp. 82–83°C (dec.). The  $^1\text{H}$  NMR spectrum showed two broad aromatic resonances at  $\delta$  6.90 (3 H) and  $\delta$  7.40 ppm (2 H) in addition to those due to triethylphosphine. The  $^{31}\text{P}$  NMR spectrum consisted of a single sharp resonance at  $\delta$  10.5 ppm.

Anal. Found: C, 47.6; H, 7.5; P, 14.0. Calcd. for C<sub>18</sub>H<sub>35</sub>NiP<sub>2</sub>Br: C, 47.82; H, 7.81; P, 13.71%.

#### *Synthesis of arylmethylbis(triethylphosphine)nickel(II)*

*trans-Phenylmethylbis(triethylphosphine)nickel(II)*. To an ethereal solution of 8 g (18 mmol) *trans*-phenyl-bromo-bis(triethylphosphine)nickel(II), was added 15 ml of 1.8 M methyllithium in ether. The solution was stirred for 30 min, always maintaining the temperature below  $-30^\circ\text{C}$ . Trimethylchlorosilane (5 ml) was added and the solvent transferred in vacuo from the reaction vessel immersed in an ice bath. The solution was concentrated until approximately 10 ml remained, whereupon the solution was recooled to  $-78^\circ\text{C}$  and the excess ethereal solution removed with a hypodermic syringe. The remaining brown-yellow solid was dried in vacuo, and the solid redissolved in hexane at room temperature. The solution was filtered, the volume reduced by evaporation on

a vacuum line and the solution recooled to  $-78^{\circ}\text{C}$ . The yellow solid was collected and recrystallized several times from hexane to afford yellow brown crystals, which are highly air-sensitive. Yield: 3 g (40%); mp.  $71.5\text{--}72^{\circ}\text{C}$  (dec.). The  $^1\text{H}$  NMR spectrum consisted of the  $\text{NiCH}_3$  resonances at  $\delta -0.76$  ppm (3 H, t,  $J = 12$  Hz) and the unresolved aromatic resonances at  $\delta 7.40$  (2 H) and  $6.90$  ppm (3 H). The  $^{31}\text{P}$  NMR spectrum consisted of a single sharp resonance at  $\delta 17.5$  ppm.

Anal. Found: C, 58.7; H, 9.6; P, 15.8. Calcd. for  $\text{C}_{19}\text{H}_{38}\text{NiP}_2$ : C, 58.94; H, 9.89; P, 16.00%.

*trans-o-Anisylmethylbis(triethylphosphine)nickel(II)*. A similar procedure was followed with 1.1 g (2.28 mmol) of *o*-anisylbromobis(triethylphosphine)-nickel(II) in 20 ml ether with 3.6 mmol methyl lithium at  $-50^{\circ}\text{C}$ . The mixture was stirred for 1 h before trimethylsilyl chloride was added and worked up in the usual manner. Recrystallization from hexane several times yielded yellow, air-sensitive material. The  $^1\text{H}$  NMR spectrum indicated the  $\text{NiCH}_3$  resonances as triplets at  $\delta -0.67$  ppm (3 H,  $J = 9$  Hz), and the methoxy resonance at  $\delta 3.50$  ppm (3 H, s).

*trans-o-Tolylmethylbis(triethylphosphine)nickel(II)*. To an ethereal solution of 1.0 g (2.15 mmol) *trans-o*-tolylbromobis(triethylphosphine)nickel(II) at  $-40^{\circ}\text{C}$  was added a 1.5 M solution (3.0 mmol) of methyl lithium under a positive pressure of argon. The solvent was removed in vacuo after stirring the solution for 60 min at this temperature. The dry pale yellow powder was obtained from hexane solution by cooling to  $-78^{\circ}\text{C}$ . Yield: 0.65 g (79%). Recrystallization afforded prismoidal brown crystals melting at  $72\text{--}73^{\circ}\text{C}$  (dec.). The  $^1\text{H}$  NMR spectrum consisted of sharp resonances for  $\text{NiCH}_3$  at  $\delta -0.72$  ppm (3 H, t,  $J = 12$  Hz); *o*- $\text{CH}_3$ :  $\delta 2.52$  ppm singlet (3 H) and two aromatic resonances:  $\delta 7.25$  (1 H) and  $\delta 6.65$  ppm (3 H). The  $^{31}\text{P}$  NMR spectrum consisted of a single sharp resonance at  $\delta 17.5$  ppm.

Anal. Found: C, 59.6; H, 10.2; P, 15.5. Calcd. for  $\text{C}_{20}\text{H}_{40}\text{NiP}_2$ : C, 59.87; H, 10.05; P, 15.44%.

### Synthesis of diaryl-bis(triethylphosphine)nickel(II)

*trans-di-o-anisyl-bis(triethylphosphine)nickel(II)*. *o*-Bromoanisole (4.0 g, 21.4 mmol) and *n*-butyllithium (20 ml of a 1.25 M solution in hexane) were mixed in 30 ml hexane. The resulting *o*-anisyllithium precipitate was removed by filtration through a sintered glass filter. The solid *o*-anisyllithium was washed several times with hexane and redissolved in 25 ml THF. The solid *o*-anisyllithium was then added to *trans*-dibromobis(triethylphosphine)nickel(II) (4.5 g, 9.9 mmol) dissolved in 30 ml of degassed, anhydrous ether under argon with the aid of a hypodermic syringe. The reaction mixture was stirred for 15 min and 100 ml of water added. The organic layer, as well as insoluble residue, were collected, and the ether removed in vacuo. The residue was then recrystallized twice from hexane to afford 0.8 g of light yellow crystals, mp.  $134\text{--}135^{\circ}\text{C}$ . The proton NMR spectrum in acetone- $d_6$  consisted of a singlet ( $\delta 3.77$  ppm, 6 H) due to the methoxy group, and unresolved multiplets for aromatic protons ( $\delta 6.47$ , 3 H;  $7.27$  ppm, 1 H). The resonances due to the ethyl groups consisted of multiplets (between  $\delta 0.87$  and  $1.17$  ppm, 30 H).

Anal. Found: C, 61.9; H, 9.0; P, 12.3. Calcd. for  $C_{20}H_{14}O_2P_2Ni$ : C, 61.32; H, 8.71; P, 12.16%.

### *Product studies*

*Thermolysis of arylmethyl-bis(triethylphosphine)nickel(II)*. The thermal decompositions were carried out at either 75 or 80°C in sealed tubes containing 0.2–0.5 M arylmethylnickel(II) in either cyclohexane, benzene or decalin solution. As the reaction progressed, the clear yellow solution turned progressively purple but remained homogeneous. Upon completion of the thermolysis, the contents of the tube were treated in either of two ways. First, it was exposed to air, and the solution filtered and analyzed by gas chromatography for the arene. Alternatively, aryl bromide was added to the purple solution, whereupon the color changed to brown and the arylbromonickel(II) was isolated in 20–30% yield.

*Induced decomposition of arylmethylnickel(II) by aryl halides*. Typically, *trans-o*-tolylmethylbis(triethylphosphine)nickel(II) (0.191 g, 0.48 mmol) was weighed into a small Schlenk flask and 1.9 ml of freshly degassed solvent added. An aliquot (0.6 ml) of this solution was transferred to a tube under argon, and a calculated amount of bromobenzene was added. The tube was degassed by successive freeze-pump-thaw cycles and sealed in vacuo. The tube was placed in a constant temperature bath and heated for 20 h. Upon opening, a known amount of internal standard (ethylbenzene) was added, and the arene analyzed by gas liquid chromatography using a 10 ft column of 15% Apiezon L at 105°C. The solution was then subjected to exhaustive vacuum distillation at ambient temperatures, and benzene reintroduced. The arylbromobis(triethylphosphine)nickel(II) was analyzed either by  $^1H$  NMR or ultraviolet spectroscopy.

### *Kinetic studies*

The rates of reductive elimination were followed by monitoring the  $^1H$  NMR spectral changes of the arylmethylnickel(II) complex. In a typical procedure, *o*-tolylmethylbis(triethylphosphine)nickel(II) (0.151 g, 0.38 mmol) was dissolved in 1.2 ml benzene containing 0.065 g (0.405 mmol) 2-methoxynaphthalene as the internal standard. Aliquots of this solution were transferred with the aid of a hypodermic syringe to NMR tubes which had previously been flushed with argon. The tubes were degassed, sealed in vacuo and heated in a constant temperature bath. At prescribed periods the tubes were removed from the bath, quickly cooled and analyzed.

The same procedure was followed for the induced decomposition, except the aryl halide was added prior to degassing and sealing the tubes.

### *Manipulation of the induction period*

In a typical procedure, arylmethylnickel(II) was weighed into a small Schlenk tube and measured amounts of degassed solvent, aryl halide, and internal standard (either 2-methoxynaphthalene, diphenylmethane or mesitylene) were added. Aliquots of this solution were transferred with the aid of a hypodermic syringe into several NMR tubes under argon. Various amounts of additive were added, and the tubes degassed and sealed in vacuo. The rates were

followed by the disappearance of the  $\text{NiCH}_3$  resonance and the shift of the methoxy or methylaryl resonance in the  $^1\text{H}$  NMR spectrum of the arylmethyl-nickel(II). The induction period was taken from the extrapolation of the induced rate of reductive elimination (see Figure 3).

### *Effect of phenyl radicals*

The thermal decomposition of phenylazotriphenylmethane (PATM) generates free phenyl radicals at  $60^\circ\text{C}$  in benzene solution with a half life of approximately 20 min, as described by eq. 10 [10]. PATM (0.087 g, 0.25 mmol) and 1,4-dihydrobenzene (0.023 g, 0.29 mmol) were added to a standard solution of *o*-anisylmethylbis(triethylphosphine)nickel(II) (0.206 mmol) and *o*-iodoanisole (2.06 mmol) in benzene. Aliquots were transferred to several Pyrex tubes (one contained 0.055 mmol  $\text{NiBr}_2$ ), which were subsequently degassed and sealed in vacuo. After heating in a constant temperature bath at  $75^\circ\text{C}$  for 3 h, the contents of the tubes were analyzed for arenes, using gas liquid chromatography with ethylbenzene as the internal standard.

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### References

- 1 P.S. Braterman and R.J. Cross, *Chem. Soc. Rev.*, 2 (1973) 271.
- 2 M.C. Baird, *J. Organometal. Chem.*, 64 (1974) 289.
- 3 R.J. Davidson, M.F. Lappert and R. Pearce, *Chem. Rev.*, 76 (1976) 219.
- 4 R.R. Schrock, G.W. Parshall, *Chem. Rev.*, 76 (1976) 243.
- 5 J.K. Kochi, *Organometallic Mechanisms and Catalysis*, Academic Press, New York, 1978.
- 6 P.W. Jolly and G. Wilke, *The Organic Chemistry of Nickel*, Vol. 1 and 2, Academic Press, New York, 1975.
- 7 G.W. Parshall, *J. Amer. Chem. Soc.*, 96 (1974) 2360.
- 8 D.G. Morrell and J.K. Kochi, *J. Amer. Chem. Soc.*, 97 (1975) 7262.
- 9 (a) R.C. Kerber, G.W. Urry and N. Kornblum, *J. Amer. Chem. Soc.*, 87 (1965) 4520. (b) N. Kornblum, R. Michel and R.C. Kerber, *J. Amer. Chem. Soc.*, 88 (1966) 5662. (c) N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, 14 (1975) 734. (d) G.A. Russell and W.C. Danen, *J. Amer. Chem. Soc.*, 88 (1966) 5663.
- 10 S.G. Cohen and C.H. Wang, *J. Amer. Chem. Soc.*, 75 (1953) 5504.
- 11 W.C. Danen, *Methods Free Radical Chem.* 5 (1974) 1.
- 12 See reference 5, Chapter 12.
- 13 T.T. Tsou and J.K. Kochi, *J. Amer. Chem. Soc.*, 101 (1979) 7547.
- 14 For a recent review, see D.E. Pennington, in *Coordination Chemistry*, Vol. 2, A.E. Martell, Ed., ACS Monograph 174, Washington, D.C., 1978, p. 476 ff.
- 15 G. van Koten and J.G. Noltes, *J. Amer. Chem. Soc.*, 101 (1979) 6593.
- 16 M. Akermark and B. Akermark, *J. Chem. Soc., Chem. Commun.*, (1978) 66.
- 17 T.T. Tsou and J.K. Kochi, *J. Amer. Chem. Soc.*, 100 (1978) 1634.
- 18 Compare also G.W. Daub, *Prog. Inorg. Chem.*, 22 (1977) 409.
- 19 T.T. Tsou and J.K. Kochi, *J. Amer. Chem. Soc.*, 101 (1979) 6319.
- 20 K.A. Jensen and B. Nygaard, *Acta Chem. Scand.* 3 (1949) 474.
- 21 A. Tamaki, S.A. Magennis and J.K. Kochi, *J. Amer. Chem. Soc.* 96 (1974) 6140.
- 22 D.F. Shriver, *The Manipulation of Air-sensitive Compounds*, McGraw-Hill, New York, 1969.
- 23 J. Chatt and B.L. Shaw, *J. Chem. Soc.* (1960) 1718.