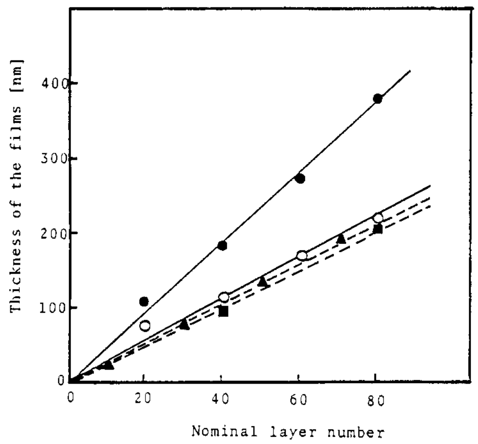

**Figure 2.** Nominal layer number vs. thickness of LB films (○) mixed film of **1** and **2** of molar ratio *r* (*r* = 1:5) deposited at 25 mN m$^{-1}$; (●) mixed films of **1** and **2** (*r* = 1:5) at 40 mN m$^{-1}$; (▲) films of pure **2** at 25 mN m$^{-1}$; (■) films of pure **2** at 40 mN m$^{-1}$.

citance of the LPF were 1.5 times larger than those of the HPF for the same layer numbers, which also showed that HPF are thicker than LPF. The thickness of various types of LB films with four different stroke numbers from 21 to 81 were measured by the stylus method (Figure 2). HPF were twice as thick as LPF, while the thickness of LPF and pure **2** deposited at 25 or 40 mN m$^{-1}$ coincided with one another. This relationship holds for the case of the smaller fraction of **1**, [**1**]:[**2**] = 1:10. In this case, it is apparent that **1**, if squeezed out from a monolayer of **2**, cannot cover the whole area of **2** in the complex layer.

From the facts described above, we may conclude that **1** is squeezed out to form islands, each serving as a pillar between two monolayers of **2** in HPF, hence the thickness of unit layer of HPF is increased to be twice that of LPF. The study of the detailed structure is in progress.

**Acknowledgment.** We thank Professor K. Fukuda and Dr. H. Nakahara for helpful comments. Thanks are also due to Drs. S. Matsuzaki and M. Matsumoto for stimulating discussions.

**Registry No. 1**, 97521-39-6; **2**, 506-30-9.

# Duality of Mechanism, Radical and Nonradical, in the Dehalogenation of Aryl Halides by Lithium 2,6-Dimethylpiperidide[1]

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*Received April 26, 1985*

Metal derivatives of dialkylamines sometimes effect hydrodehalogenation[3-8] of aryl halides. A variety of mechanisms, all of ionic type, have been proposed.

Alkoxide ions also dehalogenate aryl halides; a radical chain mechanism appears to prevail.[9-11] We visualized the possibility that the dehalogenation by metal derivatives of amines might occur by a similar sort of mechanism, the salient features of which are shown in Scheme I.

**Scheme I**

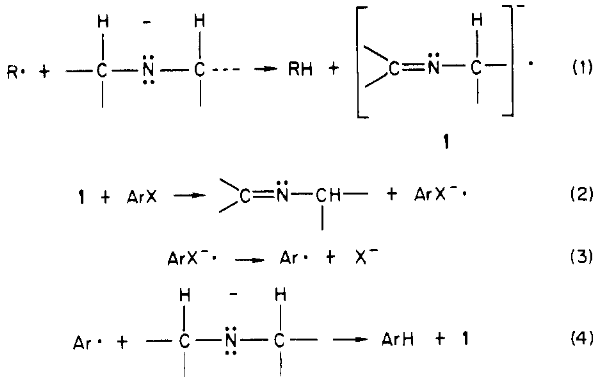


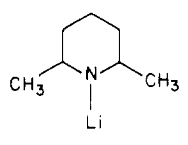
**Table I.** Reactions of Lithium 2,6-Dimethylpiperidide with Aryl Halides in 2,6-Dimethylpiperidine Solution

| ArX | other substance | temp | time, h | prod mix |  |  |
|---|---|---|---|---|---|---|
|  |  |  |  | ArX[a] | ArH | **5** or **6** |
| **3i** | nil | rt[b] | 1 | 57 | 37 | **5**, 1% |
| **3i** | $(t\text{-BuO})_2$[c] | rt | 1 | 18 | 63 | nil |
| **3i** | $Ph_2C{=}CH_2$[d] | rt | 1 | 72 | 18 | **5**, 8% |
| **3i** | PhN=NPh[c] | rt | 1 | 76 | 10 | **5**, 4% |
| **3c** | nil | reflux | 2 | 43 | 26 | **5**, 17% |
| **3c** | $(t\text{-BuO})_2$[c] | reflux | 2 | 54 | 36 | **5**, 4% |
| **3c** | $Ph_2NNPh_2$[d] | reflux | 2 | 35 | 53 | **5**, 5% |
| **3c** | $Ph_2C{=}CH_2$[d] | reflux | 2 | 46 | 20 | **5**, 21% |
| **4i** | nil | rt | 1 | 95 | 5 | nil |
| **4i** | $(t\text{-BuO})_2$[d] | rt | 1 | 72 | 27 | nil |
| **4i** | nil | reflux | 0.5 | 16 | 72 | nil |
| **4i** | 12-crown-4[e] | reflux | 0.5 | 87 | 9 | nil |
| **4b** | nil | reflux | 2 | 49 | 33 | **6**, 5% |
| **4b** | $Ph_2C{=}CH_2$[f] | reflux | 2 | 60 | 16 | **6**, 10% |
| **4b** | $Ph_2NNPh_2$[d] | reflux | 1 | 45 | 45 | *g* |
| **4b** | 12-crown-4[e] | reflux | 1 | 96 | 4 | *g* |

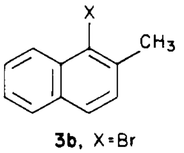
[a] Recovered, unreacted ArX. [b] rt = room temperature. [c] 20 mol %. [d] From 6 to 11 mol %. [e] 100 mol %. [f] 57 mol %. [g] Not sought.

In Scheme I, step 1, a radical abstracts a hydrogen atom from C-1 of the amide ion, generating radical ion **1**. **1** is the radical anion of an imine. Steps 2, 3, and 4 constitute a propagation cycle; in (2) an electron is transferred from **1** to the aryl halide, in (3) the resulting radical anion fragments to form the corresponding aryl radical, and in (4) the aryl radical abstracts hydrogen from C-1 of the amide, to regenerate **1**. The amide ion may be free or associated with Li$^+$, even covalently. Termination steps are implied.

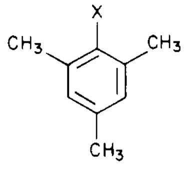
For our experiments, we chose to use lithium 2,6-dimethylpiperidide (**2**) as the amide reagent and two types of aryl halides



**2**



**3b**, X = Br
**c**, X = Cl



**4b**, X = Br
**c**, X = Cl
**h**, X = H
**i**, X = I

unable to afford aryne intermediates as test substrates: 1-halo-2-methylnaphthalenes (**3**) and mesityl halides (**4**). On treatment with **2**, in *cis*-2,6-dimethylpiperidine solution, substrates **3** and

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[1] Research support from the National Science Foundation is gratefully acknowledged.

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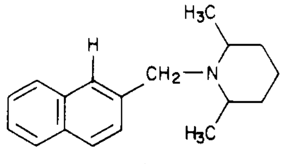
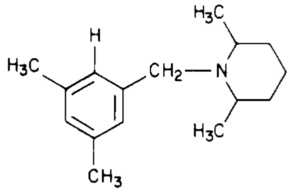
**4** gave **3h** and **4h** but also varying amounts of tele substitution products **5** and **6**, respectively. Data from some representative experiments are set forth in Table I.



**5**



**6**

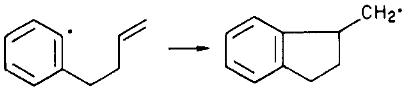
Concerning the first four entries, we note that the presence of di-*tert*-butyl peroxide causes the yield of **3h** from **3i** to increase from 37% to 63% while the presence of 1,1-diphenylethene or azobenzene lowers it respectively to 18% or 10%. Inasmuch as di-*tert*-butyl peroxide is a radical source and the other two added substances are radical and/or electron traps, these data fulfill expectations for a radical chain mechanism.

The four entries for substrate **3c** in Table I show some of the same features, but in muted form: a small augmentation of dehalogenation yield by di-*tert*-butyl peroxide, and a modest diminution by 1,1-diphenylethene. Tetraphenylhydrazine causes an *increase* in dehalogenation yield; conceivably it acts as a source of radicals (by homolysis to $Ph_2N\cdot$). It is noteworthy that the yield of substitution product **5** wanes as the yield of **3h** waxes.

The four experiments in Table I concerning **4i** show it to be less reactive than **3i** in dehalogenation. Again acceleration by di-*tert*-butyl peroxide is evident. The crown ether[12] 12-crown-4, which chelates $Li^+$ well, strongly inhibits deiodination.

The four experiments on **4b** manifest qualitatively the same efects as just discussed for **4i**, except that some tele substitution to form **6** now occurs.

Thanks to Beckwith and co-workers,[13,14] we have available another tool to probe radical character, namely, the propensity of the *o*-(3-butenyl)phenyl radical (**7**), to cyclize to 1-indanylmethyl radical (**8**). Reaction of *o*-(3-butenyl)iodobenzene[15] with **2** in 2,6-dimethylpiperidine solution (24 h at room temperature) afforded 28% of 1-methylindan as well as 27% of 3-butenylbenzene, affirming the intermediacy of **7**. But the chlorine analogue, *o*-(3-butenyl)chlorobenzene, under the same conditions gave 3-butenylbenzene (10%) free of cyclization product. Thus a nonradical mechanism is indicated for it.



**7** **8**

Dehalogenatons of **3i** and of **3c**, through the action of **2** in *N*-deuterio-2,6-dimethylpiperidine solution, afforded **3h** free of deuterium at C-1 but deuterated in the methyl group (owing to base-catalyzed hydron exchange). These results inveigh against any mechanism that would involve 1-lithio-2-methylnaphthalene or the 2-methyl-1-naphthyl anion as an intermediate.

Our experimental findings are concordant with expectations from the mechanism of Scheme I insofar as aryl iodides are concerned. One aryl chloride result is contraindicative of that mechanism, while others are weakly in accord with it. We think that some nonradical mechanism of hydrodechlorination may experience an overlay of reaction according to Scheme I when a good source of radicals is present.

The remarkable retardation of radical chain dehalogenation by 12-crown-4 suggests that tight ion pairing if not actual covalent bonding with lithium is essential if some unidentified step(s) is to occur.

Our observations furnish only meager indications of how tele substitution to form **5** or **6** occurs: In debromination of **3b** in *N*-deuterio-2,6-dimethylpiperidine at reflux (16 h), besides **3h** (48%) free of deuterium at C-1 we obtained 29% of **5** which carried deuterium at C-1. Data in Table I suggest the mechanism to be of nonradical character.

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[12] Formally, 12-crown-4 is 1,4,7,10-tetraoxacyclododecane.

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[15] The *o*-(3-butenyl)iodobenzene was prepared by Dr. G. F. Meijs, to whom we are grateful.

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## Metal Ion Complexation by Rhodium and Iridium Metallomacrocycles. The Preparation and X-ray Crystal Structures of $Rh_2(CO)_2Cl_2(\mu\text{-}Ph_2PCH_2As(Ph)CH_2PPh_2)_2$ and $[Rh_2Pd(CO)_2Cl_3(\mu\text{-}Ph_2PCH_2As(Ph)CH_2PPh_2)_2][BPh_4]$

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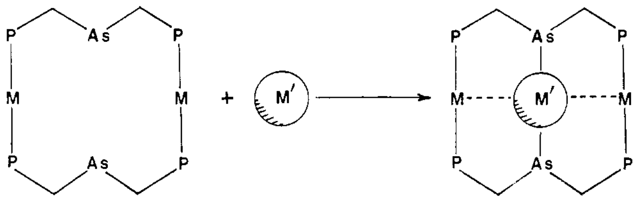
*Received February 11, 1985*

The diverse reaction chemistry that has developed around diphosphine-bridged, binuclear complexes has expanded our knowledge of metal–metal bonding, given insight into the interaction of small molecules with two metal centers, and provided models for species bound to catalytically active metal surfaces.[1,2] Polyfunctional phosphine ligands can be designed to produce more complex arrays of reactive metal centers which are expected to display multicenter metal–metal interactions and allow for multisite metal/small molecule bonding. The tripod ligand tris(diphenylphosphino)methane can stabilize or create new triangular arrays of metal centers[3,4] while bis[(diphenylphosphino)methyl]phenylphosphine[5-9] and 2,6-bis(diphenylphosphino)pyridine[10] can be used to place three or four rhodium ions into nearly linear arrays. With metal ions other than rhodium dpmp forms six-membered chelate rings which cannot, as yet, be opened up to give linear chain complexes with metal ions in close proximity.[11] Thus, to date, this class of ligands has not yielded complexes that contain linear, trinuclear arrays with any transition metals except rhodium. Here we describe the creation of metallomacrocycles **1** using the tridentate ligand bis(diphenylphosphinomethyl)phenylarsine (dpma) and the subsequent complexation, as shown in eq 1, of a third, different metal ion to form new trinuclear species **2** in which the central metal differs from the outer two. This procedure extends the range of trinuclear chains by allowing different metal ions to be placed in the center of the chain. In order to form **1** we take advantage of the



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