Radical Organometallic Phase-transfer Reactions

Vilmos Galamb and Howard Alper*†

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

The phase-transfer catalysed coupling reactions of benzylic halides, in the presence of catalytic quantities of bis(dibenzylideneacetone)palladium(0) or cobalt carbonyl, proceed *via* radical pathways.

A number of interesting metal-catalysed reactions can be effected under phase-transfer catalysis conditions.[1] The most versatile metal catalysts are those containing cobalt,[2,3] ruthenium,[4] and palladium.[5] It has been suggested that free radicals may participate in certain organometallic phase-transfer processes effected under thermal conditions. In addition, the cobalt carbonyl catalysed carbonylation of aryl and vinyl halides, in the presence of ultraviolet light, has also been postulated to proceed *via* a radical pathway.[6] We now present the first evidence for the occurrence of radical intermediates in organometallic phase-transfer reactions.

While tetrakis(triphenylphosphine)palladium(0) and Pd-(diphos)$_2$ [diphos = 1,2-bis(diphenylphosphino)ethane] catalyse the selective carbonylation of benzylic halides to acids and esters, respectively, bis(dibenzylideneacetone)-palladium(0) [Pd(dba)$_2$] induces coupling and/or dehalogenation to give hydrocarbons.[5] Radicals were believed to be involved in the latter process, a key step being the electron transfer reaction between an anionic palladium species (**1**) and the organic substrate (equation 1). Anion (**1**) is generated

$$\mathrm{ArCH_2X} + \underset{(\mathbf{1})}{\mathrm{R_4N^+Pd(OH)(dba)_2^-}} \rightarrow \mathrm{ArCH_2^{\bullet}} + {}^{\bullet}\mathrm{Pd(OH)(dba)_2} + \mathrm{R_4N^+X^-} \quad (1)$$

by hydroxide ion attack on Pd(dba)$_2$, which would make one of the two dba ligands in (**1**) monodentate. Crown-ether catalysed nucleophilic displacement (*i.e.* cyanide ion) of neutral ligands has been described by Fakley and Pidcock.[7]

It seemed conceivable that the use of the secondary halide, α-phenethyl bromide (**2**), as the organic substrate would serve as a probe of the extent of radical character of the Pd(dba)$_2$ catalysed phase-transfer reaction, since the coupled product can exist as *meso* or racemic isomers. Treatment of (**2**) with carbon monoxide, methylene chloride, 5 M NaOH, benzyltriethylammonium chloride as the phase-transfer agent, and

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† E. W. R. Steacie Fellow, 1980–82.

$$\underset{(\mathbf{2})}{\mathrm{PhCH(Me)Br}} \xrightarrow[\mathrm{CH_2Cl_2,\ 5\ M\ NaOH,\ 20\ h,\ room\ temp.,\ 1\ atm.}]{\mathrm{CO,Pd(dba)_2.PhCH_2N(C_2H_5)_3^+Cl^-}} \underset{(\mathbf{3})}{\mathrm{PhCH(Me)\text{-}CH(Me)Ph}} \quad (2)$$

$Pd(dba)_2$ as the metal catalyst [25.5/1.0 ratio of (**2**)/$Pd(dba)_2$] afforded 2,3-diphenylbutane (**3**) as the only product (no acid or ester was formed) (equation 2). Since the n.m.r. spectra of the *meso* and racemic forms are easily distinguished,[8] this method proved valuable for determining the proportion of stereoisomers. The ratio of *meso*/racemic forms was 1.00/1.10, indicating that the $Pd(dba)_2$ and phase-transfer catalysed reaction of benzylic halides is a radical process.

The coupling reaction of secondary halides, including (**2**), catalysed by cobalt carbonyl under phase-transfer conditions, has also been proposed to proceed *via* radical intermediates [$PhCHMe^\cdot$ and $^\cdot Co(CO)_4$]. Such radical species could be generated either by homolytic cleavage of $PhCH(Me)Co(CO)_4$[3] or by a single-electron transfer reaction of $R_4N^+Co(CO)_4^-$ and (**2**). We have now determined that 2,3-diphenylbutane (**3**) was formed in a 1.13/1.00 ratio of racemic/*meso* stereoisomers, by the reaction of (**2**) with carbon monoxide, toluene, 20% NaOH, benzyltriethylammonium chloride, and cobalt carbonyl [23.8/1.0 ratio of (**2**)/$Co_2(CO)_8$] at room temperature and atmospheric pressure for 22 h. Therefore the largely radical nature of this coupling reaction is established. No acid was formed in this reaction, as in the $Pd(dba)_2$ catalysed process.

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