Oxidative Addition of Alkyl Halides to Zero-Valent Palladium Complexes. Mechanisms

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Abstract: Oxidative addition reactions of alkyl halides (RX) to tetrakis(triphenylphosphine)palladium(0) afford alkylpalladium(II) complexes ($R-Pd(PPh_3)_2-X$) as primary products. The fate of the alkyl complex depends on the alkyl group present. Benzyl complexes ($R = PhCH_2-$) are stable and will undergo reactions with carbon monoxide, benzyl chloride, and acyl chlorides to give acyl palladium complexes, bibenzyl, and benzyl alkyl ketones, respectively. α-Phenethyl complexes ($R = PhCH(CH_3)-$) are not isolable because of their propensity to undergo β-elimination. A free radical decomposition leading to coupling products apparently occurs with alkyl complexes where R = 9-fluorenyl, α-carboethoxybenzyl, and trimethylsilyl, while carbanions may be involved in the decomposition of certain other alkyl complexes (R = phenacyl and indenyl).

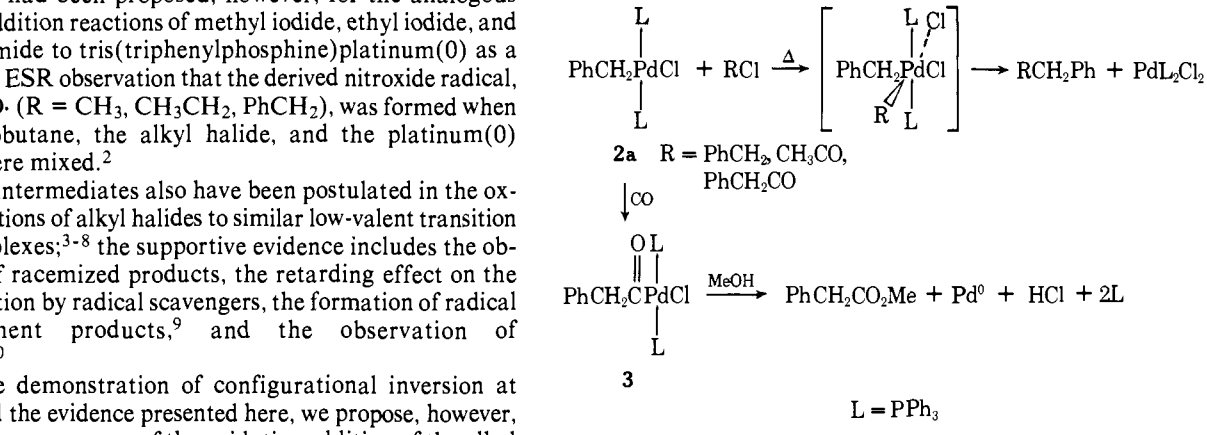
Stereospecific inversion of configuration at carbon has been demonstrated in the oxidative addition of benzyl halides to zero-valent palladium complexes.[1] A nonchain radical mechanism had been proposed, however, for the analogous oxidative addition reactions of methyl iodide, ethyl iodide, and benzyl bromide to tris(triphenylphosphine)platinum(0) as a result of the ESR observation that the derived nitroxide radical, t-Bu(R)NO· (R = CH_3, CH_3CH_2, $PhCH_2$), was formed when *tert*-nitrosobutane, the alkyl halide, and the platinum(0) complex were mixed.[2]

Radical intermediates also have been postulated in the oxidative additions of alkyl halides to similar low-valent transition metal complexes;[3-8] the supportive evidence includes the observation of racemized products, the retarding effect on the rate of reaction by radical scavengers, the formation of radical rearrangement products,[9] and the observation of CIDNP.[8,10]

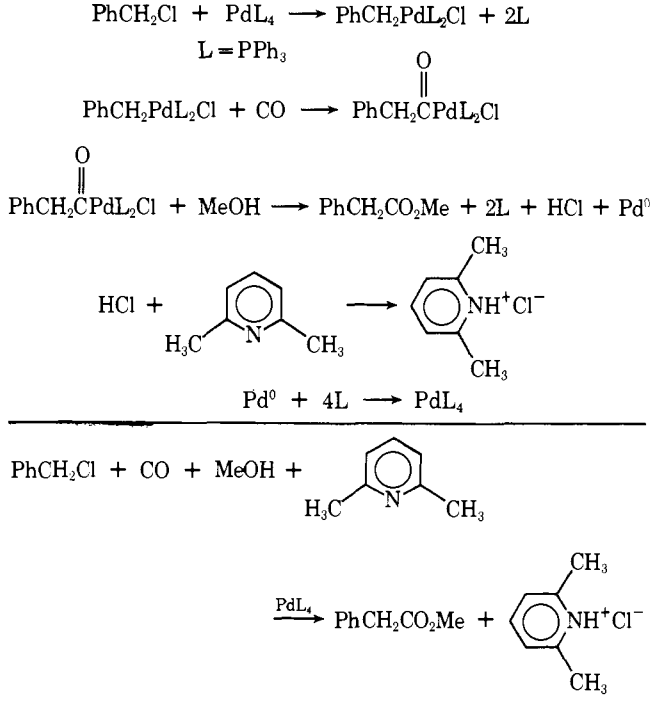
With the demonstration of configurational inversion at carbon[1] and the evidence presented here, we propose, however, that the primary process of the oxidative addition of the alkyl halides studied to palladium(0) metal complexes involves nucleophilic attack of the metal at the carbon center and that free radical species probably participate only during the decomposition of the oxidative addition product. In fact, depending on the structural characteristics of the alkyl group of the organic halide, alternative pathways for the decomposition of the oxidative adduct are possible.

Results and Discussion

Benzyl Halides. Benzyl halides undergo oxidative addition to tetrakis(triphenylphosphine)palladium(0) (**1**) to give stable benzylpalladium(II) complexes **2**[11] which are useful synthetic intermediates. For example, chloro(benzyl)bis(triphenylphosphine)palladium(II) (**2a**) undergoes reaction with benzylchloride and acyl chlorides at elevated temperatures giving bibenzyl and benzyl alkyl ketones,[12,13] respectively. A plausible mechanism for these reactions is the oxidative addition of benzyl chloride or acyl chloride at high temperature to the benzyl complex **2a** generating the unstable palladium(IV) species[14,15] which undergoes facile reductive elimination to yield dichlorobis(triphenylphosphine)palladium(II) and bibenzyl or benzyl alkyl ketone. Furthermore, the benzyl complex **2a** undergoes facile carbonylation to afford the acyl complex **3**. Methanolysis of **3** gives methyl phenylacetate with concomitant reduction of palladium(II) to palladium(0).



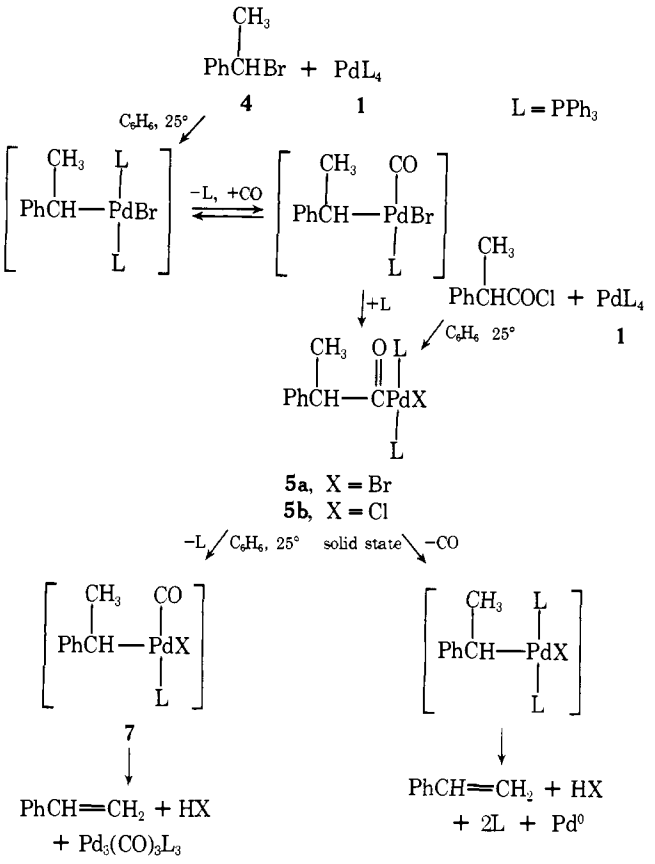
The regeneration of palladium(0) suggests the possibility of the catalytic conversion of benzyl halides to the corresponding esters. Removal of hydrogen chloride from the mixture is essential to recycling the zero-valent palladium



catalyst, however,[16] and with the addition of 2,6-lutidine, a base which is a poor nucleophile, the catalytic carbonylation[12] of benzyl chloride by tetrakis(triphenylphosphine)palladium(0) (**1**) in the presence of carbon monoxide and methanol yields methyl phenylacetate.

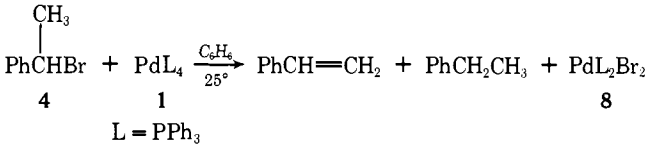
α-Phenethyl bromide (**4**) undergoes oxidative addition reaction with tetrakis(triphenylphosphine)palladium(0) (**1**) in the presence of carbon monoxide to yield the acylpalladium(II) complex **5a**[1a] (Scheme I). By comparison to benzyl bromide,

Scheme I

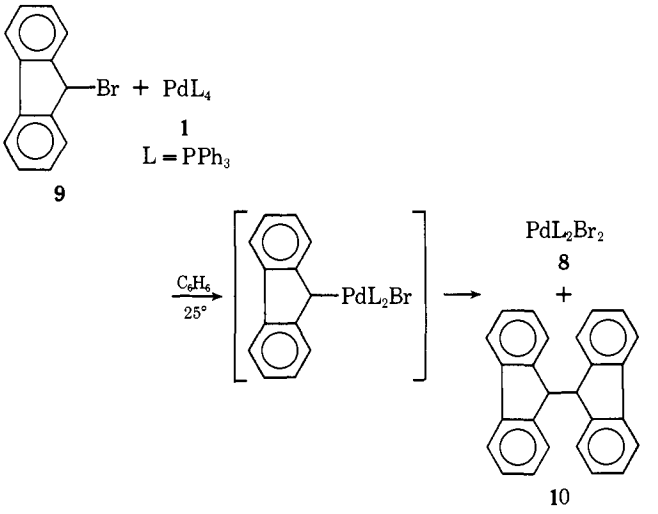


4 undergoes oxidative addition to the palladium(0) complexes (**1** or carbonyltris(triphenylphosphine)palladium(0), **6**) less efficiently. The α-substituent on the benzyl moiety reduces the reactivity of the alkyl bromide. Furthermore, when less than 2 molar equiv of α-phenethyl bromide (**4**) (relative to the palladium(0) complex) was present in solution with either **1** and carbon monoxide or **6**, a side product, the trinuclear palladium cluster complex $Pd_3(CO)_3(PPh_3)_3$ was formed. By contrast to the stable phenylacetylpalladium(II) complex (**3**), the acyl complex **5a** and its chloro analogue (**5b**), which is derivable only from the oxidative addition of α-phenylpropionyl chloride to **1**, slowly lose carbon monoxide in the solid state to yield palladium black and styrene. In benzene solution, the decomposition of the acyl complex (**5a** or **5b**) is more rapid, leading to the formation of the cluster complex, $Pd_3(CO)_3(PPh_3)_3$, and styrene. These results can be explained by the formation of intermediate **7** via ligand dissociation in solution, generating a vacant site for the migration of the alkyl group.

When the oxidative addition of the bromide **4** to complex **1** was carried out in the *absence* of carbon monoxide, dibromobis(triphenylphosphine)palladium(II) (**8**), styrene, and ethylbenzene[16,17] were obtained. No coupling product, 2,3-diphenylbutane, could be detected.



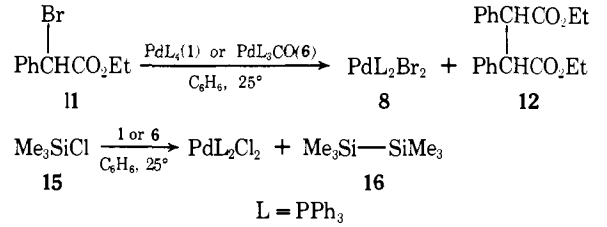
9-Bromofluorene, Ethyl α-Bromophenylacetate, and Chlorotrimethylsilane. Oxidative addition of 9-bromofluorene (**9**) to **1** afforded the dibromo complex **8**, and 9,9′-bifluorenyl (**10**)[18] (162% yield based on **1**). The decomposition of the



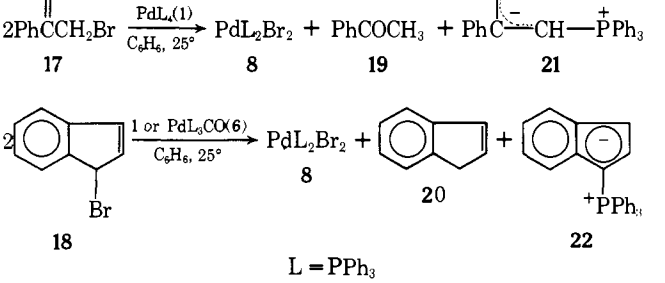
transient alkylpalladium intermediate is undoubtedly highly favorable since all attempts to promote carbon monoxide "insertion" failed to produce the desired acyl complex. In each case, only **8** and **10** were isolated.

Ethyl α-bromophenylacetate (**11**) underwent oxidative addition to **1** to give the dibromo complex **8** and the coupling product **12**[19] which was identified by its NMR spectrum to be a mixture of *erythro*- and *threo*-2,3-diphenylsuccinates. The mixture of diesters was saponified to *erythro*-2,3-diphenylsuccinic acid (**13**)[20-23] and then reduced to *erythro*-2,3-diphenyl-1,4-butanediol (**14**).[24-27] Identical results were obtainable when the palladium-carbonyl complex **6** was used in lieu of **1**.

In a similar manner, the reaction of chlorotrimethylsilane **15** and the palladium(0) complex **1** afforded the chloro analogue of **8** and hexamethyldisilane (**16**).[28] An analogous reaction has been reported for a platinum(0) complex.[29]



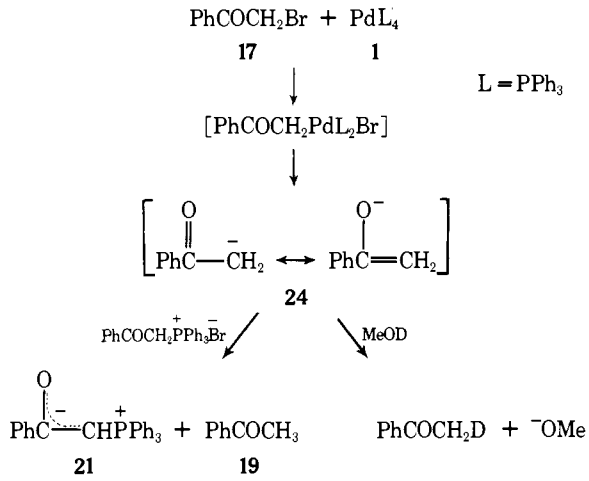
Phenacyl Bromide and 1-Bromoindene. Quite unexpectedly, the oxidative addition of phenacyl bromide (**17**) and 1-bromoindene (**18**)[30,31] to the palladium(0) complexes resulted in the reduction of the alkyl bromides to acetophenone (**19**) and indene (**20**), respectively. In addition, the stable phosphorane



ylide **21**[32] and the dibromo complex **8** were also isolated in good yield from the reaction of **17**.

When the ratio of **17** to **1** was 2.5, phenacyltriphenylphosphonium bromide **23**[32,33] (91% of theory) was obtained in addition to the dibromo complex **8**, acetophenone (**19**), and ylide **21**. The introduction of 20 molar equiv of methanol-*O-d* to the oxidative addition reactants led to the isolation of α-deuterioacetophenone. Neither phenacyl bromide (**17**) nor acetophenone (**19**) incorporated deuterium when it was mixed with methanol-*O-d* and the dibromo complex **8** under the normal conditions for oxidative addition.

Phenacyltriphenylphosphonium bromide (**23**) and indenyltriphenylphosphonium bromide[31] are known to undergo facile transformation to the respective ylides[31,32,34,35] under mildly basic conditions. The isolation of ylide **21** and the observed deuterium incorporation in product acetophenone (**19**) when methanol-*O-d* was added to the reaction imply the intervention of a carbanionic intermediate (**24**).

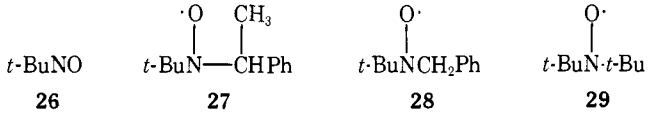


Unreactive Alkyl Halides. Oxidative addition of alkyl halides to palladium)0) complexes at 25 °C is extremely sensitive to the nature of α-substituents and of the halide ion. While benzyl halides undergo rapid addition (bromide more rapidly than chloride) to either **1** or **6** to give the expected alkyl- or acylpalladium(II) complexes, α-phenethyl bromide (**4**) requires longer reaction time and α-phenethyl chloride fails to react with either **1** or **6** at 25 °C. In the reaction of α-phenethyl chloride and **6**, the palladium complex isolated was not the starting complex but rather the cluster complex $Pd_3(CO)_3(PPh_3)_3$.

Since bromide is a better leaving group in nucleophilic displacements, the higher reactivity of the alkyl bromide is expected. That the α-substitutent lowers the reaction rate is also a consequence of an SN2 process in the oxidative addition. 1-Phenyl-2,2,2-trifluoroethyl chloride[36,37] undergoes oxidative addition with **1** only sluggishly at elevated temperatures[1b] and fails to react with **6**.[1a] These results are compatible with the explanation that the α-trifluoromethyl group both increases the steric requirement for nucleophilic displacement and destabilizes the SN2 transition state by electron withdrawal.

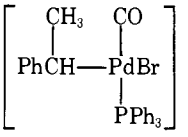
Although ethyl α-bromophenylacetate (**11**) underwent rapid reaction with **1** or **6**, the analogous compound ethyl α-bromopropionate (**25**) failed to react with either **1** or **6**. Stirring **25** and **6** under the normal conditions for oxidative addition led to a quantitative yield of the cluster complex $Pd_3(CO)_3(PPh_3)_3$, and the recovery of the α-bromoester. 2-Bromobutane also failed to react with **2** even at 60 °C under 2 atm of carbon monoxide.

Radical Intermediates from the Oxidative Addition Products. CIDNP was not observed in any of the reactions of the palladium(0) complex **1** with benzyl bromide, α-phenethyl bromide (**4**), and 9-bromofluorene (**9**). Radical trapping experiments for α-phenethyl bromide (**4**) and the benzyl halides in the presence of the palladium(0) complexes (**1** or **6**) were carried out under conditions similar to those reported for alkyl and benzyl halides in the presence of tris(triphenylphosphine)-platinum(0)[2] (Table I). On mixing α-phenethyl bromide (**4**), the palladium(0) complex **1**, and *tert*-nitrosobutane (**26**),[38] an intense signal of *tert*-butyl-α-phenethyl nitroxide (**27**)[39-41] was observed by ESR (experiment A). The same nitroxide radical **27** was also produced when the bromide **4** and the palladium–carbonyl complex **6** were mixed with **26** (experiment B). In identical experiments with benzyl chloride and bromide (experiments E, F), the ESR spectra were superimposable, showing an overlapping triplet of triplets for benzyl-*tert*-butyl nitroxide (**28**)[40-42] as well as a more intense triplet for di-*tert*-butyl nitroxide (**29**).[43-45] The spectra for solutions of **26** and the benzyl halides in the *absence* of **1** showed only a signal for **29** due to the decomposition of *tert*-nitrosobutane (**26**) (experiments C, D).



The stereochemistry[1] for the oxidative addition of benzyl-α-*d* chloride and α-phenethyl bromide to the palladium(0) complex **1** is clearly inconsistent with a radical pathway. The formation of nitroxide radicals **27** and **28** is just as consistent with a *tert*-nitrosobutane-induced radical oxidative addition or a *tert*-nitrosobutane-induced decomposition of the oxidative addition products (**2a** and **5a**), the *primary products* of the reactions of the palladium(0) complex **1** with benzyl chloride and α-phenethyl bromide, respectively. The possibility of a *tert*-nitrosobutane-induced decomposition of the oxidative addition product was demonstrated by the observation that the nitroxide radical **28** is indeed formed (experiment H) on mixing the benzylpalladium complex **2a** and *tert*-nitrosobutane.[46] *Since the oxidative addition product undergoes a reaction with tert-nitrosobutane (**26**) to afford the nitroxide radical **28**, the ESR experiments do not provide any information about the mechanism of the oxidative addition reactions.*

The acylpalladium complexes **3** and **5** are stable toward *tert*-nitrosobutane-induced radical decomposition, however (experiments J, K). The fact that mixing α-phenethyl bromide (**4**) with carbonyltris(triphenylphosphine)palladium(0) (**6**) in the presence of *tert*-nitrosobutane gave an intense ESR signal for the nitroxide radical **27** (experiment B) supports the intervention of a transient intermediate **30** during the oxidative addition of bromide **4** to the palladium–carbonyl complex **6**.

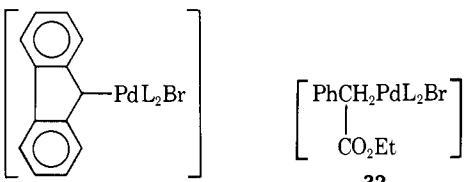


30

Although stable palladium(II) carbonyl complexes[47] are not known except in one case in which the complex is stabilized by chelation[48] the postulate of their transient existence as reaction intermediates is not without support. In fact, alkyl carbonyl complexes of platinum(II) have been isolated and identified.[49,50] In addition, α-phenethyl bromide (**4**) undergoes oxidative addition to carbonyltris(triphenylphosphine)platinum(0)[51] to give mainly a cluster complex (ir 1800 cm^{-1})[51] and a small yield of bromo(carbonyl)(α-phenethyl)(triphenylphosphine)platinum(II) (i.e., the platinum analogue of **30**).

Since **30** is structurally an alkylpalladium(II) complex, apparently it could be induced to undergo radical decomposition. In the absence of *tert*-nitrosobutane (**26**), intramolecular carbonyl "insertion" occurs significantly faster than thermal decomposition so that the acylpalladium complex **5a** is obtained. Furthermore, the intermediacy of **30** supports the formation of acylpalladium complexes (e.g., **5**) by a pathway which does not involve direct nucleophilic attack by a palladium-bonded carbonyl at the benzylic carbon. This is consistent with the fact that the carbonyl carbon is a poor nucleophile and is reactive toward bases.[52]

Each of the oxidative addition reactions of α-phenethyl bromide (**4**), 9-bromofluorene (**9**), and ethyl α-bromophenylacetate (**11**) to complex **1** was carried out under oxygen-free conditions in the presence of 2,2-diphenyl-1-picrylhydrazyl (DPPH)[53,54] (Table II). The oxidative additions of **9** and **11** to complex **1** caused a rapid color change of DPPH from deep violet to light yellow, indicating the destruction of the DPPH radical by another radical presumably generated in the reaction mixture from the decomposition of the unstable alkyl complexes **31** and **32,** the primary products of oxidative addition. The oxidative addition of bromide **4** to **1** did not cause a change in the intense color of DDPH,[55] in accord with a mechanism which *excludes a radical pathway for the decomposition of the oxidative addition product* and that a radical pathway is not important in the oxidative addition reaction; therefore, formation of radicals during the oxidative addition of benzyl chloride and α-phenethyl bromide to complex **1** in the presence of *tert*-nitrosobutane (vide supra) is clearly a *tert*-nitrosobutane-induced process.



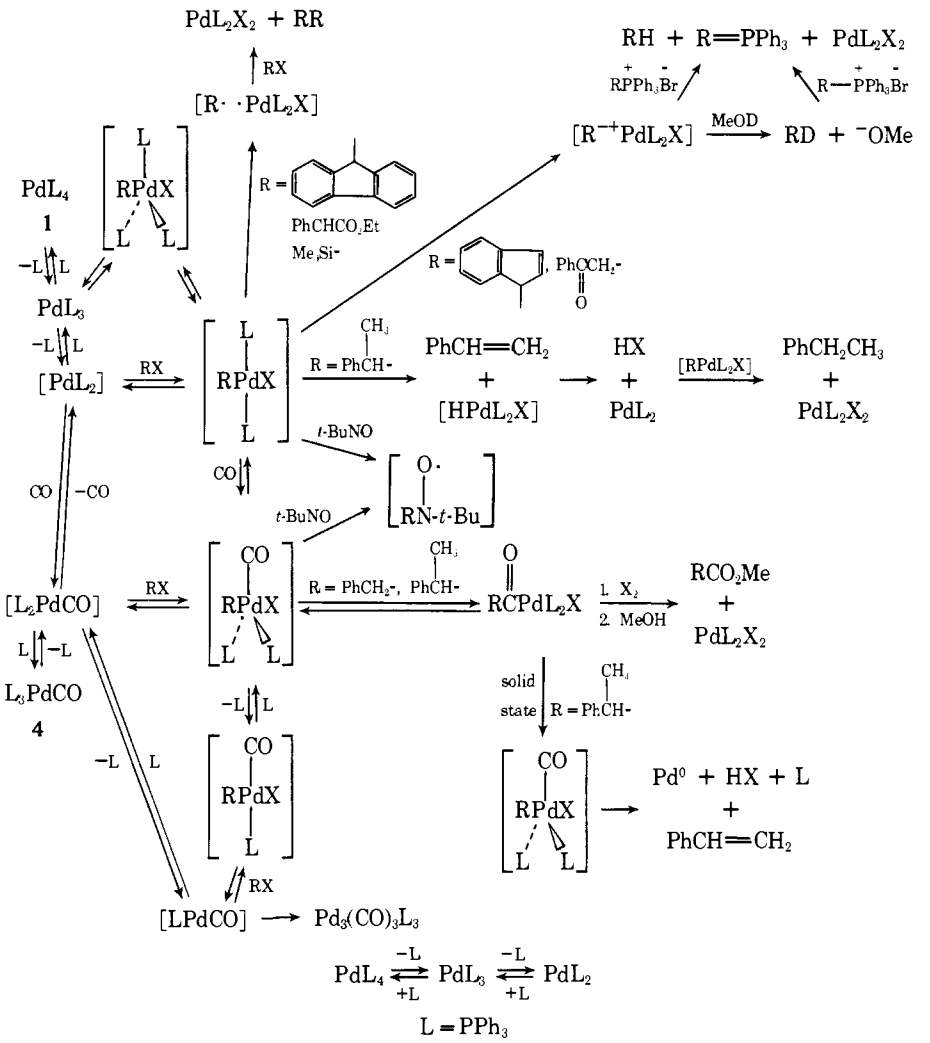
31 **32**

L = PPh_3

At low conversion, the copolymerization of styrene and methyl methacrylate in a 1:1 monomer ratio yields a copolymer whose composition depends on the polymerization mechanism.[57,58] A cationic catalyst leads to a styrene-rich copolymer, an anionic catalyst to a methyl methacrylate-rich copolymer, and a free radical initiator to an alternating 1:1 copolymer. Copolymerization of styrene and methyl methacrylate was carried out under anaerobic conditions at 25 °C to 2% conversion in the presence of 9-bromofluorene (**9**) and complex **1**. The elemental analysis,[59] infrared[59] spectrum, and ^1H[60,61] and ^{13}C NMR[61] spectra were consistent with a 1:1 styrene–methyl methacrylate alternating copolymer. A similar experiment carried out in the presence of α-phenethyl bromide (**4**) and complex **1** did not afford copolymer. These results support the postulate that radical intermediates are present in the reaction mixture, and probably are generated by decomposition of the oxidative addition product of **9** to complex **1,** but not in the oxidative addition reaction itself.

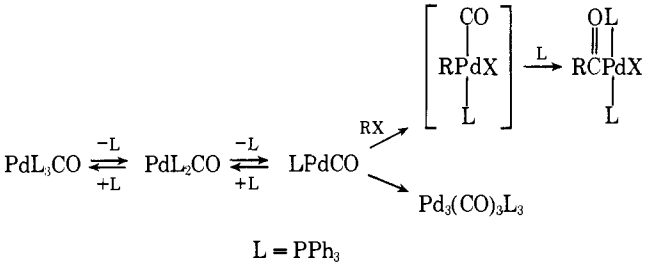
Mechanisms. Square planar tetrakis(triphenylphosphine)-palladium(0) (**1**) is coordinatively saturated. Ligand dissociation generates the reactive coordinatively unsaturated

Scheme II



species in solution at room temperature;[62-67] the equilibria can be displaced in favor of the bis-ligated species[67-69] in the presence of the alkyl halide. Subsequent oxidative addition of the alkyl halide to palladium generates the alkyl complex, *the fate of which depends on the nature of the alkyl group.* Alternatively, oxidative addition can take place with the tris-ligated species generating a five-coordinate palladium(II) species[70,71] which undergoes subsequent ligand dissociation to give the square planar complex.

Carbonyltris(triphenyphosphine)palladium(0) (**6**) undergoes similar ligand dissociation to give initially a reactive tris-ligated palladium–carbonyl complex.[72] By analogy to complex **1,** displacement of the equilibria in favor of the bis-ligated species is possible in the presence of the alkyl halide. Oxidative addition of the alkyl halide to the bis-ligated species leads ultimately to the stable acyl complex, or the bis-ligated



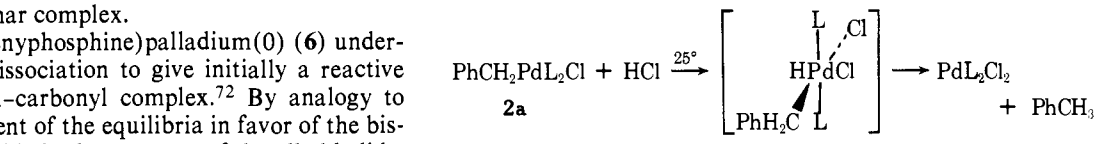
species trimerizes in the presence of unreactive alkyl halide, e.g., α-phenethyl chloride (vide supra). An alternative mechanism involves oxidative addition of the alkyl halide to the tris-ligated palladium–carbonyl species giving a five-coordinate intermediate which undergoes intramolecular carbonyl insertion to give the acyl complex. Support for the participation of a five-coordinate intermediate is provided by the results of the solid state decomposition of the acyl complex **5a** (and its chloro analogue **5b**). The first step for decarbonylation must be the acyl–alkyl rearrangement. In solution, this process is facilitated by ligand dissociation, a step which is unlikely to occur in the solid state (Scheme I).

The observation of CIDNP in the oxidative addition of isopropyl iodide to tris(triethylphosphine)platinum(0) (**33**) and -palladium(0) (**34**) *has not necessarily demonstrated* that the primary process of oxidative addition is free radical.[8] A mechanism which invokes initial nucleophilic attack of zero-valent platinum or palladium to the alkyl halide and subsequent free radical decomposition of the oxidative addition product can equally account for the observation of CIDNP and the formation of products characteristic of free radical disproportionation and coupling.

The general reactivity pattern for the reaction of alkyl halides with the zero-valent platinum complex **33** has been shown to be primary > secondary.[7] Although it has been suggested that the major path for secondary alkyl halides involves a *bis-ligated* $Pt(PEt_3)_2$ species (the low concentration of which accounts for the slower rates), the observed rate order is also that expected for an SN2 pathway.

The observation that the rate of oxidative addition is retarded by radical scavengers such as duroquinone and galvanoxyl can be explained by inhibition of the radical chain reaction[8] by trapping the radicals generated from the decomposition of the oxidative addition product.

The fate of the alkyl palladium complex obtained from the oxidative addition of alkyl halide to zero-valent palladium is dictated by the alkyl group involved. Benzyl halides give stable benzylpalladium(II) complexes **2.** The initial products of decomposition of the oxidative addition product obtained from α-phenethyl bromide (**4**) and complex **1** are styrene and a hydridopalladium complex but no coupling product. Thus a β-elimination[73,74] is the decomposition pathway. The hydridopalladium complex regenerates a palladium(0) species by reductive elimination of hydrogen bromide which undergoes addition to another molecule of the oxidative addition product leading ultimately to ethylbenzene and the dibromo complex **8** via a palladium(IV) species. The feasibility of this latter reaction pathway is demonstrated by the fact that the reaction of hydrogen chloride and chloro(benzyl)bis(triphenylphosphine)palladium(II) (**2a**) affords toluene.



The oxidative addition products of **1** with 9-bromofluorene (**9**), ethyl α-bromophenylacetate (**11**), and chlorotrimethylsilane (**15**) decompose to give coupling products. Although the mechanism for decomposition of the adduct from **15** is uncertain, the other two adducts probably decompose via a radical mechanism as evidenced by the results obtained from the DPPH and copolymerization experiments. The driving force for the decomposition of the oxidative addition products of phenacyl bromide **17** and 1-bromoindene **18** is the formation of the stable enolate anion **24.**

Experimental Section

The preparation of, and reaction involving, air-sensitive tetrakis(triphenylphosphine)palladium(0) (**1**) and carbonyltris(triphenylphosphine)palladium(0) (**6**) was carried out under appropriate inert atmospheres (nitrogen or carbon monoxide). All solvents used for oxidative addition reactions were purified and degassed.

Reaction of Chloro(benzyl)bis(triphenylphosphine)palladium(II) (2a) with Benzyl Chloride in Benzene at Reflux. Formation of Bibenzyl. A solution of 6.07 g (8.02 mmol) of chloro(benzyl)bis(triphenylphosphine)palladium(II)[11] and 1.09 g (8.62 mmol, 1.08 equiv) of benzyl chloride in 100 ml of degassed anhydrous benzene was heated to reflux under nitrogen for 90 h. The mixture was cooled and the yellow complex was removed by filtration. The filtrate was concentrated and the residual brown oil consisted (NMR) only of bibenzyl and unreacted benzyl chloride (40:60).

Reaction of Chloro(benzyl)bis(triphenylphosphine)palladium(II) (2a) with Acetyl Chloride. Formation of Phenylacetone and Dichlorobis(triphenylphosphine)palladium(II). A solution of 0.645 g (0.852 mmol) of chloro(benzyl)bis(triphenylphosphine)palladium(II) and 2 ml of freshly distilled acetyl chloride in 25 ml of degassed anhydrous toluene was heated at reflux under nitrogen for 20 h. The mixture was cooled and the volatile materials (fraction 1) were transferred under reduced pressure to a liquid nitrogen cold trap. The yellow solid dichlorobis(triphenylphosphine)palladium(II) (Anal. Calcd for $C_{36}H_{30}Cl_2P_2Pd$: C, 61.60; H, 4.30. Found: C, 60.61; H, 4.66) was washed thoroughly with acetone, and the washings were combined and concentrated (fraction 2).

GLC analysis (80 °C, 10 ft × 0.325 in., 20% SE-30 on Chromosorb W 60/80) of fraction 1 showed no acetone or biacetyl. GLC analysis of fraction 2 (same column at 200 °C) showed the presence of benzyl chloride (7.8% yield) and phenylacetone (14.8% yield) by comparison of retention time (coinjection).

A solution of 0.112 g (0.148 mmol) of chloro(benzyl)bis(triphenylphosphine)palladium(II) and 1 ml each of acetyl chloride and 2,6-lutidine in 10 ml of degassed toluene was heated at reflux under nitrogen for 24 h. The solid was filtered and the filtrate was washed with 10% hydrochloric acid and water and then dried over calcium chloride. GLC analysis of the concentrated filtrate (200 °C, 10 ft × 0.325 in., 20% SE-30 on Chromosorb W 60/80) showed a 73% yield of phenylacetone and a trace amount of benzyl chloride. The ketone was isolated by preparative GLC and its identity was confirmed by NMR ($CDCl_3$) δ 7.22 (s, 5 H, aromatic), 3.58 (s, 2 H, $PhCH_2CO$), and 2.04 ppm (s, 3 H, $COCH_3$).

Reaction of Chloro(benzyl)bis(triphenylphosphine)palladium(II) (2a) with Phenylacetyl Chloride. Formation of Dibenzyl Ketone. The same procedure described above was used as in the preparation of phenylacetone from chloro(benzyl)bis(triphenylphosphine)palladium(II) and acetyl chloride. Routine workup led to an oil which was shown

by GLC (200 °C, 10 ft × 0.325 in., 20% DEGS on Chromosorb W 60/80) to contain dibenzyl ketone (156% yield based on chloro(benzyl)bis(triphenylphosphine)palladium(II)).

Oxidative Addition of α-Phenethyl Bromide to Tetrakis(triphenylphosphine)palladium(0) in the Absence of Carbon Monoxide. Formation of Styrene, Ethylbenzene, and Dibromobis(triphenylphosphine)palladium(II) (8). To a degassed benzene solution of 1.03 g (0.889 mmol) of tetrakis(triphenylphosphine)palladium(0)[75] was added 0.575 g (3.11 mmol, 3.49 equiv) of freshly distilled α-phenethyl bromide. After 2.5 h at 25 °C, the orange solution turned cloudy and then a yellow precipitate formed. After 20 h, 0.644 g (91.6%) of dibromobis(triphenylphosphine)palladium(II) (**8**) was isolated by filtration, washed with ether, and air-dried, mp 230–240 °C dec. Anal. Calcd for $C_{36}H_{30}Br_2P_2Pd$: C, 54.66; H, 3.82. Found: C, 54.82, 54.34; H, 3.49, 3.50.

A preparative scale experiment was carried out using a 300-ml degassed anhydrous benzene solution of 11.60 g (10.05 mmol) of tetrakis(triphenylphosphine)palladium(0)[75] and 3.804 g (20.56 mmol, 2.046 equiv) of α-phenethyl bromide. After 2.5 h, a heavy yellow precipitate formed and after 18 h, 300 ml of hexane was added to the mixture. Dibromobis(triphenylphosphine)palladium(II) (**8**) (7.048 g, 8.931 mmol, 88.86%) was obtained after filtration and washing with ether, mp 230–250 °C dec.

The yellow filtrate was concentrated by distillation of the solvent. The residue was washed three times with pentane. The pentane washings were combined and concentrated by distillation of the solvent. The residual oil was then distilled into a cold trap (−78 °C) under reduced pressure (bp 21 °C (0.5 mmHg)). The trap material was shown to be a mixture of 60% styrene and 40% ethylbenzene by NMR. GLC analysis (130 °C, 10 ft × 0.375 in., 20% FFAP/Chromosorb W 60/80) indicated two components were present. The styrene peak was confirmed by retention time comparison with an authentic sample. The other peak at a shorter retention time was isolated by preparative GLC (same column) and identified as ethylbenzene: NMR ($CDCl_3$) δ 7.20 (s, 5 H, aromatic), 2.67 (q, 2 H, J = 7.5 Hz, PhCH_2–) and 1.25 ppm (t, 3 H, J = 7.5 Hz, –CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 106 (90.0), 91 (100), 78 (40.7), 77 (40.7), 65 (55.0), and 51 (65.0).

Decomposition of Halo(α-phenylpropionyl)bis(triphenylphosphine)palladium(II). (a) In Solution. Nitrogen was bubbled through a 120-ml benzene slurry of 2.34 g (2.93 mmol) of chloro(α-phenylpropionyl)bis(triphenylphosphine)palladium(II) (**5b**) during which time the initial cream-colored slurry became orange. After 3.5 h, an orange complex, $Pd_3(CO)_3(PPh_3)_3$, was removed by filtration: mp 125–128 °C; ir ($CHCl_3$) 1870 cm^{-1} (Pd–CO). Anal. Calcd for $C_{57}H_{45}O_3P_3Pd_3$: C, 57.48; H, 3.81. Found: C, 56.99; H, 4.09.

The filtrate was concentrated to a dark brown residue by distillation of the solvent. The residue was extracted three times with pentane and the pentane extracts were combined, concentrated, and distilled (22 °C (0.5 mmHg)) to afford 115 mg (1.11 mmol, 37.9%) of styrene, identifiable by comparison of its NMR spectrum with that of an authentic sample. Similar results were obtained with the bromo complex **5a**.

(b) In the Solid State. A 2.82 g (3.54 mmol) sample of chloro(α-phenylpropionyl)bis(triphenylphosphine)palladium(II) (**5b**) which was allowed to stand at 25 °C for 18 days turned black. Repeated washing with ether removed the organic material from the black residue. The etheral washing was concentrated to a mobile liquid which was shown by NMR to contain triphenylphosphine and styrene (2:1). The calculated ratio of aromatic to vinyl absorptions, 11.67:1.00; found by integration, (10.78 ± 0.05):1.00. Similar results were obtained with the bromo complex **5a**.

Oxidative Addition Reaction of 9-Bromofluorene (9) to Palladium(0) Complexes. Formation of Dibromobis(triphenylphosphine)palladium(II) (8) and 9,9′-Bifuorenyl (10). (a) To Tetrakis(triphenylphosphine)palladium(0). To 50 ml of a degassed benzene solution of 1.053 g (0.913 mmol) of tetrakis(triphenylphosphine)palladium(0)[75] was added 0.798 g (3.26 mmol, 3.57 equiv) of 9-bromofluorene. After 5 min, the orange solution turned yellow and a precipitate appeared. After 16 h, the complex, dibromobis(triphenylphosphine)palladium(II) (**8**), was isolated by filtration, mp 230–250 °C dec. Anal. Calcd for $C_{36}H_{30}Br_2P_2Pd$: C, 54.66; H, 3.82. Found: C, 53.88; H, 3.43.

The filtrate was concentrated to give a mixture of crystalline solids which was dissolved in hot ethanol. Upon cooling at 25 °C, white needles of 9,9′-bifluorenyl (**10**) were obtained: mp 259–265 °C (lit. 243.5–245 °C);[18] mass spectrum (70 eV) *m/e* (rel intensity) 330 (20.4), 165 (100.0); NMR ($CDCl_3$) δ 7.75–6.81 (m, 8 H, aromatic) and 4.78 ppm (s, 1 H, C*H*). Anal. Calcd for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.63; H, 5.37.

(b) To Tetrakis(triphenylphosphine)palladium(0) under Carbon Monoxide. To 50 ml of a carbon monoxide-saturated benzene solution of 1.26 g (1.10 mmol) of tetrakis(triphenylphosphine)palladium(0)[75] was added 1.00 g (4.09 mmol, 3.74 equiv) of 2-bromofluorene (**9**) and the mixture was stirred under 1 atm of carbon monoxide at 25 °C. After 5 min, a yellow solid, dibromobis(triphenylphosphine)palladium(II) (**8**) began to form and was removed by filtration after 13 h (0.723 g, 0.902 mmol, 82.3%), mp 230–250 °C dec; Anal. Calcd for $C_{36}H_{30}Br_2P_2Pd$: C, 54.66; H, 3.82. Found: C, 54.28; H, 3.23.

The filtrate was worked up as described above, leading to the isolation of 9,9′-bifluorenyl (**10**) which was identified by comparison of its mass spectrum with that of an authentic sample.

(c) To Carbonyltris(triphenylphosphine)palladium(0). To 50 ml of a carbon monoxide-saturated benzene solution of 1.53 g (1.66 mmol) of carbonyltris(triphenylphosphine)palladium(0)[76] was added 1.42 g (5.80 mmol, 3.49 equiv) of 9-bromofluorene (**9**). Precipitation of a yellow complex occurred after 5 min. After 2 h, the yellow complex dibromobis(triphenylphosphine)palladium(11) (1.13 g, 1.27 mmol, 76.5%) was filtered: mp 245–255 °C dec. The filtrate was worked up as described to yield 9,9′-bifluorenyl (**10**) identified by its mass spectrum.

(d) To Tetrakis(triphenylphosphine)palladium(0) under 3 Atm of Carbon Monoxide. A 1.12-g (0.963 mmol) quantity of tetrakis(triphenylphosphine)palladium(0)[76] was dissolved in 50 ml of carbon monoxide-saturated benzene solution under 3 atm of carbon monoxide. 9-Bromofluorene (1.07 g, 4.38 mmol) was introduced as a benzene solution by injection through a gas-tight hypodermic syringe. A precipitate formed after 5 min. After 24 h, 0.691 g (0.874 mmol, 90.8%) of dibromobis(triphenylphosphine)palladium(II) (**8**) was isolated: mp 250–265 °C dec. Similar workup of the filtrate as described yielded 9,9′-bifluorenyl (**10**) which was identified by its mass spectrum.

Oxidative Addition of Ethyl α-Bromophenylacetate (11) to Tetrakis(triphenylphosphine)palladium(0). Formation of Diethyl 2,3-Diphenylsuccinates (12) and Dibromobis(triphenylphosphine)-palladium(II) (8). A 10.1 g (8.76 mmol) sample of tetrakis(triphenylphosphine)palladium(0)[75] was partially dissolved in 300 ml of degassed anhydrous benzene. Addition of 5.11 g (21.0 mmol) of ethyl α-bromophenylacetate caused complete dissolution of the yellow complex, giving a dark orange solution. After 10 min, the solution became turbid and precipitation occurred after 30 min. After 14 h, 200 ml of pentane was added to the mixture and the mixture was filtered. The yellow complex (5.70 g, 7.2 mmol, 82.3%) was identified as dibromobis(triphenylphosphine)palladium(II) (**8**) by ir and elemental analysis, mp 245 °C dec. Anal. Calcd for $C_{36}H_{30}Br_2P_2Pd$: C, 54.66; H, 3.83. Found: C, 53.24, 53.44; H, 3.63, 3.80.

The filtrate was concentrated by distillation of the solvent. NMR ($CDCl_3$) of the crude product indicated total absence of starting material and the presence of *erythro*- and *threo*-diethyl-2,3-diphenylsuccinates (**12**).[34] The crude product was mixed with a 5% aqueous solution of potassium hydroxide and the mixture was heated at reflux for 36 h. Cooling to room temperature yielded a heavy precipitate of triphenylphosphine oxide which was removed by filtration. The filtrate was washed with ether and neutralized with concentrated hydrochloric acid to afford a white precipitate which was taken up in methylene chloride and reprecipitated with the addition of ether. The white product was identified as *erythro*-2,3-diphenylsuccinic acid (**13**): mp 199–200 °C; ir ($CHCl_3$) 3600–3100 (broad, OH), 1690 (sharp, C=O) and 1300–950 cm^{-1} (broad, C—O—C); NMR (Me_2SO-d_6) δ 7.70–7.08 (m, 6 H, aromatic and acid proton) and 4.31 ppm (s, 1 H, Ph C*H*–); mass spectrum (70 eV) molecular ion absent, base peak *m/e* 180 (M − $2CO_2H$), identical with mass spectrum of an authentic sample.

A 51.2-mg (0.190 mmol) sample of 2,3-diphenylsuccinic acid (**13**) was allowed to react with 30.0 mg (0.790 mmol) of lithium aluminum hydride in refluxing anhydrous benzene under nitrogen for 22 h. The mixture was hydrolyzed with water and the benzene fraction was washed with 10% hydrochloric acid and water. After drying and concentration, a white solid was obtained which was crystallized from pentane–ether to afford 14.5 mg (0.0599 mmol, 31.5%) of *erythro*-2,3-diphenyl-1,4-butanediol (**14**): mp 141–143 °C (lit. 142–143.5 °C);[27] NMR ($CDCl_3$) δ 7.23 (bs, 10 H, phenyl), 3.58–3.33 (distorted d, 4 H, CH_2OH), 3.17–2.83 (m, 2 H, PhC*H*CH_2OH) and 1.37 (bs,

2 H, O*H*, exchanged with D_2O); mass spectrum (70 eV) *m/e* (rel intensity) 242 ($M\cdot^+$, 0), 224 (21.9), 206 (9.3), 194 (10.5), 193 (15.2), 178 (10.3), 120 (13.5), 115 (17.0), 105 (31.6), 104 (100.0), 103 (15.8), 91 (38.0).

Oxidative Addition of Chlorotrimethylsilane to Tetrakis(triphenylphosphine)palladium(0). Formation of Hexamethyldisilane (16) and Dichlorobis(triphenylphosphine)palladium(II). To a slurry of 8.31 g (7.20 mmol) of tetrakis(triphenylphosphine)palladium(0)[75] in 300 ml of degassed methylene chloride was added 2.78 g (25.6 mmol, 3.55 equiv) of chlorotrimethylsilane (**15**) under nitrogen. The immediate dissolution of the suspension occurred to yield a clear yellow solution. After 72 h, the precipitated yellow complex, dichlorobis(triphenylphosphine)palladium(II) was filtered: mp 259–260 °C dec. Anal. Calcd for $C_{36}H_{30}Cl_2P_2Pd$: C, 61.60; H, 4.30. Found: C, 61.64; H, 4.40.

The filtrate was concentrated by distillation and the concentrate was mixed with pentane to precipitate additional yellow complex. The filtered pentane solution was further concentrated by distillation of the solvent. The residual oil was fractionally distilled. The first distillate (major fraction) (76–84 °C (760 mmHg)) was predominantly hexamethyldisilane (**16**) as shown by GLC (115 °C, 10 ft × 0.375 in., 20% FFAP on Chromosorb W 60/80): NMR ($CDCl_3$) δ 0.08 (s); mass spectrum (70 eV) parent ion *m/e* 146, base peak *m/e* 73.

The second distillate (minor fraction) (27–28 °C (4.5 mmHg)) contained two components which were not identified.

Oxidative Addition of Phenacyl Bromide to Tetrakis(triphenylphosphine)palladium(0). Formation of Benzoylmethylene Triphenylphosphorane Ylide (21), Acetophenone (19), and Dibromobis(triphenylphosphine)palladium(II) (8). Into 300 ml of degassed anhydrous benzene containing 24.2 g (21.0 mmol) of tetrakis(triphenylphosphine)palladium(0)[75] was added 10.5 g (52.5 mmol, 2.51 equiv) of freshly recrystallized phenacyl bromide (**17**). Immediately a clear dark orange solution resulted which was stirred under nitrogen for 18 h. A yellow complex precipitated. Pentane was added to the mixture to ensure complete precipitation. The precipitate was filtered and washed with ether to afford 20.6 g (123%) of product which was then washed twice with ethanol and then ether. The product was recrystallized from chloroform–pentane to give 15.3 g (19.4 mmol, 92.4%) of dibromobis(triphenylphosphine)palladium(II) (**8**): mp 260–265 °C dec.

The ethanol washing obtained from the treatment of the crude yellow complex was evaporated to yield 4.40 g (9.54 mmol, 91.0%) of phenacyltriphenylphosphonium bromide (**23**): mp 280–281 °C (lit. 279–280 °C),[32] which gave a positive silver nitrate test: ir ($CHCl_3$) 1678 cm^{-1} (carbonyl); NMR ($CDCl_3$/20% CD_3CN) δ 7.25–8.28 (m, 20 H, aromatic) and 5.97 ppm (d, J_{HP} = 13.0 Hz, 2 *H*, PCH_2COPh); mass spectrum (70 eV) *m/e* (rel intensity) 490 ($M\cdot^+$, 0), 380 (49.6), 379 (57.4), 354 (15.6), 303 (87.2), 278 (35.5), 262 (29.1), 204 (26.2), 180 (100).

The ether–pentane washings obtained from the initial extraction of the yellow complex were combined and concentrated. The crude material was washed with ether to yield an ether-insoluble white powder, benzoylmethylenetriphenylphosphorane ylide (**21**) (7.24 g, 19.1 mmol, 90.9% of theory): mp 177–179 °C (lit. 178–180 °C);[32] NMR ($CDCl_3$) only aromatic absorptions; mass spectrum (70 eV) 380 ($M\cdot^+$). The ether washing was concentrated to an oil which was purified by distillation (34.5–35.5 °C (0.5 mmHg)) to give 1.30 g (10.8 mmol, 51.7%) of acetophenone (**19**): NMR ($CDCl_3$) δ 8.08–7.83 (m, 2 H, ortho H's), 7.62–7.23 (m, 3 H, para and meta H's) and 2.52 ppm (s, 3 H, CH_3CO), mass spectrum (70 eV) *m/e* (rel intensity) 120 ($M\cdot^+$, 23.8), 105 (100), 77 (96.0).

The experiment was repeated with 2.16 g (1.87 mmol) of tetrakis(triphenylphosphine)palladium(0) and 0.747 g (3.75 mmol, 2.01 equiv) of phenacyl bromide (**17**) in 50 ml of olefin and toluene-free anhydrous benzene. The reaction mixture was stirred under nitrogen at 25 °C and after 2 h, the initial orange color of the solution turned opaque yellow. The mixture was diluted with pentane and filtered to give the yellow complex dibromobis(triphenylphosphine)palladium(II) (**8**) (1.39 g, 1.76 mmol, 94.0%) and a colorless filtrate which upon evaporation yielded 0.532 g (1.40 mmol, 74.9%) of white crystalline benzoylmethylenetriphenylphosphorane ylide (**21**) mp 176–177 °C (first crop) 170–172 °C (second crop). Both crops gave negative silver nitrate test and identical mass spectra (70 eV): *m/e* 380 ($M\cdot^+$), 278, 262, 185; NMR ($CDCl_3$) only aromatic absorptions; ir ($CHCl_3$) 1515 cm^{-1} (intense, PhCOCH=P). Anal. Calcd for $C_{26}H_{21}OP$: C, 82.09; H, 5.56. Found: C, 82.86; H, 5.52.

Repetition of the experiment with the introduction of methanol-*O-d* (in an equivalent amount of 20 times that of α-phenacyl bromide) led to the isolation of dibromobis(triphenylphosphine)palladium(II) (**8**) benzoylmethylenetriphenylphosphorane ylide (**21**) and α-deuterioacetophenone: NMR ($CDCl_3$) δ 8.08–7.83 (m, 2 H, ortho H's), 7.63–7.23 (m, 3 H, para and meta H's), and 2.52 ppm (t, 2 H, $COCH_2D$, J_{HD} = 2.0 Hz).

Attempted Hydrogen–Deuterium Exchange between Phenacyl Bromide (17) and Acetophenone (19) with Methanol-*O-d* in the Presence of Dibromobis(triphenylphosphine)palladium(II) (8). A mixture of 0.207 g (1.04 mmol) of phenacyl bromide (**17**) and 0.408 g (0.520 mmol) of dibromobis(triphenylphosphine)palladium(II) (**8**) in 10 ml of degassed anhydrous benzene containing 1.20 g (38.7 mmol) of methanol-*O-d* (99% *d*) was stirred at 25 °C under nitrogen for 24 h. The dibromo complex was filtered (90.5% recovery) and the filtrate was concentrated to an oil. NMR analysis revealed only the presence of starting material. Integration verified the absence of hydrogen–deuterium exchange.

A similar experiment was carried out with 0.260 g (2.17 mmol) of acetophenone (**19**), 0.856 g (1.08 mmol) of dibromobis(triphenylphosphine)palladium(II) (**8**), 1.20 g (38.7 mmol) of methanol-*O-d* (99% *d*), and 10 ml of degassed anhydrous benzene. NMR analysis of the concentrated filtrate after removal of the yellow complex revealed only the presence of acetophenone and integration confirmed the absence of hydrogen–deuterium exchange.

Oxidative Addition of 1-Bromoindene (18) to Tetrakis(triphenylphosphine)palladium(0). Formation of Indene (20) and Dibromobis(triphenylphosphine)palladium(II) (8). A solution of 0.842 g (4.32 mmol, 2.12 equiv) of 1-bromoindene[30] and 2.35 g (2.04 mmol) of tetrakis(triphenylphosphine)palladium(0) in 30 ml of degassed anhydrous benzene was stirred under nitrogen at room temperature for 17 h. The mixture was diluted with hexane and filtered to afford 1.58 g (2.00 mmol, 98.0%) of dibromobis(triphenylphosphine)palladium(II) (**8**). The filtrate was concentrated to a brown oil which was distilled into a liquid nitrogen cold trap. The distillate showed an NMR spectrum superimposable to that of an authentic sample of indene (**20**): NMR ($CDCl_3$) δ 7.58–7.05 (m, 4 H, aromatic), 7.05–6.75 and 6.58–6.38 (m, total 2 H, olefinic), and 3.30 ppm (distorted s, 2 H, allylic).

Attempted Oxidative Addition of α-Phenethyl Chloride to Carbonyltris(triphenylphosphine)palladium(0). A solution of 1.43 g (1.55 mmol) of carbonyltris(triphenylphosphine)palladium(0)[76] in 25 ml of carbon monoxide-saturated benzene containing 0.740 g (5.28 mmol, 3.41 equiv) of α-phenethyl chloride was stirred under carbon monoxide at 25 °C for 48 h. Addition of hexane to the mixture precipitated a yellow-orange complex which did not contain the 1670-cm^{-1} infrared absorption but an intense 1870-cm^{-1} band corresponding to that of a trinuclear palladium–carbonyl cluster complex $Pd_3(CO)_3(PPh_3)_3$: 0.600 g (0.504 mmol, 97.5%); mp 126–130 °C dec. Anal. Calcd for $C_{57}H_{45}O_3P_3Pd_3$: C, 57.48; H, 3.81. Found: C, 57.75; H, 4.03.

The filtrate was concentrated to an oil which was purified by distillation to afford 0.600 g (4.29 mmol, 81.2%) of α-phenethyl chloride.

Radical Trapping Experiments (Table I). The general procedure for the radical trapping experiments with *tert*-nitrosobutane (**26**) is illustrated with benzyl chloride and chloro(benzyl)bis(triphenylphosphine)palladium(II) (**2a**).

tert-Nitrosobutane (**26**) was prepared by the oxidation of *tert*-butylamine with hydrogen peroxide in the presence of sodium tungstate dihydrate.[38]

(a) Benzyl Chloride. To a solution of 25 mg (0.20 mmol) of benzyl chloride and 1.0 mg (0.011 mmol) of *tert*-nitrosobutane in 2 ml of degassed benzene was added 230 mg (0.20 mmol) of tetrakis(triphenylphosphine)palladium(0) (**1**) under nitrogen. After 4 h, the ESR spectrum of the reaction mixture showed a triplet for di-*tert*-butyl nitroxide (**29**) and a less intense triplet of triplets for benzyl-*tert*-butyl nitroxide (**28**). No ESR signal was observed after 24 h.

The ESR spectrum for a solution of 12 mg (0.10 mmol) of benzyl chloride, 26 mg (0.10 mmol) of triphenylphosphine, and 1.0 mg (0.011 mmol) of *tert*-nitrosobutane in 2 ml of degassed benzene showed only a weak signal for di-*tert*-butyl nitroxide (**29**), the signal becoming intense after 24 h.

(b) Chloro(benzyl)bis(triphenylphosphine)palladium(II) (2a). To a solution of 4.0 mg (0.046 mmol) of *tert*-nitrosobutane in 2 ml of degassed benzene was added 152 mg (0.200 mmol) of chloro(benzyl)bis(triphenylphosphine)palladium(II) (**2a**) under nitrogen. After 5 h, the ESR spectrum of the mixture showed a triplet for di-*tert*-butyl nitroxide (**29**) and a less intense triplet of triplets for benzyl-*tert*-butyl

Table I. Electron Spin Resonance of Some Alkyl-*tert*-butyl Nitroxides Produced by Radical Trapping

Experiment	Reactants	Time of reaction	Nitroxide	Value of hfsc
A	PdL_4 + $PhCH(CH_3)Br$ + *t*-BuNo 1 4 26	15 min	$PhCH(CH_3)N(O\cdot)$-*t*-Bu 27	$a_N = 15.12 \pm 0.03$ $a_{CH}^H = 3.68 \pm 0.05$
B	PdL_3CO + 4 + 26 6	30 min	27	$a_N = 14.93 \pm 0.13$ $a_{CH}^H = 3.60 \pm 0.07$
C	4 + 26	4 h then 24 h	*t*-$BuN(O\cdot)$-*t*-Bu 29	$a_N = 15.56 \pm 0.14$
D	$PhCH_2Cl$ + 26	4 h then 24 h	29	$a_N = 15.56 \pm 0.14$
E	1 + $PhCH_2Cl$ + 26	4 h	29 + $PhCH_2N(O\cdot)$-*t*-Bu 28	$a_N = 15.63$ $a_{CH_2}^H = 7.54$
F	1 + $PhCH_2Br$ + 26	30 min	29 + 28	$a_N = 15.06 \pm 0.20$ $a_{CH_2}^H = 7.52 \pm 0.18$
G	1 + CH_3I + 26	30 min	29 + $CH_3N(O\cdot)$-*t*-Bu	$a_N = 15.91 \pm 0.07$ $a_{CH_3}^H = 11.83 \pm 0.13$
H	$PhCH_2PdL_2Cl$ + 26	5 h	29 + 28	$a_N = 15.26 \pm 0.05$ $a_{CH_2}^H = 7.63 \pm 0.05$
I	$PhCH_2PdL_2Br$ + 26	30 min then 3 h	29 + Ph(D)C(O·)-N-*t*-Bu H	$a_N = 15.04 \pm 0.25$ $a_{CHD}^H = 7.61 \pm 0.14$ $a_{CDH}^D = 1.15 \pm 2.07$
J	$PhCH(CH_3)C(=O)PdL_2Br$ (5a) + 26	5 h	29 only	
K	$PhCHDC(=O)PdL_2Cl$ + 26	5 h	29 only	
L	$PhCH(CH_3)Cl$ + 1 + 26	30 min	29 + 27 (v. weak)	

nitroxide (**28**).

Oxidative Addition of α-Phenethyl Bromide to Carbonyltris(triphenylphosphine)platinum(0). Formation of Bromo(carbonyl)(α-phenethyl)(triphenylphosphine)platinum(II). A solution of 0.487 g (0.483 mmol) of carbonyltris(triphenylphosphine)platinum(0)[51] and 0.441 g (2.78 mmol, 4.94 equiv) of α-phenethyl bromide in 25 ml of carbon monoxide-saturated benzene was stirred at 25 °C for 26 h. Dilution of the mixture with hexane gave a yellow solid which was isolated by filtration. The filtrate was evaporated to dryness yielding an impure yellow solid (ir ($CHCl_3$) 1800 cm^{-1}). The solid isolated by filtration was purified by column chromatography on alumina using a mixture of dioxane and hexane as eluent. The yellow complex was bromo(carbonyl)(α-phenethyl)(triphenylphosphine)platinum(II) (ca. 20 mg, 0.03 mmol, 6%), ir ($CHCl_3$) 2100 cm^{-1}. Anal. Calcd for $C_{26}H_{24}BrOPPt$: C, 47.42; H, 3.65. Found: C, 46.44, 47.23; H, 3.45, 3.43.

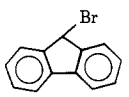
General Procedure for the Reaction of DPPH with the Oxidative Addition Product. The Reaction of 9-Bromofluorene (9) and Tetrakis(triphenylphosphine)palladium(0) in the Presence of DPPH. Reactions were carried out in the dark using freshly distilled reagents in degassed anhydrous benzene in a sealed glass apparatus[77] consisting of two connecting ampoules. A breakable seal was constructed at the connector such that the reactants could be placed and sealed off inside the appropriate ampoules. Breakage of the seal afterwards allowed mixing of the reactants. The same apparatus was used for the polymerization experiments.

Into one ampoule were placed 0.267 g (1.09 mmol) of 9-bromofluorene (**9**) and 10 ml of a 10^{-2} M deep violet solution of 2,2-diphenyl-1-picrylhydrazyl (DPPH)[53,54] in benzene. The solution was degassed by four freeze–pump–thaw cycles and the ampoule was sealed. Into the other ampoule was placed 0.128 g (0.111 mmol) of tetrakis(triphenylphosphine)palladium(0) in 3 ml oxygen-free anhydrous benzene. The solutions was similarly degassed and the ampoule was sealed. Breakage of the seal in the connector of the apparatus allowed mixing of the contents in the two ampoules. Instantaneous disappearance of the deep violet color occurred. A light orange-yellow solution was obtained.

Similar experiments with **2a**, **4**, and **11** gave the results shown in Table II.

Copolymerization of Styrene and Methyl Methacrylate in the Presence of 9-Bromofluorene (9) and Tetrakis(triphenylphosphine)-palladium(0) (1). Into one ampoule of the glass apparatus[77] were placed 2.0 g (20 mmol) of freshly distilled methyl methacrylate, 1.2 g (20 mmol) of freshly distilled styrene, and 100 mg (0.41 mmol) of freshly recrystallized 9-bromofluorene (**9**). The mixture was degassed by four freeze–pump–thaw cycles at 1–2 μ Hg and the ampoule was sealed. Into the other ampoule was introduced a 10-ml quantity of a 3×10^{-2} M solution of tetrakis(triphenylphosphine)palladium(0) (**1**) in oxygen-free anhydrous benzene (0.3 mmol). The solution was similarly degassed and the ampoule was sealed. The contents of the ampoules were allowed to mix through the breakage seal in the connector of the glass apparatus. After standing in the dark at 25 °C for 18 h, the mixture was mixed with 100 ml of vigorously stirred methanol. A white precipitate was obtained which was purified by twice dissolving it in benzene and reprecipitating with methanol. The final product was washed with ether and dried to afford 42 mg (1% conversion) of polymer. A second run using the same quantities and degassing procedure but allowing 45 h for reaction afford 44 mg of polymer after purification. A third run after 45 h afforded 94 mg (2% conversion) of polymer after purification.

Table II. Reaction of Oxidative Addition Products with DPPH

Solution A[a]	Solution B[a]	Color change after mixing
$PhCH(CH_3)Br$, to DPPH 4	PdL_4	No change after 3 days
4 + DPPH	—	No change after 3 days
$PhCH_2PdL_2Cl$ (29)	DPPH	No change after 3 days
 9	DPPH	PdL_4	Violet to light yellow[b]
$PhCH(Br)CO_2Et$ (11), DPPH	PdL_4	Violet to Light yellow[b]

[a] The solutions were degassed by at least three freeze–pump–thaw cycles. [b] Color change occurred within 0.5 h.

All three samples of polymer had identical ir spectra: ir ($CHCl_3$) 1720 (sharp, intense) and 1300–1050 cm^{-1} (broad, intense) were ascribable to the methyl methacrylate unit; 1600, 1490, 1450, 1380, 1020, and 690 cm^{-1} were ascribable to the styryl unit. The polymer had an NMR spectrum that was superimposable to that of an authentic sample of a 1:1 alternating copolymer of styrene and methyl methacrylate, synthesized under free radical (AIBN catalyzed) conditions: NMR ($CDCl_3$) broad absorptions at δ 7.09 (5 H, phenyl), 3.48, 3.28, 2.90, 2.23 (CO_2CH_3), 1.65 ($-CCH_2CH(Ph)-$), 1.32 ($-CCH_2CH(Ph)CH_2-$) and 0.58 ppm ($CH_3C(CO_2Me)CH_2-$); total nonaromatic integration was 11 H.

^{13}C NMR ($CDCl_3$) δ 177.2–175.7 (broad m, carbonyl carbon), 146.6–143.6 (broad m, quaternary carbon on phenyl), 128.2 (s, phenyl), 126.0 (s, phenyl), 51.4–50.0 (sharp m, $CH_2C(CH_3)(CO_2CH_3)-$), 46.1–44.1 (sharp m, $CH_2C(CH_3)(CO_2CH_3)-$), 40.0–38.2 (broad m, $CH_2CH(Ph)CH_2-$), and 21.8–18.2 ppm (3 broad s, CH_3). Anal. Calcd for $(C_{13}H_{16}O_2)_n$: C, 76.12; H, 7.90. Found: C, 76.72, 77.52; H, 7.99, 7.92.

Reaction of Chloro(benzyl)bis(triphenylphosphine)palladium(II) (2a) with Hydrogen Chloride. Formation of Toluene. A suspension of 1.5

g (2.0 mmol) of chloro(benzyl)bis(triphenylphosphine)palladium(II) in 100 ml of pentane was treated with 100 ml of concentrated hydrochloric acid. The heterogeneous mixture was vigorously stirred for 30 min. Filtering the yellow complex afforded a two-phase colorless liquid. The pentane layer was separated, washed with water, and dried over magnesium sulfate. Distillation of solvent afforded a residual yellow oil which was purified by GLC (120 °C, 10 ft × 0.375 in., 20% Carbowax-20M on Chromosorb W 60/80) to afford toluene: NMR ($CDCl_3$) δ 7.21 (s, 5 H, aromatic) and 2.35 ppm (s, 3 H, CH_3).

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