Reaction of α,ω-Di-Grignard Reagents with Silver(I) Salts Forms Carbocyclic Rings[1]

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Reaction of α,ω-alkane di-Grignard reagents with silver(I) triflate in tetrahydrofuran solution provides a practical synthesis for representative four-, five-, and six-membered carbocyclic rings. The reaction works less well for medium-ring compounds.

The reaction of primary alkylmagnesium and -lithium reagents with silver(I) salts results in carbon–carbon bond formation by a reaction involving initial formation of an alkylsilver(I) reagent, followed by concerted carbon–silver bond breaking and carbon–carbon bond forming.[2–4] This reaction occurs under mild conditions (20 °C <5 min) in high yields. Free alkyl radicals are not intermediates. Although it is restricted to primary alkyl moieties,[5] within this class it is one of the cleanest oxidative methods for forming carbon–carbon bonds from Grignard and organolithium reagents.

This paper explores the utility of the coupling of α,ω-di-Grignard reagents using silver(I) salts as a method for preparing carbocyclic structures. We had originally hoped that the fact that the decompositions of the intermediate organosilver(I) compounds undoubtedly proceed within aggregates might permit the synthesis of medium rings. In fact, this reaction does *not* provide a practical synthesis of medium ring compounds. It does, however, provide a useful method of making four-, five-, and six-membered rings, and warrants consideration in circumstances in which the functionality introduced into the products by the standard methods of ring formation is not desirable.

Results and Discussion

The most useful precursors to the α,ω-di-Grignard reagents were α,ω-dichlorides, prepared, in turn, from α,ω-diols. We explored a number of routes for the conversion of diols to chlorides, and found the most general to be the displacement of tosylate or mesylate using lithium chloride in HMPA.[6] Occasionally direct reaction between diols and thionyl chloride was used, but this reaction produced cyclic ethers when applied to many of the substrates of interest. Grignard reagents were used as the organometallic starting materials rather than dilithium reagents because organomagnesium compounds are more easily prepared, more soluble, and more stable to storage in ethers than organolithium compounds. Two points concerning the preparation of the Grignard reagents deserve mention. First, a detailed examination of the mechanism of formation of Grignard reagents, presently in progress in our laboratory, indicates that the highest yields of these materials are obtained by reaction of alkyl chlorides with magnesium in refluxing THF, rather than by the more commonly used reaction of alkyl bromides with magnesium in diethyl ether at 0 °C. Much of the work described in this paper used the latter procedure, but we now believe yields obtained by the former to be 10–15% higher. Second, many di-Grignard reagents are either insoluble in, or form two liquid phases with, diethyl ether. They are much more soluble in THF. Thus, the most useful reagents for the ring closure procedures discussed here are solutions of alkane di(magnesium chlorides) in THF.

Ring closure reactions were carried out by adding the solution of di-Grignard reagent to a solution containing a slight excess of a soluble silver(I) salt in THF at −78 or 0 °C. Several experiments were carried out using tetrakis[iodo(tri-*n*-butylphosphine)silver(I)]; these experiments led to adequate yields of product, as assayed by GLC. For practical synthetic work, however, it is clear that silver(I) triflate is the most useful reagent. It is easily prepared and dried, stable, and soluble in THF at concentration greater than 1 M. Further, triflate ion is easily removed in workup: separation of tri-*n*-butylphosphine and its silver salts from products can prove a major nuisance.

The major experimental difficulty encountered in these reactions is avoiding adventitious hydrolysis and oxidation of the solutions of organometallic reagents during their manipulation. Loss of Grignard (or organosilver) reagent in handling proved to be the major factor in limiting the yield of the desired cyclized product, particularly in experiments designed to improve the yield of medium ring cycloalkanes by adding the Grignard reagents to the silver salts using high dilution techniques.

Table I compares the yields of cycloalkanes obtained by reaction of α,ω-alkane di-Grignard reagents with $[IAgPBu_3]_4$ in THF. These experiments were carried out by mixing the Grignard reagent and a 10% excess of silver(I) salt at −78 °C and allowing the resulting solutions of α,ω-alkanedisilver(I) reagents to decompose while warming to room temperature. The important conclusion from these data is that the yield of cycloalkane product formed on thermal decomposition of α,ω-alkanesilver(I) reagents depends strongly on ring size; yields of four- and five-membered rings are good; those for medium rings are poor. Although it is possible to obtain modest yields of cyclodecane and cyclododecane by working with dilute solutions, the experimental problems encountered in preparing, manipulating, and recovering products from solutions that originally contain air-sensitive organometallic reagents at concentrations less than 10^{-2} N are such that these procedures are not practical.

Table II gives further examples of this coupling reaction. These experiments used silver triflate as silver(I) salt under conditions considered practical for synthetic applications. The yields represent conversions from starting alkyl halide to product. These yields are sufficient to establish that the reaction provides a practical, although specialized, alternative to the more usual chemical and photochemical methods for preparing four-, five-, and six-membered rings.

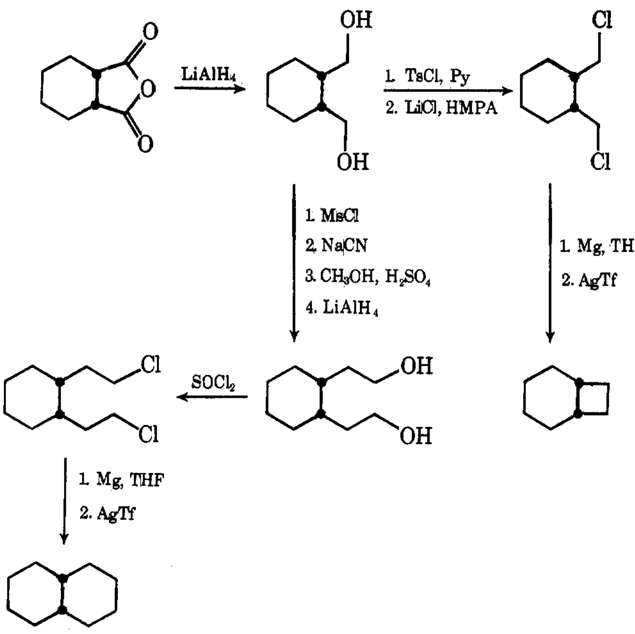
The Experimental Section of this paper contains details only for the preparations of the two alkyl halides included in the representative reaction sequences outlined by Scheme I, and for the conversion of these halides to Grignard reagents and thence to hydrocarbons by treatment with silver(I) triflate. The other transformations summarized in Scheme I are described fully in supplementary material to this paper. Details of the other procedures leading to the data in Tables I and II are sufficiently similar and repetitive that they do not warrant publication. They can, however, be found by consulting the thesis on which this work is based.[7]

Table I. Yields of Cycloalkanes by Reaction between $XMg(CH_2)_nMgX$ and $IAgPBu_3$ in THF

Registry no.	n	X	Concn, N × 10^{2a}	Product	Registry no.	Yield, %[b]
23708-47-6	4	Br	5.0	Cyclobutane	287-23-0	93
23708-48-7	5	Br	2.5	Cyclopentane	287-92-3	83
59448-46-3	6	Cl	2.5	Cyclohexane	110-82-7	43
59321-71-0	7	Br	2.5	Cycloheptane	291-64-5	23
45037-87-4	8	Br	2.5	Cyclooctane	292-64-8	2
59448-47-4	9	Cl	2.5	Cyclononane	293-55-0	<1
23708-54-5	10	Br	0.77	Cyclodecane	293-96-9	10–15[c]
59434-46-7	12	Br	0.77	Cyclododecane	294-62-2	10–15[c]

[a] Concentrations are those estimated for the alkanedisilver(I) intermediates, based on the normality of the starting di-Grignard reagent and the final volume of the reaction mixture. [b] Yields are GLC determinations and are based on the normality of the starting solutions of Grignard reagents. [c] The yields of cyclodecane and cyclododecane varied, depending on the details of the experimental procedure used.

Scheme I. Representative Synthetic Procedures



Experimental Section

General Methods. Melting points and boiling points are uncorrected. All reactions involving organometallic compounds were carried out under prepurified nitrogen or argon. Solvents were reagent grade. THF was distilled from a dark purple solution of disodium benzophenone dianion under argon before use. Diethyl ether was distilled under nitrogen from lithium aluminum hydride; hexamethylphosphoramide was distilled from sodium at reduced pressure;[8] pyridine and benzene were dried over Linde 4A molecular sieves. All solvents were transferred using hypodermic syringes or stainless steel cannulas and were stored under prepurified argon or nitrogen. Alkyl halides were purified by passing through a short column of Woelm alumina (activity grade I) immediately before conversion to Grignard reagents. Grignard reagents were stored under argon in Schlenck tubes, and manipulated using standard procedures.[9] Grignard reagents were titrated using the Eastham procedure.[10] Normalities are expressed for di-Grignard reagents as equivalents of RMgX. Infrared spectra were recorded in 0.1-mm sodium chloride solution cells using carbon tetrachloride as the solvent. NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. Analytical GLC analyses were carried out with Hewlett-Packard Model 810 and Perkin-Elmer Model 990 gas chromatographs equipped with flame ionization detectors.

Tetrakis[iodo(tri-*n*-butylphosphine)silver(I)] was prepared following the procedure of Mann, Wells, and Purdie.[11]

Silver trifluoromethylsulfonate was prepared according to a procedure adapted from Haszeldine and Kidd.[12] Distilled trifluoromethanesulfonic acid (60 g, 0.4 mol) was added slowly to 300 ml of water in a 500-ml flask equipped with a Teflon-coated magnetic stirring bar and cooled in an ice bath.[13] Finely powdered silver oxide (48.5 g, 0.21 mol) was added in portions; the bath was removed and stirring was continued for 25 min in the dark. The suspension was filtered through a sintered glass funnel and the filtrate was washed with 100 ml of distilled water. Water was removed under reduced pressure and the residue was dissolved in 250 ml of acetone. The acetone solution was filtered through a sintered glass funnel and the solvent was evaporated. The product was ground to a fine white powder and dried (100 °C, 0.025 Torr, 6 h), yielding 87.9 g (98%) of silver triflate. Product was stored in a desiccator with exclusion of light.

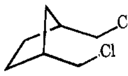
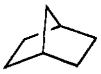
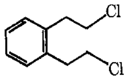
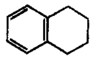
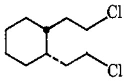
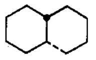
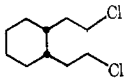
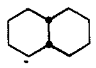
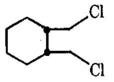
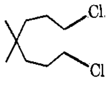
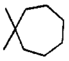
General Procedure for Preparation of Grignard Reagents. Preparation of the Grignard Reagent from *trans*-1,2-Bis(2-chloroethyl)cyclohexane. *trans*-1,2-Bis(2-chloroethyl)cyclohexane (15.7 g, 0.075 mol), which had been passed through a short column of Woelm activity grade I alumina, was transferred under argon by syringe to a 60-ml dropping funnel fitted to a dry, round-bottomed, three-necked flask equipped with a Teflon-coated magnetic stirring bar and charged with 7.3 g (0.3 g-atom) of magnesium powder. An argon bubbler was attached to the flask and 25 ml of dry THF was added, followed by 0.5 ml of dibromoethane. After the reaction with dibromoethane had ceased, the THF was removed by forced siphon and was replaced with 150 ml of fresh THF. The addition of the dichloride was made to the stirred suspension of magnesium in THF over 4 h. When all the halide had been added, the dropping funnel was rinsed with 3 ml of THF and stirring was continued overnight.

General Procedure for Preparation of Cycloalkanes with Tetrakis[iodo(tri-*n*-butylphosphine)silver(I)] at High Dilution. Synthesis of Cyclododecane. A THF solution of the di-Grignard reagent (1 ml, 0.85 N) prepared from 1,12-dibromododecane was diluted to a total volume of 75 ml with dry THF. This solution was added from a dropping funnel over 1.5 h to a magnetically stirred solution containing 0.41 g (0.935 mmol) of tetrakis[iodo(tri-*n*-butylphosphine)silver(I)] and 50 ml of THF, which was cooled in a dry ice bath and protected by a nitrogen atmosphere. When the addition was complete, the bath was removed and the solution was allowed to warm to room temperature. GLC analysis using internal standards indicated that cyclododecane had been formed in 10% yield. Dodecane was also present in 71% yield, presumably as the result of adventitious hydrolysis of the di-Grignard or alkylsilver(I) reagent during the course of the reaction. In general, yields of cyclodecane and of cyclododecane prepared by this procedure were maximized when the di-Grignard concentration was approximately 10^{-2} N. Higher concentrations resulted in less hydrolysis but lower yields of cycloalkanes, while lower concentrations were more prone toward hydrolysis.

***cis*-1,2-Bis(2-chloroethyl)cyclohexane.** Thionyl chloride (71.5 g, 0.6 mol) was added over 0.5 h to a stirred solution of 24.5 g (0.142 mol) of *cis*-1,2-bis(2-hydroxyethyl)cyclohexane and 500 ml of dry benzene which was protected with a $CaSO_4$ drying tube. The reaction mixture was stirred for 6 h at room temperature and then heated at reflux for 4 h. The cooled reaction mixture was transferred cautiously to 500 ml of water and neutralized with solid sodium bicarbonate. The organic phase was separated and was washed with two 250-ml portions of water and with 100 ml of saturated sodium chloride solution. The organic phase was dried ($MgSO_4$), filtered and concentrated, and the crude dichloride was distilled to yield 21 g (71%) of pure material (bp 69–71 °C, 0.15 Torr): ir (CCl_4) 3000 (vw), 930 (s), 2860 (w), 2670 (w), 1448 (m), 1375 (w), 1347 (w), 1323 (w), 1280 (m), 1190 (w), 1035 (w), 937 (w), 857 (w), 713 (w), 661 cm^{-1}; (m); NMR ($CDCl_3$) δ 3.50 (poorly resolved t, 2), 1.73 (poorly resolved t, 2), 1.46 (broad s, 5).

***cis*-Decalin.** A THF solution (800 ml, ca 0.2 N) of the di-Grignard reagent from *cis*-1,2-bis(2-chloroethyl)cyclohexane (16.7 g, 0.08 mol) was added in drops to 160 ml of a chilled (ice bath) THF solution of $AgOSO_2CF_3$ (45.2 g, 0.18 mol), which was vigorously stirred under

Table II. Yields of Cycloalkanes by Reaction between Di-Grignard Reagents and CF_3SO_3Ag in THF

Starting halide	Registry no.	Concn, N[a]	Product	Registry no.	Yield, %[b]
1,4-Dibromobutane	110-52-1	0.21	Cyclobutane		84
1,5-Dibromopentane	111-24-0	0.21	Cyclopentane		80
1,6-Dichlorohexane	2163-00-0	0.21	Cyclohexane		55
	59434-47-8	0.80		279-23-2	82
	59448-77-0	0.50		119-64-2	70
	59434-48-9	0.20		493-02-7	(67)
	59434-49-0	0.20		493-01-6	(57)
	38300-68-4	0.69		28282-35-1	(61)
	59434-50-3	0.22			0

[a] Concentrations are estimated based on the quantity of alkyl halide used in preparing the di-Grignard reagent, the volume of the reaction solution containing the disilver reagent, and the assumption that the overall conversion of alkane dihalide to alkanedisilver reagent occurred in 90% yield. [b] Yields not in parentheses are GLC yields; yields in parentheses are isolated yields. Both are based on starting alkyl halide.

argon with a Teflon-coated magnetic stirring bar. When the addition was completed, the reaction mixture was allowed to warm to room temperature and filtered through a pad of Celite. The solution was passed through a short alumina column and concentrated under reduced pressure at 25 °C to ca. 75 ml. Water (150 ml) and pentane (150 ml) were added and the phases were separated. The aqueous phase was extracted with three 50-ml portions of pentane and the combined organic phase was then washed with water (2 × 50 ml) and saturated aqueous sodium chloride solution (25 ml) and dried ($MgSO_4$). After filtering and concentrating, the product was distilled through a Holtzman column [bp 81–83 °C, 19 Torr (lit.[14] bp 196 °C, 760 Torr)], yield 6.3 g (57%). NMR and ir spectra were indistinguishable from those of an authentic sample of *cis*-decalin.

***cis*-1,2-Bis(hydroxymethyl)cyclohexane Ditosylate.** *cis*-1,2-Bis(hydroxymethyl)cyclohexane (44 g, 0.306 mol) and 300 ml of pyridine were cooled under argon to 0 °C. A solution of *p*-toluenesulfonyl chloride (143 g, 0.75 mol) and 400 ml of pyridine was added to the diol solution over a period of 3 h. The reaction mixture was stored at 0 °C for 12 h and was then poured into a mixture of 700 ml of concentrated HCl and 800 g of crushed ice. The mixture was extracted with three 300-ml portions of methylene chloride and the organic phase was washed with three 400-ml portions of water and 200 ml of saturated aqueous sodium chloride solution. After drying ($MgSO_4$), filtering, and evaporating the solvent, the ditosylate was recrystallized from a mixture of pentane and methylene chloride (4:1 v/v) at −78 °C: mp 83.5–84.5 °C (lit.[15] mp 84–85 °C); yield 89 g (64%); ir ($CHCl_3$) 3020 (w), 2935 (m), 2865 (w), 1600 (m), 1450 (m), 1360 (s), 1309 (w), 1290 (w), 1175 (s), 1098 (m), 955 (s), 555 cm^{-1} (m); NMR ($CDCl_3$) δ 7.53 (AB q, 4) 3.87 (d, 2), 2.47 (s, 3) 2.16–1.60 (broad m, 1), 1.37 (broad s, 4).

***cis*-1,2-Bis(chloromethyl)cyclohexane.** *cis*-1,2-Bis(hydroxymethyl)cyclohexane ditosylate (89 g, 0.192 mol), lithium chloride (68 g, 1.6 mol), and 400 ml of HMPA were heated to 100 °C and stirred under argon for 12 h. The cooled reaction mixture was added to 1.2 l of water and extracted with four 400-ml portions of pentane. The pentane extracts were combined and washed with three 800-ml portions of water and with 200 ml of saturated sodium chloride solution. The solution was dried ($MgSO_4$), filtered, and concentrated. Distillation (139–140 °C, 30 Torr) afforded 31.5 g (90%) of the dichloride: ir (CCl_4) 2985 (w), 2955 (m), 2870 (w), 1445 (m), 1322 (m), 1195 (w), 1140 (w), 1110 (w), 1060 (w), 717 cm^{-1} (m); NMR ($CDCl_3$) δ 3.50 (d, 2), 2.20 (broad s, 1), 1.53 (broad s, 8).

Bicyclo[4.2.0]octane. A THF solution (450 ml) of the di-Grignard reagent prepared from *cis*-1,2-bis(chloromethyl)cyclohexane (28 g, 0.155 mol) was added over 2 h to a vigorously stirred solution of $AgOSO_2CF_3$ (87.6 g, 0.341 mol) and THF (90 ml) cooled in an ice bath and protected by an argon atmosphere. When the addition was completed, the bath was removed, and the reaction mixture was allowed to warm to room temperature. After filtration through a pad of Celite, the solution was passed through a column containing 100 g of alumina, which was subsequently washed with 100 ml of pentane. This solution was concentrated to approximately 150 ml by distillation through a 36-cm Holtzman column. The residue was poured into 100 ml of water and the layers were separated. The aqueous phase was extracted with five 30-ml portions of pentane. The combined organic phases were washed with two 50-ml portions of water and 25 ml of saturated sodium chloride solution, dried ($MgSO_4$), and filtered. The solution was distilled through a 36-cm Holtzman column, yielding 10.4 g (61%) of bicyclo[4.2.0]octane, bp 135.5–137 °C (lit.[16] bp 136–137.5 °C). The NMR and ir spectra of this material were indistinguishable from those of a sample prepared by hydrogenation of Δ^7-bicyclo[4.2.0]octene.[17,18]

Registry No.—1,7-Dibromoheptane, 4549-31-9; 1,8-dibromooctane, 4549-32-0; 1,9-dichlorononane, 821-99-8; 1,10-dibromodecane, 4101-68-2; 1,12-dibromododecane, 3344-70-5; α,ω-butanedisilver(I), 59434-51-4; α,ω-pentanedisilver(I), 59434-56-9; α,ω-hexanedisilver(I), 59434-53-6; α,ω-heptanedisilver(I), 59434-54-7; α,ω-octanedisilver(I), 59434-55-8; α,ω-nonanedisilver(I), 59434-56-9; α,ω-decanedisilver(I), 59434-57-0; α,ω-dodecanedisilver(I), 59434-58-1; 1,3-bis(silvermethyl)cyclopentane, 59434-59-2; 1,2-bis(2-silverethyl)benzene, 59434-60-5; *trans*-1,2-bis(2-silverethyl)cyclohexane, 59434-61-6; *cis*-1,2-bis(2-silverethyl)cyclohexane, 59434-62-7; *cis*-1,2-bis(silvermethyl)cyclohexane, 59434-63-8; 1,3-bis(chloromethyl)cyclopentane Grignard reagent, 59434-64-9; 1,2-bis(2-chloroethyl)benzene Grignard reagent, 59434-65-0; *trans*-1,2-bis(2-chloroethyl)cyclohexane Grignard reagent, 59434-66-1; *cis*-1,2-bis(2-chloroethyl)cyclohexane Grignard reagent, 59434-67-2; *cis*-1,2-bis(chloromethyl)cyclohexane Grignard reagent, 59434-68-3; 4,4-dimethyl-1,7-dichloroheptane Grignard reagent, 59434-69-4; tetrakis[iodo(tri-*n*-butylphosphine)silver(I)], 59448-71-4; silver triflate, 2923-28-6; *cis*-1,2-bis(2-hydroxyethyl)cyclohexane, 59434-70-7; *cis*-1,2-bis(hydroxymethyl)cyclohexane ditosylate, 59461-66-4; *cis*-1,2-bis(hydroxymethyl)cyclohexane, 15753-50-1; *p*-toluenesulfonyl chloride, 98-59-9.

Supplementary Material Available. Experimental procedures for the preparations of compounds listed in Scheme I and not described in the Experimental Section (3 pages). Ordering information is given on any current masthead page.

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Linear Carboxylic Acid Esters from α Olefins. 2. Catalysis by Homogeneous Palladium Complexes

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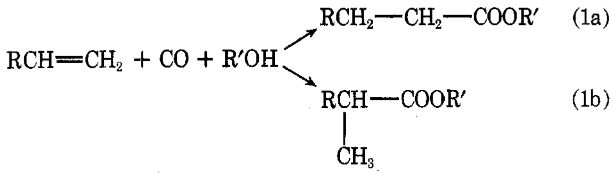
Regioselective carbonylation of α olefins is catalyzed by a series of ligand-stabilized palladium(II)–group 4B metal halide complexes of the composition $[(p\text{-}XC_6H_4)_3P]_2PdCl_2{-}MCl_2$ (where X = H, CH_3, CH_3O, and Cl, and M = Sn or Ge) and by related complexes. For the synthesis of linear carboxylic acid esters the sensitivity of the carbonylation to palladium catalyst composition, the structure of the olefin substrate and that of the nucleophilic coreactant have been examined in relation to observed kinetics and the isolation of active intermediates.

In a previous paper[1] we described the synthesis of linear carboxylic acid esters from linear α olefins in high yields (eq 1a) catalyzed by a novel class of ligand-stabilized



$$RCH{=}CH_2 + CO + R'OH \longrightarrow RCH_2{-}CH_2{-}COOR' \quad (1a)$$

$$RCH{=}CH_2 + CO + R'OH \longrightarrow \underset{\displaystyle CH_3}{\underset{|}{RCH}}{-}COOR' \quad (1b)$$

platinum(II)–group 4B metal halide carbonylation catalysts. These highly regioselective catalysts, typified by $[(C_6H_5)_3As]_2PtCl_2{-}SnCl_2$, afford up to 98 mol % selectivity to the linear ester. We report herein the extension of that work to palladium chemistry, and the development of a series of highly active ligand-stabilized palladium(II)–group 4B metal halide catalysts. These catalysts also yield linear esters in 85–89 mol % selectivity but have the intrinsic advantages of requiring lower CO pressures, greater flexibility regarding olefin feed stock, and lower cost.

Palladium salts have, in recent years, found extensive application as carbonylation catalysts.[2–7] Where the addition is to an α olefin of three or more carbons, however, most catalysts, e.g., $PdCl_2$[8] and $PdCl_2[P(C_6H_5)_3]_2$,[5] yield a mixture of normal and iso acid derivatives and generally it is the iso ester that predominates (eq 1b).[3] The use of more selective palladium bimetallic catalysts which ensure higher selectivity to linear acid derivatives has been recognized in the patent literature.[9–12]

Results

Effect of Palladium Catalyst Structure. By analogy with earlier studies[1] a broad range of palladium bimetallic complexes have been screened for carbonylation activity. Palladium bonded to group 5B and 6B tertiary donor ligands containing aryl, substituted aryl, alkyl, and aryloxy radicals in combination with group 4B metal halides has been considered.[11] Methyl octanoate synthesis was selected as the model reaction. Table I illustrates the importance of catalyst structure upon both activity and selectivity to linear ester. Under typical screening conditions linear ester selectivity varies from a low of 44% up to 89 mol %. Yields of methyl octanoate also vary widely, but exceed 70 mol % for at least four palladium complexes, viz., $[(C_6H_5)_3P]_2PdCl_2{-}SnCl_2$, $[(p\text{-}CH_3C_6H_4)_3P]_2PdCl_2{-}SnCl_2$, $[(p\text{-}CH_3OC_6H_4)_3P]_2PdCl_2{-}SnCl_2$, and $[(C_6H_5)_3P]_2PdCl_2{-}GeCl_2$ (expt 1–3, 10). Total ester yields, which include 10–13% methyl 2-methylheptanoate and 1–2% methyl 2-ethylhexanoate, are in excess of 85 mol % for each of these catalysts. The remaining products are isomerized heptenes, primarily *cis*- and *trans*-2-heptenes.

No simple correlations have been found between catalyst performance and either the size or electronic character of the coordinated ligands, although both properties are clearly important. For a series of substituted arylphosphine complexes, differences in the effective size of the coordinated ligands may have a critical effect upon the degree of steric crowding and consequently upon catalyst reactivity. This is illustrated by the more than 20-fold difference in ester yield between otherwise similar ortho- and para-substituted methoxyphenylphosphine complexes, viz., $[(o\text{-}CH_3OC_6H_4)_3P]_2PdCl_2{-}SnCl_2$ and $[(p\text{-}CH_3OC_6H_4)_3P]_2PdCl_2{-}SnCl_2$ (expt

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