A New Platinum Complex Catalyzed Reaction Involving Nucleophilic Substitution at the Central Carbon Atom of the π-Allyl Ligand

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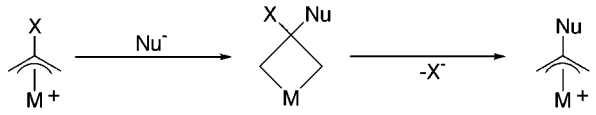
The reaction of 2-chloro-allyl acetate with sodium ethyl acetoacetate in the presence of a platinum(0) complex gave furan derivatives. The key feature of this new platinum-catalyzed reaction is the nucleophilic substitution at the central carbon atom of π-allyl complexes. The regioselectivity of the nucleophilic attacks (central or terminal) is dependent on the pK_a of the nucleophile. In addition, a labeling experiment revealed that a rapid syn−anti isomerization of the (π-allyl) platinum complexes occurs.

Introduction

The extensive investigations of reactions of π-allyl transition metal complexes with nucleophiles has led to a number of synthetically useful methods for the introduction of three-carbon units into organic compounds. Typically, the nucleophilic attack takes place at the terminal carbon atom of π-allyl complexes to give allylated products.[1] The recent report of a nucleophilic attack at the central carbon atom of π-allyl complexes has attracted attention. This process converts π-allyl complexes into a variety of metalacyclobutanes[2] and, in some cases, leads to the formation of cyclopropane derivatives via reductive elimination with metallacyclobutanes.[3] In the majority of these examples, the attached group on the central carbon atom was a hydrogen atom and, in a few cases, an alkyl group. If, however, group X (Scheme 1) represents a viable leaving group, this could substantially alter the reaction pathway. Thus, nucleophilic substitution would be expected to proceed via nucleophilic attack at the central carbon atom of the π-allyl complex (**I**) followed by the elimination of X^- from metalacyclobutane (**II**), rather than cyclopropane, giving rise to a reductive elimination.

Scheme 1



I **II** **III**

In a preliminary communication we reported the first example of this type of reaction.[4] In the presence of a platinum catalyst, the reaction of 2-chloro-allyl acetate with 2 equiv of sodium diethyl methylmalonate gave a doubly alkylated product, and in the case of sodium ethyl benzoyl acetate, a furan derivative was obtained. More recently, three examples of nucleophilic substitutions of this type at the central carbon atom have been reported by other groups. Bäckvall reported the stoichiometric reaction of (π-allyl) palladium complexes with sodium diethyl methylmalonate,[5] and Chen reported the formation of trimethylenemethane platinum complexes.[6] Organ reported the palladium-catalyzed reaction of 2,3-dibromopropene with phenoxides as nucleophiles.[7] In this paper, we report further results of the platinum-catalyzed reaction of 2-chloro-allyl acetate with a variety of carbon nucleophiles. Our findings show that the regioselectivity of the nucleophilic attack on the central or terminal carbon is dependent on the nature of the nucleophiles used.

Results and Discussion

2-Chloro-allyl acetate **1** was chosen as the simplest allyl acetate with a leaving group on the central carbon.

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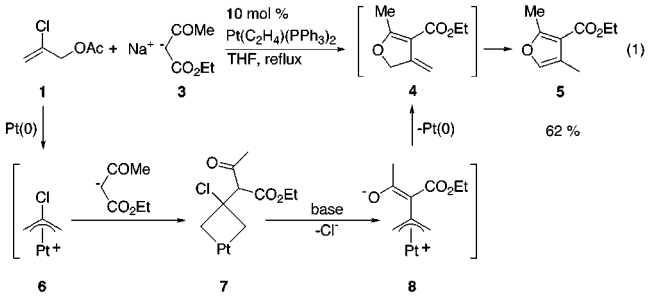
Table 1. Variation of Ligands

entry	ligand	time (h)	yield (%)[a] of **5**
1	PPh_3	2	85(83[b])
2	$P(OMe)_3$	8	73
3	dppe	21	n.r.[c]
4	dppb	18	20[d]
5	dppf	28	61[d]
6	TMEDA	20	n.r.
7	bipy	18	n.r.

[a] GC yield. [b] Isolated yield. [c] No reaction. [d] Allyl acetate was not consumed completely.

The reaction of **1** with sodium diethyl malonate **2** in the presence of a platinum complex such as $Pt(C_2H_4)(PPh_3)_2$ resulted in no reaction.[8] In contrast, however the reaction of 2-chloro-allyl acetate **1** (1.0 mmol) with 2 equiv of sodium ethyl acetoacetate **3** in the presence of $Pt(C_2H_4)(PPh_3)_2$ (0.1 mmol) as catalyst in THF at reflux gave ethyl 2,4-dimethyl-3-furoate **5** as the result of a nucleophilic attack at the central carbon (eq 1).



This reaction proceeds as follows. First, a nucleophilic attack at the central carbon atom of 2-chloro-(π-allyl) platinum(II) **6** gives platinacyclobutane **7**. The elimination of a chloride anion in **7**, followed by deprotonation by the excess nucleophile, which serves as a base, affords 2-alkylated (π-allyl) platinum(II) **8**. (In fact, it must also exist in trimethylenemethane−platinum form.) An enolate O-cyclization, followed by exo to endo double-bond isomerization would have given furan **5**.[9]

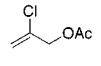
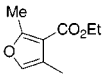
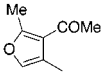
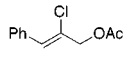
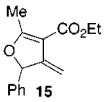
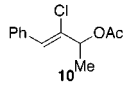
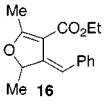
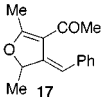
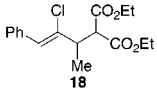
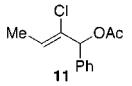
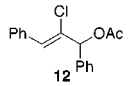
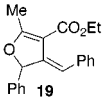
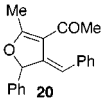
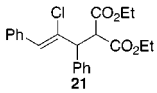
Several different ligands for platinum(0) were examined in this reaction (eq 1) using platinum complexes prepared in situ from $Pt(dba)_2$ (10 mol %) and an appropriate ligand (20 mol % for the monodentate, 10 mol % for the bidentate) as catalyst instead of $Pt(C_2H_4)(PPh_3)_2$ (Table 1). The use of PPh_3 gave the highest yield (entry 1). Platinum−bidentate phosphine ligand systems, such as $Pt(dba)_2$−dppe, −dppb, and −dppf, gave moderate to poor yields (entries 3−5). No reaction was observed with σ-donor nitrogen ligands, such as TMEDA or bipyridyl, although some nitrogen ligands have been reported to be effective for the attack on a central carbon.[5]

With $Pt(C_2H_4)(PPh_3)_2$ (10 mol %) as the catalyst, reactions of 1,3-substituted allyl acetates (1.0 mmol) with some carbon nucleophiles (2.0 mmol) were carried out under the same condition as were used for the reaction of eq 1. These results are summarized in Table 2.

(8) The lack of reaction appears to be due to stable trimethylenemethane−plainum complex formation through nucleophilic substitution at the central carbon atom of the π-allyl ligand, followed by deprotonation. Actually, the stoichiometric reaction of 2-chloro-(π-allyl) platinum complex with sodium diethyl malonate gave a trimethylenemethane−platinum complex in 21% yield.

(9) A preliminary result of a similar reaction using sodium ethyl benzoyl acetate has been reported; see ref 4.

Table 2. Platinum-Catalyzed Reaction of 2-Chloro-allyl Acetates with Carbon Nucleophiles[a]

entry	allylacetate	NuH	time(h)	product	yield(%)
1	 **1**	 **3**	2	 **5**	62
2	**1**	 **13**	5	 **14**	43[b]
3	 **9**	**3**	5	 **15**	58
4	 **10**	**3**	0.25	 **16**	76
5	**10**	**13**	4	 **17**	82
6	**10**	 **2**	2	 **18**	71
7	 **11**	**3**	21	**16**	55
8	 **12**	**3**	6	 **19**	84
9	**12**	**13**	48	 **20**	76[c]
10	**12**	**2**	12	 **21**	58[b]

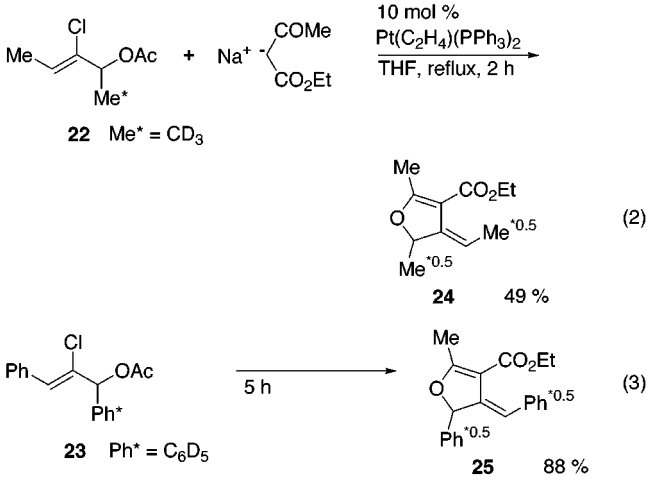
[a] Reactions were run as follows: protonated nucleophile (2.0 mmol) was added to a suspension of NaH (2.0 mmol) in THF at 0 °C. After the solution was stirred for 30 min at room temperature, $Pt(C_2H_4)(PPh_3)_2$ (0.1 mmol) and allyl acetate (1.0 mmol) were added. [b] In refluxing dioxane. No reaction in THF. [c] This product underwent isomerization within 30 min in $CDCl_3$ to the corresponding furan derivative.

Allyl acetate **1** reacted with sodium acetylacetonate **13** to give a furan derivative **14** in dioxane at reflux, whereas no reaction took place in refluxing THF (entry 2). The reaction of 3-phenylallyl acetate **9** with sodium ethyl acetoacetate **3** gave the 2,3-dihydrofuran derivative **15**, which was formed through enolate O-cyclization at the terminal carbon atom, which carries a phenyl group in π-allyl ligand (entry 3). It is likely that the regioselectivity of enolate O-cyclization onto C1 or C3 termini is dependent on the stabilization of the partial positive charge on the terminal carbon, in this case, the phenyl group. The reactions of 1-methyl-3-phenylallyl acetate **10** with nucleophiles were also examined (entries 4−6). Interestingly, with nucleophiles bearing an acetyl group, the corresponding dihydrofurans **16** and **17** were obtained. The cyclization took place at the terminal carbon carrying the smaller substituent, i.e., a methyl group. Thus, steric

congestion appears to compete with phenyl stabilization. It is noteworthy that sodium diethyl malonate **2** did not undergo attack at the central carbon atom but attacked at the terminal carbon atom in a classic manner (entry 6). A similar result was obtained in the reaction where 1,3-diphenylallyl acetate **12** was used as the substrate (entry 10). At present, the reason for why the regioselectivity of nucleophilic attack (central or terminal) varies with the nature of the nucleophile used is unclear. Recently, Bäckvall has reported that the site of nucleophilic attack (central or terminal) in the reaction of a 2-chloro-(π-allyl) palladium complex with carbon nucleophiles changed with the type of ligand.[5] Central attack was observed when bipyridyl or TMEDA was used as the ligand, but terminal attack occurred with a phosphine ligand. Calculation for (π-allyl) palladium complexes with the σ-donor nitrogen ligands indicated that the LUMO is the molecular orbital with a large coefficient at the central carbon. They proposed that the nucleophilic attack at the central carbon is frontier orbital controlled. However, the data herein suggest that the regioselectivity of nucleophilic attack on (π-allyl) platinum complexes varies with the structure of the nucleophiles. It seems likely that the energy level of the nucleophile's HOMO also is a factor in determining whether the central or terminal carbon atom of the π-allyl ligand is attacked. Thus, when the difference of energy level between the nucleophile's HOMO and LUMO of π-allyl complexes is sufficiently small to allow the interaction of molecular orbitals, central attack will be observed. The pK_a values for **13**, **3**, and **2** are 9, 11, and 13, respectively, and relate, in part, to the strength of their nucleophilicity. To make the relation of regioselectivities with the pK_a values clearly, cyclic β-dicarbonyls (1,3-cyclohexanedione, Meldrum's acid) were used but unfortunately resulted in no reaction.

The reaction with 1-phenyl-3-methylallyl acetate **11** (which is an isomer of **10** with a reversed substitution pattern) afforded the same product **16** (entries 7 and 4). It thus appears that the product was obtained via a common π-allyl intermediate, derived from both **10** and **11**, and this suggests that the syn−anti stereochemistry in the intermediate is easily interconvertible.[10]

Similar results relative to regio- and stereochemistry were obtained for the symmetrically substituted allyl aceates that were unsymmetrically labeled (**22** and **23**). The deuterium was incorporated equally into the two substituents (eq 2 and 3).



Conclusion

The data herein provide clear evidence for the platinum-catalyzed reaction of 2-chloro-allyl acetate with stabilized carbon nucleophiles. This reaction is a new type of catalytic reaction, in which the nucleophilic substitution at the central carbon atom of π-allyl complexes predominates. The site of nucleophilic attack on either the central or terminal carbon atom appears to depend on the small difference in the pK_a of the nucleophiles.

Experimental Section

Materials. Protonated nucleophiles, diethyl malonate **2**, ethyl acetoacetate **3**, and acetylacetone **13**, were purificated by distillation. THF and dioxane were distilled over Na−benzophenone or CaH prior to use. Pt(C_2H_4)(PPh_3)$_2$[11] and Pt(dba)$_2$[12] were prepared according to published procedures.

Preparation of 2-Chloro-allyl Acetates. 2-Chloro-2-propenyl Acetate (1). A mixture of 2,3-dichloro-1-propene (11.1 g, 100 mmol) and K_2CO_3 (15.2 g, 110 mmol) in water (100 mL) was stirred at reflux temperature for 12 h. After cooling to room temperature, the mixture was extracted with diethyl ether, and the combined organic layer was dried over $MgSO_4$ and concentrated in vacuo to give a yellow oil. The residue was distilled under atmospheric pressure to give 2-chloro-2-propen-1-ol (8.51 g, 92 mmol, bp 127−129 °C). To a mixture of this alcohol (8.51 g) and triethylamine (40 mL, 287 mmol) in diethyl ether (100 mL) at 0 °C was added acetyl chloride (14.2 mL, 200 mmol) dropwise, and the resulting solution was stirred at room temperature for 1 h. After 2 N HCl (200 mL) was added to the reaction mixture, it was extracted with diethyl ether, and the combined organic layer was dried over $MgSO_4$ and concentrated in vacuo to give a yellow oil. The residue was distilled under reduced pressure to give 2-chloro-2-propenyl-acetate **1** (8.34 g, 62 mmol, overall 62% yield, bp 79−80 °C/100 mmHg). This material is also commercially available (Aldrich Chemical Co. 29077−7).

2-Chloro-3-phenyl-2-propenyl Acetate (9). First, 2 N HCl (30 mL) was added dropwise to a solution of α-chlorocinnamaldehyde (8.33 g, 50 mmol) and $NaBH_3CN$ (7.54 g, 120 mmol) in methanol (100 mL) at room temperature, followed by stirring for 1 h.[13] The reaction mixture was concentrated in vacuo, the residue was extracted with diethyl ether, and the combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent, hexane/ethyl acetate = 10/1) to give 2-chloro-3-phenyl-2-propen-1-ol (4.45 g, 26.4 mmol). This alcohol was acetylated as described for **1** (3.81 g, 18 mmol, overall 36% yield) to give a white solid, mp 44−45 °C, bp 102 °C/2 mmHg. ^{1}H NMR ($CDCl_3$): δ 2.15 (s, 3H), 4.81 (s, 2H), 6.78 (s, 1H), 7.28−7.41 (m, 3H), 7.64 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 20.8, 68.5, 127.5, 128.3, 128.3, 128.4, 129.2, 133.7, 170.3. IR (KBr): 2944 bw, 1734 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 212 (M^+ + 2, 4), 210 (M^+, 12), 168 (18), 115 (100), 77 (15). HRMS Found: 210.0437. Calcd for $C_{11}H_{11}O_2Cl$: 210.0448.

2-Acetoxy-3-chloro-4-phenyl-3-butene (10). To the Grignard reagent MeMgI [prepared in situ from Mg (1.46 g, 60 mmol) and iodomethane (8.52 g, 60 mmol)] in diethyl ether (100 mL) at room temperature was added a diethyl ether

(10) We consider that the elimination of a chloride anion in intermediate **7** requires flipping of **7**. The reactions of cyclic allyl acetate (2-chloro-2-cyclohexenyl acetate, which is not able to flip in intermediate **7**) with carbon nucleophiles from diethyl malonate **2**, ethyl acetoacetate **3**, and acetylacetone **13** were investigated, and in the case of **2** and **13**, only terminal attack leading to allylation was observed as expected. However, only in the case of sodium ethyl acetoacetate **3** as nucleophile, product by central attack was observed in 13% yield, with allylated product in 73% yield (not identified except for ^{1}H NMR spectrum). This result is not understood as of now and must be investigated in detail.

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solution of α-chlorocinnamaldehyde (5.0 g, 30 mmol). The mixture was stirred for 12 h, and a saturated aqueous solution (100 mL) of NH_4Cl was added, followed by extraction with diethyl ether. The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was distilled under reduced pressure to give 3-chloro-4-phenyl-3-buten-2-ol (5.10 g, 28 mmol). This alcohol was acetylated as described for **1** in an overall yield of 90% (6.10 g, 27 mmol) to give a colorless liquid, bp 80 °C/0.1 mmHg. ^{1}H NMR ($CDCl_3$): δ 1.51 (d, J = 6.3 Hz, 3H), 2.11 (s, 3H), 5.59 (q, J = 6.3 Hz, 1H), 6.78 (s, 1H), 7.29−7.39 (m, 3H), 7.60 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 19.0, 21.2, 73.7, 126.6, 128.2, 128.3, 129.4, 132.5, 133.9, 170.0. IR (neat): 2990 m, 1746 bs cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 226 (M^+ + 2, 1.5), 225 (M^+ + 1, 0.8), 224 (M^+, 5.3), 189 (11), 129 (100), 77 (14). Anal. Calcd for $C_{12}H_{13}O_2Cl$: C, 64.15; H, 5.83; Cl, 15.78. Found: C, 64.15; H, 5.83; Cl, 15.79.

1-Acetoxy-2-chloro-1-phenyl-2-butene (11). A solution of *trans*-1-ethoxy-1-propene (10.4 g, 120 mmol) and bromotrichloromethane (24 g, 120 mmol) in diethyl ether (50 mL) was cooled to −78 °C. To this stirred solution was added methyllithium (1.0 M in diethyl ether, 150 mL, 150 mmol) dropwise over a 1 h period. After 1 h at the same temperature, water (50 mL) was added. The resulting solution was extracted with diethyl ether, and the combined ether layer was dried over $MgSO_4$. The ether was evaporated, and the residue was distilled under reduced pressure to give 1,1-dichloro-2-ethoxy-3-methylcyclopropane[14] (15.9 g, 94 mmol). *trans*-2-Chloro-1,1-diethoxy-2-butene[14] was prepared in 63% yield (10.5 g, 59 mmol) from 1,1-dichloro-2-ethoxy-3-methylcyclopropane and sodium ethoxide [generated in situ from Na (2.81 g, 122 mmol) and solvent ethanol] in ethanol (50 mL) at reflux for 12 h. This acetal in 1 N HCl (50 mL) was stirred for 0.5 h at room temperature. The mixture was extracted with pentane and dried over $MgSO_4$. Evaporation of the pentane followed by distillation gave *trans*-2-chloro-2-butenal[14] (5.85 g, 56 mmol). This aldehyde was phenylated and acetylated in the same manner as described for **10** using bromobenzene instead of iodomethane in 99% yield (12.4 g, 55 mmol, overall 46% yield) to give a colorless liquid, bp 95 °C/0.1 mmHg. ^{1}H NMR ($CDCl_3$): δ 1.79 (d, J = 6.6 Hz, 3H), 2.16 (s, 3H), 5.95 (q, J = 6.6 Hz, 1H), 6.38 (s, 1H), 7.32−7.38 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 13.8, 21.1, 77.4, 117.4, 124.8, 127.0, 128.4, 132.9, 137.0, 169.6. IR (neat): 2928 bm, 1748 bs cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 224 (M^+, 0.5), 189 (12), 129 (100), 77 (23). Anal. Calcd for $C_{12}H_{13}O_2Cl$: C, 64.15; H, 5.83; Cl, 15.78. Found: C, 63.93; H, 5.74; Cl, 15.76.

2-Chloro-1,3-diphenyl-2-propenyl Acetate (12). The use of bromobenzene instead of iodomethane in the same manner as described for **10** gave **12** in 98% yield (7.22 g, 29.5 mmol) as a colorless liquid. R_f 0.23 (hexane/ethyl acetate = 10/1). ^{1}H NMR ($CDCl_3$): δ 2.20 (s, 3H), 6.52 (s, 1H), 6.88 (s, 1H), 7.26−7.48 (m, 8H), 7.65 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 21.1, 78.2, 127.1, 127.5, 128.2, 128.4, 128.5, 128.6, 129.4, 131.2, 133.8, 136.9, 169.5. IR (neat): 3030 w, 1743 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 288 (M^+ + 2, 0.6), 286 (M^+, 1.6), 244 (19), 191 (100), 77(100). HRMS Found: 286.0756. Calcd for $C_{17}H_{15}O_2Cl$: 286.0761.

2-Acetoxy-3-chloro-1,1,1-trideuterio-3-pentene (22). The use of iodomethane-d_3 instead of bromobenzene in the same manner as described for **11** gave **22** in 77% yield (3.81 g, 23 mmol) from *trans*-2-chloro-2-butenal (3.13 g, 30 mmol) as a colorless liquid, bp 90−92 °C/50 mmHg. ^{1}H NMR ($CDCl_3$): δ 1.76 (d, J = 6.5 Hz, 3H), 2.07 (s, 3H), 5.44 (bs, 1H), 5.91 (q, J = 6.5 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 13.7, 17.9, 21.2, 72.6, 123.6, 134.1, 170.0. IR (neat): 2930 bm, 1739 bs, 1666 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 166 (M^+ + 2, 0.2), 130 (68), 70 (100). HRMS Found: 165.0635. Calcd for $C_7H_8O_2D_3Cl$: 165.0636.

2-Chloro-1-(2,3,4,5,6-pentadeuterio-phenyl)-3-phenyl-2-propenyl Acetate (23). The use of bromobenzene-d_5 instead of bromobenzene in the same manner as described for **12** gave **23** quantitatively (5.74 g, 23 mmol) from α-chlorocinnamaldehyde (3.83 g, 23 mmol) as a colorless liquid. R_f 0.23 (hexane/ethyl acetate = 10/1). ^{1}H NMR ($CDCl_3$): δ 2.20 (s, 3H), 6.52 (s, 1H), 6.89 (s, 1H), 7.29−7.40 (m, 3H), 7.63−7.66 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 21.1, 78.1, 127.5, 128.2, 128.4, 129.4, 131.2, 133.8, 136.7, 169.5. IR (neat): 2940 w, 1752 bs, 1646 m cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 291 (M^+, 1.1), 249 (12), 196 (100). HRMS Found: 291.1071. Calcd for $C_{17}H_{10}O_2D_5Cl$: 291.1074.

Typical Procedure. Ethyl acetoacetate (260 mg, 2.0 mmol) was added to a suspension of NaH (60 wt % in mineral oil, 80 mg, 2.0 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at room temperature for 30 min, at which time $Pt(C_2H_4)(PPh_3)_2$ (74.7 mg, 0.1 mmol) was added. 2-Chloro-allyl acetate **1** (134.5 mg, 1.0 mmol) was added, and the flask was then immersed in an oil bath at 80 °C. The reaction was monitored by analytical GC, and after 2 h the substrate had been completely consumed. After the reaction mixture was cooled to room temperature, water (10 mL) was added. The resulting solution was extracted with diethyl ether, and the combined organic layer was dried over $MgSO_4$ and concentrated in vacuo to give yellow oil. The residue was subjected to column chromatography on silica gel (eluent, hexane/ethyl acetate = 10/1) to give ethyl 2,4-dimethyl-3-furoate **5** (101 mg, 62% yield) as a clear oil.

Ethyl 2,4-Dimethyl-3-furoate (5): colorless liquid; bp 100 °C/16 mmHg. ^{1}H NMR ($CDCl_3$): δ 1.35 (t, J = 7.1 Hz, 3H), 2.13 (d, J = 1.4 Hz, 3H), 2.53 (s, 3H), 4.28 (q, J = 7.1 Hz, 2H), 7.03 (d, J = 1.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 10.0, 14.3, 59.8, 113.5, 121.2, 137.6, 160.0, 164.8. IR (neat): 2978 bm, 1724 bs, 1613 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 169 (M^+ + 1, 60), 123 (100). Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.15; H, 7.39.

3-Acetyl-2,4-dimethylfuran (14): colorless liquid; bp 90−95 °C/12 mmHg. ^{1}H NMR ($CDCl_3$): δ 2.16 (d, J = 1.4 Hz, 3H), 2.42 (s, 3H), 2.54 (s, 3H), 7.02 (d, J = 1.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 10.7, 15.3, 30.9, 120.3, 122.4, 137.9, 159.1, 194.8. IR (neat): 2964 m, 2930 m, 1670 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 140 (M^+ + 2, 2), 139 (M^+ + 1, 2), 138 (M^+, 18), 123 (100). HRMS Found: 138.0681. Calcd for $C_8H_{10}O_2$: 138.0680.

4-Ethoxycarbonyl-5-methyl-3-methylene-2-phenyl-2,3-dihydrofuran (15): colorless liquid. R_f 0.28 (hexane/ethyl acetate = 10/1). ^{1}H NMR ($CDCl_3$): δ 1.35 (t, J = 7.3 Hz, 3H), 2.40 (s, 3H), 4.28 (q, J = 7.3 Hz, 2H), 4.53 (d, J = 3.0 Hz, 1H), 5.53 (d, J = 3.2 Hz, 1H), 5.94 (dd, J = 3.0 Hz, J = 3.2 Hz, 1H), 7.30−7.40 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 14.3, 15.6, 59.8, 88.2, 101.2, 106.6, 127.3, 128.7, 128.8, 139.4, 147.0, 164.9, 175.5. IR (neat): 2966 m, 1702 m, 1614 m cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 246 (M^+ + 2, 2), 245 (M^++1, 18), 244 (M^+, 100), 216 (23), 77 (55). HRMS Found: 244.1100. Calcd for $C_{15}H_{16}O_3$: 244.1099.

3-Benzylidene-2,5-dimethyl-4-ethoxycarbonyl-2,3-dihydrofuran (16): white solid; mp 56−58 °C. R_f 0.23 (hexane/ethyl acetate = 10/1). ^{1}H NMR ($CDCl_3$): δ 0.67 (t, J = 7.3 Hz, 3H), 1.53 (d, J = 6.8 Hz, 3H), 2.23 (s, 3H), 3.62 (m, 2H), 5.27 (dq, J = 2.7 Hz, J = 6.8 Hz, 1H), 5.98 (d, J = 2.7 Hz, 1H), 7.00−7.20 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 13.2, 14.6, 21.8, 60.0, 84.4, 107.2, 112.8, 125.9, 127.7, 127.7, 138.9, 141.4, 165.5, 173.9. IR (KBr): 2984 bw, 1694 s, 1610 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 259 (M^+ + 1, 6), 258 (M^+, 31), 229 (11), 212 (100). Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.51; H, 7.04.

4-Acethyl-3-benzylidene-2,5-dimethyl-2,3-dihydrofuran (17): colorless liquid. R_f 0.29 (hexane/ethyl acetate = 5/1). ^{1}H NMR ($CDCl_3$): δ 1.54 (s, 3H), 2.14 (s, 3H), 1.54 (d, J = 6.5 Hz, 3H), 5.25 (dq, J = 2.5 Hz, J = 6.5 Hz, 1H), 6.02 (d, J = 2.5 Hz, 1H), 7.10−7.30 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 14.5, 21.7, 29.7, 84.2, 113.1, 116.9, 126.5, 127.8, 128.6, 138.7, 143.4, 171.7, 197.7. IR (neat): 2978 m, 2926 w, 1668 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 229 (M^+ + 1, 16), 228 (M^+, 100), 214 (11). HRMS Found: 228.1148. Calcd for $C_{15}H_{16}O_2$: 228.1149.

Diethyl 2-[3-(1-phenyl-2-chloro)-1-butenyl]malonate (18): yellow liquid. R_f 0.15 (hexane/ethyl acetate = 10/1). ^{1}H NMR ($CDCl_3$): δ 1.19 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H), 1.30 (d, J = 6.8 Hz, 3H), 3.42 (dq, J = 6.8 Hz, J = 10.6

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Hz, 1H), 3.70 (d, J = 10.6 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 6.64 (s, 1H), 7.24−7.58 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 14.1, 17.2, 44.3, 56.1, 61.5, 61.6, 126.4, 127.8, 128.1, 129.1, 134.5, 135.2, 167.7, 168.8. IR (neat): 2984 m, 1737 bs cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 324 (M^+, 6), 289 (46), 129 (100). Anal. Calcd for $C_{17}H_{21}O_4Cl$: C, 62.86; H, 6.52; Cl, 10.92. Found: C, 62.74; H, 6.59; Cl, 10.96.

3-Benzylidene-4-ethoxycarbonyl-5-methyl-2-phenyl-2,3-dihydrofuran (19): colorless liquid. R_f 0.21 (hexane/ethyl acetate = 10/1). ^{1}H NMR ($CDCl_3$): δ 0.68 (t, J = 7.0 Hz, 3H), 2.31 (s, 3H), 3.66 (m, 2H), 5.87 (d, J = 2.4 Hz, 1H), 6.10 (d, J = 2.4 Hz, 1H), 7.05−7.25 (m, 5H), 7.40 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 13.2, 14.5, 60.2, 89.7, 107.9, 116.2, 126.1, 127.6, 127.7, 128.8, 128.9, 138.7, 139.4, 140.0, 165.2, 173.9. IR (neat): 2982 bm, 1705 s, 1610 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 321 ($M^+ + 1$, 75), 320 (M^+, 59), 275 (41), 204 (100), 77 (23). HRMS Found: 320.1421. Calcd for $C_{21}H_{20}O_3$: 320.1411.

4-Acethyl-3-benzylidene-5-methyl-2-phenyl-2,3-dihydrofuran (20): white solid. R_f 0.14 (hexane/ethyl acetate = 10/1). ^{1}H NMR ($CDCl_3$): δ 1.58 (s, 3H), 2.22 (s, 3H), 6.08 (d, J = 2.7 Hz, 1H), 5.93 (d, J = 2.7 Hz 1H), 7.10−7.40 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 14.4, 29.7, 89.4, 116.3, 117.4, 126.7, 127.3, 127.7, 128.5, 128.8, 128.9, 138.4, 139.3, 141.9, 171.7, 197.3.

Diethyl 2-[1-(1,3-Diphenyl-2-chloro)-2-propenyl]malonate (21): yellow liquid. R_f 0.11 (hexane/ethyl acetate = 10/1). ^{1}H NMR ($CDCl_3$): δ 1.00 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H), 3.98 (q, J = 7.1 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 4.57 (d, J = 6.0 Hz, 1H), 4.36 (d, J = 6.0 Hz, 1H), 6.81 (s, 1H), 7.25−7.57 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 13.7, 14.1, 54.9, 55.0, 61.6, 61.9, 126.6, 127.7, 127.9, 128.1, 128.4, 129.2, 133.4, 134.4, 137.7, 166.9, 167.4. IR (neat): 2984 bm, 1736 bs cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 388 ($M^+ + 2$, 1), 387 ($M^+ + 1$, 1), 386 (M^+, 3), 351 (24), 277 (100). Anal. Calcd for $C_{22}H_{23}O_4Cl$: C, 68.30; H, 5.99; Cl, 9.16. Found: C, 68.29; H, 6.16; Cl, 9.06.

3-Methylidene-2,5-dimethyl-4-ethoxycarbonyl-2,3-dihydrofuran (24): colorless liquid. R_f 0.28 (hexane/ethyl acetate = 10/1). ^{1}H NMR ($CDCl_3$): δ 1.34 (t, J = 7.3 Hz, 3H, CH_3), 1.38 (d, J = 6.5 Hz, 1.5H, CH_3/CD_3 = 1/1), 1.76 (dd, J = 7.3 Hz, J = 2.7 Hz, 1.5H, CH_3/CD_3 = 1/1), 2.20 (s, 3H, CH_3), 4.25 (q, J = 7.3 Hz, 2H, CH_2), 4.91−4.97 (m, 1H, CH), 4.99−5.07 (m, 1H, 2-H). ^{13}C NMR ($CDCl_3$): δ 14.3 (CH_3), 14.6 (CH_3/CD_3 = 1/1), 15.2 (CH_3), 21.9 (CH_3/CD_3 = 1/1), 59.9 (CH_2), 83.6, 83.7 (2-C), 106.6 (4-C), 109.0, 109.1 (CH), 139.6 (5-C), 165.6 (CO), 172.5 (3-C). IR (neat): 2982 bm, 1711 s, 1619 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 200 ($M^+ + 1$, 13), 199 (M^+, 100), 171 (13). HRMS Found: 199.1289. Calcd for $C_{11}H_{13}O_3D_3$: 199.1288.

3-Benzylidene-4-ethoxycarbonyl-5-methyl-2-phenyl-2,3-dihydrofuran (25): colorless liquid. R_f 0.21 (hexane/ethyl acetate = 10/1). ^{1}H NMR ($CDCl_3$): δ 0.68 (t, J = 7.0 Hz, 3H, CH_3), 2.31 (s, 3H, CH_3), 3.66 (m, 2H, CH_2), 5.87 (d, J = 2.4 Hz, 1H, CH), 6.10 (d, J = 2.4 Hz, 1H, 2-H), 7.05−7.25 (m, 2.5H, Ph/Ph-*d*5 = 1/1), 7.40 (m, 2.5H, Ph/Ph-*d*5 = 1/1).

Reaction with Pt(dba)$_2$ and Appropriate Ligand as Catalyst. PPh_3 (26.2 mg, 0.1 mmol) was added to a suspension of Pt(dba)$_2$ (33.2 mg, 0.05 mmol) in THF (1 mL). The mixture was stirred at room temperature for 30 min. To this solution was added 2-chloro-allyl acetate **1** (67.5 mg, 0.5 mmol). Sodium ethyl acetoacetate [generated from ethyl acetoacetate (130 mg, 1.0 mmol) and NaH (60 wt % in mineral oil, 40 mg, 1.0 mmol) in THF (4 mL) at 0 °C] was slowly added, and the flask was then immersed in an oil bath at 80 °C. The reaction was monitored by analytical GC, and after 2 h the substrate had been completely consumed. Yields were determined by GC with *n*-pentadecane as an internal standard.

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Supporting Information Available: The detailed experimental procedures and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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