a hydrogen permit this substituent to serve as a regiochemical control element!

**Acknowledgment.** We wish to thank the National Science Foundation for their generous support of our programs. M. L. thanks the Natural Sciences and Engineering Research Council of Canada for a predoctoral fellowship.

**Registry No.** 1, 72047-94-0; 2, 86970-30-1; 2-carbomethoxycyclopentanone sodium salt, 86970-29-8; $Me_3SiCH{=}CHCH_2OAc$, 80401-14-5; $Me_3SiCH{=}CHCH(OAc)SiMe_3$, 86970-25-4; $Me_3SiCH{=}CHCH(OAc)CO_2Bu$, 86970-26-5; $CH_3CH_2CH_2CH(OAc)CH{=}CH\ CO_2Me$, 86970-27-6; $CH_2E_2$, 108-59-8; $CH_3CHE_2$, 609-02-9; $Me_3SiCH{=}CHCH_2CHE_2$, 86970-31-2; $Me_3SiCH(CHE_2)CH{=}CH_2$, 86970-32-3; (*E*)-$Me_3SiCH{=}CHCH(SiMe_3)CHE_2$, 86422-29-9; (*E*)-$Me_3SiCH{=}CHCH(SiMe_3)CE_2CH_3$, 86970-33-4; (*E*)-$Me_3SiCH(CHE_2)CH{=}CHCO_2Bu$, 86970-34-5; (*E*)-$Me_3SiCH{=}CHCH(CE_2CH_3)CO_2Bu$, 86970-35-6; (*E*)-$CH_3CH_2CH_2CH(CHE_2)CH{=}CHCO_2Me$, 86970-36-7; (*E*)-$CH_3CH_2CH_2CH(CE_2CH_3)CH{=}CHCO_2Me$, 86970-37-8; $Mo(CO)_6$, 13939-06-5; methyl 3-(1-acetyloxycylohexyl)propenoate, 86970-28-7; $C_6H_{10}{=}CHCH(CE_2CH_3)CO_2Me$, 86970-38-9; (*E*)-2-methyl-2-[1-(carbomethoxyethenyl)cyclohexyl]propandioic acid dimethyl ester, 86970-39-0; (*E*)-2-[1-(carbomethoxyethenyl)-cyclohexyl]propanedioic acid dimethyl ester, 86970-40-3.

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## Addition of Carboxylic Acids to Alkynes Catalyzed by Ruthenium Complexes. Vinyl Ester Formation

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*Summary:* $Ru_3(CO)_{12}$ as well as $[Ru(CO)_2(O_2CCH_3)]_n$ are catalyst precursors for the addition of aliphatic and aromatic carboxylic acids to di- and monosubstituted acetylenes which yields vinyl esters. The kinetic product results from a cis addition to the triple bond; a rearranged product is also formed.

Catalysis involving transition-metal complexes is a rapidly growing field of chemistry.[1] In this communication we present preliminary data concerning a new catalytic system. It is based on $Ru_3(CO)_{12}$ which serves as a catalyst precursor in an addition reaction of carboxylic acids to alkynes. The reaction is exemplified with diphenylacetylene and acetic acid (eq 1); the reaction conditions

$$PhC{\equiv}CPh + AcOH \xrightarrow{Ru_3(CO)_{12}} \underset{1\ (E+Z)}{PhCH{=}C(OAc)Ph} + \underset{2}{Ph_2C{=}C(OAc)H} \quad (1)$$

are described in Table I, footnote *a*. The reaction is conveniently monitored by GLC, and eventually the mixture was separated by chromatography (silica; $CH_2Cl_2$–petroleum ether). The properties of the isolated substances (MS, IR, NMR) are consistent with structures 1 (*E* and *Z*) and 2, and the melting points are identical with those reported in the literature.[2-4] The product distributions and other experimental data are presented in Table I (entry 1). Other carboxylic acids and also different alkynes exhibit similar behavior (Table I). In most of the cases the products were separated (silica) and purified, and their structures were assigned by comparing the spectral data with that of the known 1 (*E* and *Z*) and 2.[5]

The following additional experiments were performed:

1. Several control experiments, omitting the catalyst, have revealed only traces (<1%) of vinyl esters.

2. GLC monitoring of the reaction (entry 1) has indicated a slow conversion of the $E \rightarrow Z$ isomer. This was also verified in a separate experiment, by subjecting (*E*)-α-(benzoyloxy)stilbene to the original reaction conditions.

3. When subjected to the original reaction conditions, a mixture of (*E*)- and (*Z*)-α-acetoxystilbenes did *not* produce the rearranged product 2. From the experimental data presented we can derive the following conclusions:

a. $Ru_3(CO)_{12}$ is a catalyst precursor for the addition of carboxylic acids to alkynes, generating vinyl esters. The reaction seems to be a general one, in as much as various aliphatic and aromatic carboxylic acids, as well as structurally diverse alkynes, are reactive (Table I). In general, the conversions are good and the stereoselectivity is variable.

b. An interesting isomeric rearranged product, viz., 2, accompanies the *E* and *Z* vinyl ester mixtures. It is a *primary* product that is being formed in parallel with the normal vinyl esters. To the best of our knowledge, such a reaction is without precedent in organic chemistry.

c. Most probably the kinetically controlled product results from a cis addition of the acids to the triple bond.

d. The addition of carboxylic acids to alkynes is known to be catalyzed by strong acids, Lewis acids, and electrophiles.[2,6] Notably, mercury salts, where organomercurials are serving as intermediates, are useful catalysts; in many cases stoichiometric quantities of mercury salts are used.[2,6] We believe that our catalytic system is more complex in as much as $RuCl_3$, which may be considered as a Lewis acid catalyst, is totally inactive in the above addition reaction.

e. The reactions listed in Table I have not been parameterized. It is noteworthy that practically quantitative yields were recorded in entries 8–10 (Table I). Entry 8 represents the only unsymmetrical alkyne that was examined. Although listed as a rearranged product, α-(benzoyloxy)styrene (23%) may have actually resulted from the inverse addition of benzoic acid to phenylacetylene. Neither are we sure that the β-(benzoyloxy)styrenes are not, in fact, rearranged products. Nevertheless, it is noteworthy that the major product of this reaction is β-(benzoyloxy)styrene (77%)—a formally anti-Markovnikov addition product. This observation also supports our previous contention that the addition is not induced by simple acid catalysis.

Since only one product was isolated in entries 9 and 10, it is difficult to characterize them stereochemically.[5] We have assigned the *E* configuration to 4-acetoxy-4-octene (entry 9). Its vinyl proton resonates at 5.13 ppm compared to 5.04 ppm for (*E*)-2-acetoxy-4,4-dimethyl-2-pentene[6] and 4.79 ppm for the *Z* isomer.[6] The assigned configuration is consistent with cis addition of acetic acid to 4-octyne.

Some insight into the reaction under investigation may be gained by examining reaction 2. This type of reaction, with various acids, was studied by several investigators.[7,8]

(1) Parshall, G. W. "Homogenous Catalysis"; Wiley: New York, 1980.
(2) Bach, R. D.; Woodward, R. A.; Anderson, T. J.; Glick, M. D. *J. Org. Chem.* **1982**, *47*, 3707.
(3) Barnes, R. P.; Cooper, S. R.; Tulane, V. J.; Delaney, H. *J. Org. Chem.* **1943**, *8*, 153.
(4) Mičović, V. M.; Rogič, M. M.; Mihailović, M. L. *Tetrahedron* **1957**, *1*, 340.
(5) The vinyl proton resonance is a reliable structural indicator. For (*E*)- and (*Z*)-α-acetoxystilbenes and 1-acetoxy-2,2-diphenylethylene δ-($CDCl_3$) 6.45, 6.70, and 7.63, respectively. Very similar chemical shifts were recorded for all other vinyl esters, thus enabling structural assignments to be made.
(6) Larock, R. C.; Oertle, K.; Beatty, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 1966 and references cited therein.

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**Table I. Experimental Data for the Reactions of Carboxylic Acids and Alkynes Catalyzed by Ru Complexes[a]**

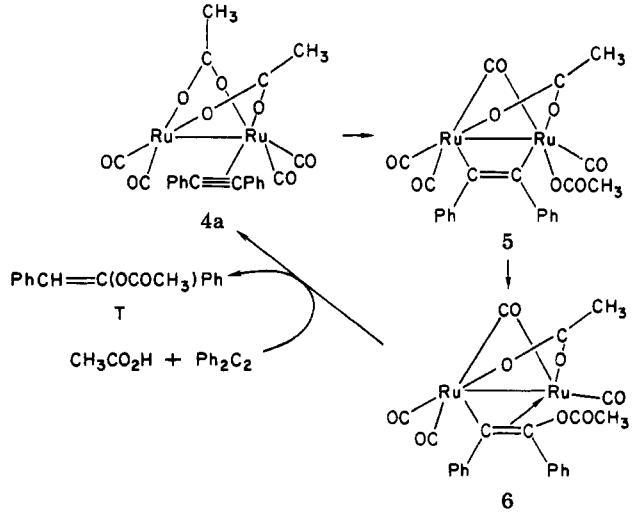
| entry | acid | alkyne | cat. | time, h | conversn, % | vinyl esters' distribution, % | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | *E* isomer | *Z* isomer | rearranged product | |
| 1 | $CH_3CO_2H$ | PhC≡CPh | $Ru_3(CO)_{12}$ | 22 | 55 | 82 | 9 | 9 | |
| 2 | $CH_3CO_2H$ | PhC≡CPh | $[Ru(CO)_2(CH_3CO_2)]_n$ | 19 | 50 | 85 | 7 | 8 | |
| 3 | $(CH_3)_3CCO_2H$ | PhC≡CPh | $Ru_3(CO)_{12}$ | 20 | 77 | 87 | 12 | 1 | |
| 4 | $PhCO_2H$ | PhC≡CPh | $Ru_3(CO)_{12}$ | 17 | 81 | 14 | 65 | 21 | |
| 5 | $PhCO_2H$ | PhC≡CPh | $[Ru(CO)_2(CH_3CO_2)]_n$ | 20 | 66 | 20 | 60 | 20 | |
| 6 | 4-F-$C_6H_4CO_2H$ | PhC≡CPh | $Ru_3(CO)_{12}$ | 19 | 45 | | 42[b] | 58 | |
| 7 | 4-Me-$C_6H_4CO_2H$ | PhC≡CPh | $Ru_3(CO)_{12}$ | 19 | 40 | | 80[b] | 20 | |
| 8 | $PhCO_2H$ | PhC≡CH | $Ru_3(CO)_{12}$ | 17 | 96 | 62 | 15 | 23 | |
| 9 | $CH_3CO_2H$ | $(n\text{-}C_3H_7)_2C_2$ | $Ru_3(CO)_{12}$ | 17 | 92 | 100 | | | |
| 10 | $CH_3CO_2H$ | $(CO_2Me)_2C_2$ | $Ru_3(CO)_{12}$ | 17 | 95 | | 100[c] | | |

[a] Reaction conditions: [acid] = [alkyne] = 0.2 M; [catalyst] = $4 \times 10^{-3}$ M in toluene. The reaction was carried out in a glass-lined closed stainless-steel reactor (45 mL) under a nitrogen blanket at 145 °C. Conversions were determined by isolation of products and unreacted alkynes. All vinyl esters exhibit stretching bands at 1720–1770 $cm^{-1}$. [b] Combined % of *E* and *Z* vinyl esters. [c] $\nu(CCl_4)$ 1784, 1740, 1660 $cm^{-1}$; $\delta(CDCl_3)$ 2.18 (s, 3 H), 3.68 (s, 3 H), 3.73 (s, 3 H), 5.97 (s, 1 H); *m/e* 171 ($M^+ - OCH_3$), 143 ($M^+ - O_2C$). The configuration of this isomer has not yet been determined.

$$CH_3CO_2H + Ru_3(CO)_{12} \rightarrow \underset{\mathbf{3}}{[Ru(CO)_2(O_2CCH_3)]_n} \xrightarrow{L} \underset{\mathbf{4}}{[Ru(L)(CO)_2(O_2CCH_3)]_2} \quad (2)$$

A yellow insoluble polymer (**3**) was isolated and could be depolymerized with various ligands (**4**).[7] Indeed, the insoluble polymer **3** was also isolated by us from the reaction mixture of entry 1 (Table I). Furthermore, polymer **3**, which was separately prepared and characterized (IR), is also active in reaction 1 (Table I, entries 2 and 5).

Although the reaction is apparently heterogenous, the insoluble polymer **3** may, in the presence of an alkyne ligand, depolymerize, in analogy with the reported transformation **3** → **4** (L = CO, amines, phosphines),[7,8] giving rise to **4a**. The structure of **4a** is analogous to that which




was determined by Schumann et al.[8] for $[Ru(\mu\text{-}O_2CC_3H_7)(CO)_2(t\text{-}Bu_3P)]_2$, in which the phosphine ligands were replaced by the alkyne; the latter may function either as a two- (**4a**) or four-electron ligand. Being a reactive ligand the alkyne in **4a** may undergo an oxidative addition to generate **5** (a structurally similar Rh dimer was reported[9]). By a reductive elimination step, the acetoxy group is transferred from Ru → C, giving rise to **6**. Protolysis of the Ru–C bond in **6** will liberate the vinyl acetate and reform the coordinatively unsaturated dimer $[Ru(\mu\text{-}O_2CCH_3)(CO)_2]_2$. The latter will, by capturing another alkyne molecule, regenerate **4a**.

The catalytic reactivity of the polymer **3** in reaction 1, which may be in equilibrium with the proposed **4a**, has been experimentally established. Although the rest of the transformations and structures presented in the above mechanistic scheme are in accordance with established principles of organometallic chemistry, they should be regarded as tentative ones until experimental support will be adduced.

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**Registry No.** (**E**)-**1**, 24647-07-2; (**Z**)-**1**, 13892-81-4; **2**, 86846-73-3; **3**, 26317-70-4; $CH_3CO_2H$, 64-19-7; $(CH_3)_3CCO_2H$, 75-98-9; $PhCO_2H$, 65-85-0; 4-F-$C_6H_4CO_2H$, 456-22-4; 4-Me-$C_6H_4CO_2H$, 99-94-5; PhC≡CPh, 501-65-5; PhC≡CH, 536-74-3; $(n\text{-}C_3H_7)_2C_2$, 1942-45-6; $(CO_2Me)_2C_2$, 762-42-5; $Ru_3(CO)_{12}$, 15243-33-1; (**E**)-

(7) Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I. G. *J. Chem. Soc. A 1969*, 2761.
(8) Schumann, H.; Opitz, J.; Pickardt, J. *J. Organomet. Chem.* **1977**, *128*, 253.
(9) Mague, J. T.; Devries, S. H. *Inorg. Chem.* **1982**, *21*, 1632.

α-[(2,2-dimethylpropanoyl)oxy]stilbene, 86846-74-4; (*Z*)-α-[(2,2-dimethylpropanoyl)oxy]stilbene, 86846-75-5; (*E*)-α-(benzoyloxy)stilbene, 86846-76-6; (*Z*)-α-(benzoyloxy)stilbene, 86846-77-7; 1-(benzoyloxy)-2,2-diphenylethylene, 86123-17-3; (*E*)-α-[(*p*-fluorobenzoyl)oxy]stilbene, 86846-78-8; (*Z*)-α-[(*p*-fluorobenzoyl)oxy]stilbene, 86846-79-9; 1-[(*p*-fluorobenzoyl)oxy]-2,2-diphenylethylene, 86846-80-2; (*E*)-α-[(*p*-methylbenzoyl)oxy]-stilbene, 86846-81-3; (*Z*)-α-[(*p*-methylbenzoyl)oxy]stilbene, 86846-82-4; 1-[(*p*-methylbenzoyl)oxy]-2,2-diphenylethylene, 86846-83-5; (*E*)-β-(benzoyloxy)styrene, 86846-84-6; (*Z*)-β-(benzoyloxy)styrene, 84262-78-2; α-(benzoyloxy)styrene, 838-58-4; (*E*)-4-acetoxy-4-octene, 86846-85-7; dimethyl 2-acetoxy-2-butenedioate, 78704-24-2.

## Lithiation and Derivatization of Group 4A Bent-Sandwich Molecules

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*Summary:* Dilithiation of stannocene, $(\eta^5\text{-}C_5H_5)_2Sn$, produces the synthetically useful 1,1′-dilithiostannocene, **1**. Treatment of **1** with 2 equiv of $Me_3SiCl$ or $(i\text{-}Pr_2N)_2PCl$ affords the disubstituted derivatives $(Me_3SiC_5H_4)_2Sn$ (**2**) and $((i\text{-}Pr_2N)_2PC_5H_4)_2Sn$ (**3**), respectively. The structure of **3** has been determined by X-ray diffraction.

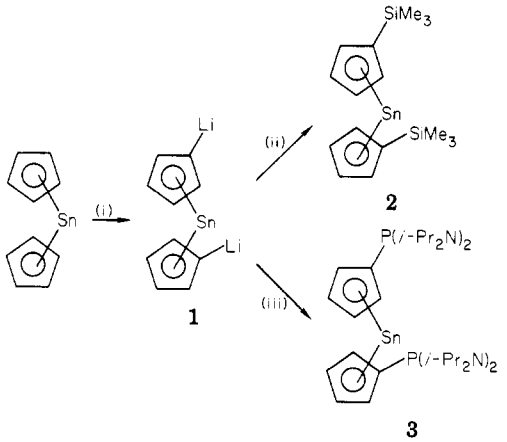
Interest in the reactivity of annulene complexes of the main-group elements has focused principally on ligative behavior, protolytic cleavage, oxidative addition, and ligand exchange reactions.[1] However Xα-SW calculations on bent-sandwich[2] and open-faced-sandwich[3] $\eta^5\text{-}C_5H_5$ compounds indicate that the HOMO is primarily ring localized. Thus, main-group annulene complexes should exhibit a ring substitution chemistry. To the best of our knowledge only two ring substitution reactions of bent-sandwich molecules have been documented, viz., the reaction of $(\eta^5\text{-}C_5H_5)_2Sn$ with $Me_3SnNEt_2$[4] and $[(i\text{-}Pr_2N)_2P][AlCl_4]$.[5] We now report that, like ferrocene,[6] $(\eta^5\text{-}C_5H_5)_2Sn$ readily forms a synthetically useful, 1,1′-dilithio derivative.

A THF solution of $(\eta^5\text{-}C_5H_5)_2Sn$ was treated with 2 equiv. of *n*-BuLi at −78 °C. The $^1H$ and $^{13}C\{^1H\}$ NMR spectra of the resulting dark red solution comprised singlets at δ 5.6 and 102.9, respectively, indicating that 1,1′-dilithiostannocene (**1**) is fluxional at 30 °C (see later).

The dilithium compound **1** is reactive toward main-group organometallic chlorides. Treatment of **1** with 2 equiv of $Me_3SiCl$ in THF at −78 °C caused an immediate discharge of the red color. After the solution was warmed to room temperature and the THF removed, the light yellow residue was extracted with *n*-hexane. Distillation of the resulting yellow oil (bp 115 °C at $5 \times 10^{-3}$ torr) afforded 30–40% yields of 1,1′-bis(trimethylsilyl)stannocene, **2**.[7] Compound **2** can also be prepared via the reaction of $Me_3SiC_5H_4Li$ with $SnCl_2$ in THF solution at 0 °C, thus supporting the above formulation.

Treatment of **1** with 2 equiv of $(i\text{-}Pr_2N)_2PCl$ in THF at −78 °C followed by removal of solvent and recrystallization from *n*-hexane afforded 30–40% yields of yellow crystalline 1,1′-bis((diisopropylamino)phosphido)stannocene, **3**, mp 162–164 °C (see Scheme I).[8] The structure of **3** was es-

Scheme I[a]




[a] (i) 2 *n*-BuLi; (ii) $2Me_3SiCl$; (iii) $2(i\text{-}Pr_2N)_2PCl$.

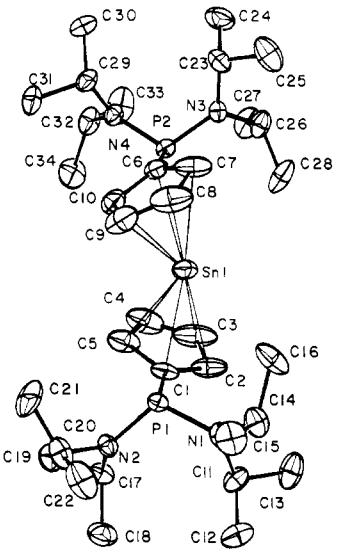



**Figure 1.** Structure of $[(i\text{-}Pr_2N)_2PC_5H_4]_2Sn$ (**3**) showing the atom numbering scheme. The hydrogen atoms are omitted. Important parameters include Sn(1)–C = 2.527 (8) – 2.807 (8) Å, C(1)–P(1) = 1.822 (7) Å, C(6)–P(2) = 1.824 (8) Å, P(1)–N(1) = 1.681 (8) Å, P(1)–N(2) = 1.686 (5) Å, P(2)–N(3) = 1.687 (6) Å, and P(2)–N(4) = 1.679 (5) Å.

(1) For a review of the reactivity of bent-sandwich molecules see: (a) Connolly, J. W.; Hoff, C. *Adv. Organomet. Chem.* **1981**, *19*, 123. For examples of the reactivity of open-faced sandwich molecules see: (b) Habeeb, J. J.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1975**, 1815. (c) Conteras, J. G.; Tuck, D. G. *Inorg. Chem.* **1973**, *12*, 2596.

(2) Baxter, S. G.; Cowley, A. H.; Lasch, J. G.; Lattman, M.; Sharum, W. P.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 4064.

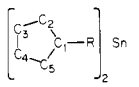
(3) Lattman, M.; Cowley, A. H. *Inorg. Chem.*, in press.

(4) Bulten, E. J.; Budding, H. A. *J. Organomet. Chem.* **1978**, *157*, C3.

(5) Cowley, A. H.; Kemp, R. A.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 3239.

(6) See, for example: Benkeser, R. A.; Goggin, D.; Scholl, G. *J. Am. Chem. Soc.* **1954**, *76*, 4025. Nesmeyanov, A. N.; Perevalova, E. G.; Golovinya, E. G.; Nesmayanova, D. A. *Dokl. Akad. Nauk SSSR* **1954**, *97*, 659. Rausch, M. D.; Ciappenelli, D. J. *J. Organomet. Chem.* **1967**, *10*, 127.

(7) Anal. Calcd for $C_{16}H_{26}Si_2Sn$: C, 48.7; H, 6.6. Found: C, 48.6; H, 6.8. $^1H$ NMR (200 MHz): δ 0.30 (s, 18 H, $SiMe_3$), 6.05 (m, 4 H, $H_{2,5}$ or $H_{3,4}$), 6.15 (m, 4 H, $H_{2,5}$ or $H_{3,4}$). $^{13}C\{^1H\}$ NMR (20 MHz): δ 1.4 ($SiMe_3$), 114.3 ($C_{2,5}$ or $C_{3,4}$), 117.5 ($C_{2,5}$ or $C_{3,4}$), 121.9 ($C_1$).




(8) **3**: $^1H$ NMR (90 MHz) δ 1.05 (d, 12 H, Me (*i*-Pr group), $^3J_{HH}$ = 6.9 Hz), 1.20 (d, 12 H, Me′, $^3J_{HH}$ = 6.9 Hz), 3.40 (m, 4 H, $Me_2CH$), 5.90 (m, 4 H, $H_{2,5}$ or $H_{3,4}$), 6.10 (m, 4 H, $H_{2,5}$ or $H_{3,4}$); $^{13}C\{^1H\}$ NMR (20 MHz) δ 24.4 (d, Me, $^3J_{PC}$ = 10.3 Hz), 24.7 (d, Me′, $^3J_{PC}$ = 9.7 Hz), 47.5 (d, $Me_2CH$, $^2J_{PC}$ = 11.4 Hz), 110.4 (d, $C_{2,5}$ or $C_{3,4}$, $J_{PC}$ = 6.0 Hz), 115.0 (d, $C_{2,5}$ or $C_{3,4}$, $J_{PC}$ = 15.9 Hz), 132.6 (d, $C_1$, $^1J_{PC}$ = 6.4 Hz); $^{31}P\{^1H\}$ NMR (36.4 MHz) δ (relative to 85% $H_3PO_4$) 46.6.

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