Vinylplatinum Carbenes and Nitriles, Platinoxacyclic Complexes, and Heck-Type Coupling Products Formed via Reaction of (σ-2-Propenyl)bis(triphenylphosphine)platinum(II) Triflate with Alkynols, Nitriles, and Acrylate Esters. Molecular Structure of $[(PPh_3)_2\overline{PtCH_2C(O})OCH_3][OTf]$

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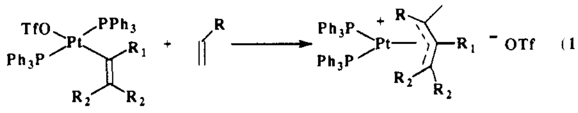
The reaction of (2-propenyl)bis(triphenylphosphine)platinum(II) triflate (**1a**) with several unsaturated organic substrates such as alkynols, nitriles, and acrylate esters has been examined. Alkynols **3a** (3-butyn-1-ol) and **3b** ((±)-4-pentyn-2-ol) provide the vinyl carbene species [*trans*-$Pt({=}\overline{C(CH_2)_3O})(2\text{-propenyl})(PPh_3)_2[OTf]$ (**4a**) and [*trans*-$Pt({=}\overline{C(CH_2)_2CH(CH_3)O})(2\text{-propenyl})(PPh_3)_2][OTf]$ (**4b**). Reaction with nitriles **5a** (acrylonitrile) and **5b** (ethyl cyanoacetate) provide [(acrylonitrile)(2-propenyl)$(PPh_3)_2Pt][OTf]$ (**6a**) and [(ethyl cyanoacetate)(2-propenyl)$(PPh_3)_2Pt][OTf]$ (**6b**), each of which is bonded through the nitrogen lone pair. Reaction with methyl and ethyl acrylates (**7a** and **7b**, respectively) results in the formation of the "chelated" platinum acrylate complexes $[(PPh_3)_2\overline{PtCH_2CH_2C(O})OCH_3][OTf]$ (**8a**) and $[(PPh_3)_2\overline{PtCH_2CH_2C(O})OCH_2CH_3][OTf]$ (**8b**) in 63 and 58% isolated yields, respectively. The structure of complex **8a** was unambiguously determined by X-ray analysis of a single crystal. Complex **8a** crystallizes in the orthorhombic space group $C222_1$ with $a = 17.433(3)$ Å, $b = 17.964(4)$ Å, $c = 25.047(4)$ Å, and $Z = 8.0$. The structure was solved and refined to $R = 0.0521$ and $R_w = 0.0674$ with 5645 observed reflections. The formation of **8a** and **8b** involves cleavage of the original σ-vinyl bond, transfer of a hydride to the acrylate, and release of the Heck-type coupling products $CH_2{=}C(CH_3)CH{=}CHCO_2R$ (**10a**, R = CH_3; **10b**, R = CH_2CH_3). We present a mechanism of formation for complexes **8a**, **8b**, **10a**, and **10b** as well as reactions of **8a** with carbon monoxide.

Introduction

Triflate complexes of transition metals have been the subject of an increasing number of investigations.[1] Previous studies from this and other laboratories[1c] have demonstrated the versatility of triflates coordinated to iridium, rhodium, and platinum in substitution reactions leading to several types of products: a novel heterobimetallic complex of iridium and platinum;[2] water complexes of rhodium and iridium;[3] (σ-vinyl)(σ-alkynyl)platinum(II) complexes;[4] platinum carbonyls;[5] and carbene complexes derived from iridium, rhodium, and platinum methyl complexes.[6] We also recently reported the reaction of platinum(II) triflates with simple alkenes to form a variety of allyl species under very mild conditions (eq 1).[7] Encouraged by the versatility thus far observed, we sought to further develop the potential of the platinum triflate species. Therefore, we extended our investigations to include several other unsaturated organic compounds. Herein we report the reaction of (2-propenyl)bis(triphenylphosphine)platinum(II) triflate (**1a**) with alkynols to afford vinyl alkoxycarbene complexes, as well as reactions with electron-deficient olefins to produce both chelated and novel lone-pair-coordinated complexes.



(1)

1 a: $R_1 = CH_3$, $R_2 = H$
b: $R_1 = H$, $R_2 = CH_3$
c: $R_1 = {}^tBu$, $R_2 = H$

2: R = H or CH_3

Results and Discussion

The facile C–C bond formation between two unsaturated units to produce η^3-allyl complexes[7] prompted us to attempt reactions with alkynes as well as olefins in order to investigate the potential synthesis of functionalized allyl and allenyl complexes. While alkynols **3a** and **3b** afforded alkoxycarbene complexes **4a** and **4b**, respectively (eq 2), simple alkynes such as phenylacetylene, 1-propyne, and

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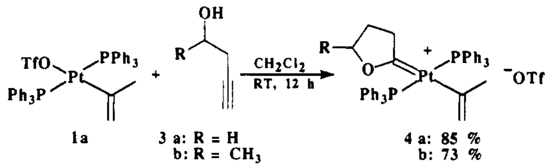
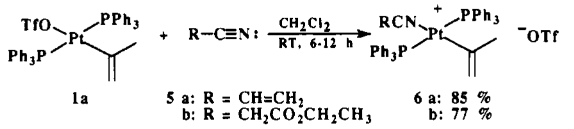


(2)

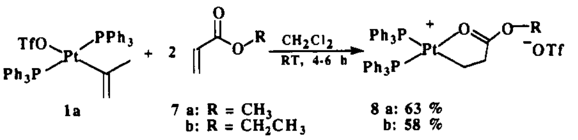
3,3-dimethyl-1-butyne provided complex product mixtures. Although platinum alkoxycarbene complexes have been known for approximately 20 years, platinum alkyl species rather than σ-vinyl complexes are the usual precursors.[8a,b] The generally accepted mechanism for the formation of alkoxycarbene complexes is shown in Figure 1.[8c,d] Dissociation of the triflate in polar solvents and coordination of the free alkyne to the open coordination site lead to an intermediate which can be visualized as either **A** or **A′**. Rearrangement to the vinylidene complex **B** and/or **B′** followed by intramolecular attack of the alcohol oxygen and protonation leads to the observed products. The difference in reactivities of alkynols and simple alkynes may be due to instability of the vinylidene intermediate in the case of the (σ-vinyl)platinum species. This intermediate probably decomposes in the absence of an intramolecular alcohol.

In an attempt to synthesize functionalized η^3-allyl complexes via our mild procedure, we reacted acrylonitrile (**5a**) with platinum complex **1a**. However, this afforded complex **6a**, in which the acrylonitrile is bonded through the nitrogen lone pair. This mode of coordination was determined by the change in the infrared absorption of the nitrile from 2230 to 2264 cm^{-1} as well as the change in the chemical shift of the nitrile carbon from 117.3 to 120.9 ppm in the ^{13}C{^{1}H} NMR spectrum. This compound is analogous to the acetonitrile complex that we recently reported.[5a] Likewise, reaction of ethyl cyanoacetate (**5b**) with complex **1a** resulted in another very stable nitrile complex **6b** (eq 3). It was characterized in the same manner as **6a**, and further details can be found in the Experimental Section.



(3)

Acrylate esters **7a** and **7b** were also reacted with **1a** (eq 4). The reaction of excess methyl acrylate (**7a**) with platinum complex **1a** led to the clean formation of a new product with loss of the original σ-2-propenyl moiety, as indicated by the absence of characteristic σ-vinyl resonances in the ^{1}H NMR spectrum. Complex **8a** was crystallized by addition of toluene and hexane or ether to the original CH$_2$Cl$_2$ reaction mixture followed by refrigeration.[9] A similar complex, **8b**, was produced in the reaction with ethyl acrylate (**7b**).



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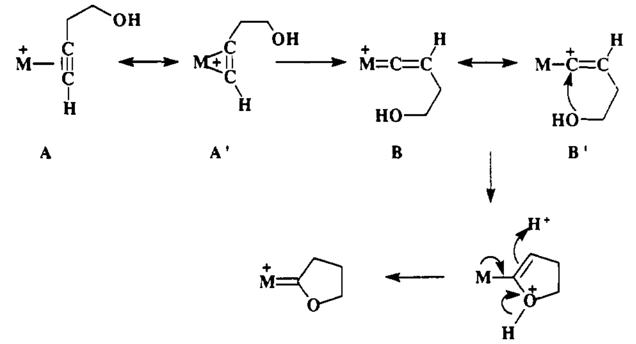

Figure 1. Proposed mechanism of formation for complexes **4a** and **4b** from **1a** and alkynols.

The IR spectra of these complexes clearly establish the presence of an anionic triflate. Strong absorptions near 1270 and 635 cm^{-1} are assigned to the S=O stretches of anionic triflates[1a] while covalent triflates display characteristic absorptions near 1215 and 645 cm^{-1}.[10] Chelation by the carbonyl oxygen in **8a**, and thus displacement of the triflate, is indicated by a very strong absorption at 1602 cm^{-1}. The C=O stretch of free acrylate **7a** appears at 1733 cm^{-1}, and the shift of the carbonyl oxygen for **8a** indicates a decrease in bond order due to coordination.[11] The 1602-cm^{-1} value is typical of metal-coordinated carbonyls.[12]

The ^{31}P NMR spectra display the characteristic AB splitting pattern of complexes with inequivalent phosphorus nuclei; ^{195}Pt satellites are also present. The most significant feature of these spectra is the drastic difference between the chemical shift and J_{PtP} values for the two phosphorus nuclei. The phosphorus *trans* to the coordinated carbonyl of **8a** resonates at 12.0 ppm; it is assigned on the basis of its very large platinum coupling constant of 4877 Hz.[9a] The phosphorus *trans* to the alkyl portion is located at 30.9 ppm and has a $^1J_{PtP}$ of 1915 Hz. The assignments of these doublets is readily made since the $^1J_{PtP}$ coupling constant is inversely proportional to the *trans* influence of the ligands.[11b] The ^{13}C{^{1}H} NMR spectra show complex splitting patterns due to the inequivalent phosphorus atoms, but all expected resonances are present. The ^{1}H NMR spectra are also complex, but all resonances are assigned.

Confirmation of the chelated structure was made by X-ray analysis of a crystal grown by vapor diffusion of pentane into a CH$_2$Cl$_2$/toluene solution of **8a**. An ORTEP diagram of **8a** is shown in Figure 2, and a summary of crystallographic data and selected bond lengths and angles are reported in Tables I–III.

The Pt–C bond length of the square planar complex, **8a**, is 2.11(2) Å and the Pt–O distance is 2.12(1) Å. However, as presaged by the vastly different ^{31}P NMR chemical shifts (*vide supra*) and corresponding Pt–P coupling constants, the two phosphorus nuclei have

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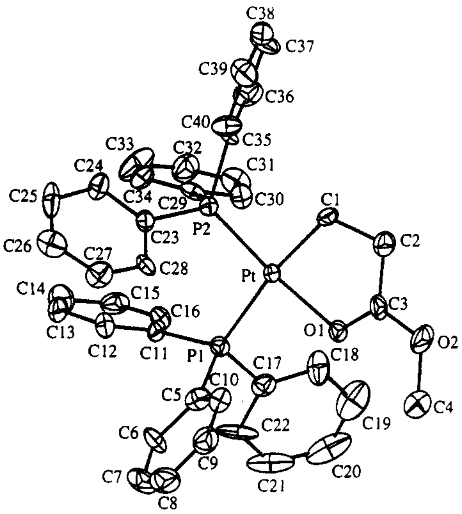


Figure 2. ORTEP diagram of complex **8a**. The triflate moiety has been omitted for clarity.

Table I. Summary of Crystallographic Data for 8a

mol formula	$C_{41}H_{37}O_5F_3P_2SPt$
mol wt	955.846
crystal system	orthorhombic
space group	$C222_1$
space group no.	20
cell dimens	
a, Å	17.433(3)
b, Å	17.964(4)
c, Å	25.047(4)
V, Å^3	7843.57
Z	8.0
d_{calcd}, g/cm^3	1.619
crystal dimens, mm	0.28 × 0.24 × 0.21
abs coeff, cm^{-1}	38.008
radiation: type; λ, Å	Mo; 0.709 30
no. of reflns measd	5645
2θ range, deg	4.00–58.00
scan technique	$\theta/2\theta$
scan width, deg	0.8000 + 0.3400 tan θ
data collection position	bisecting, ω = 0
decay cor	none
min % transm	74.1236
max % trans	99.8936
av % transm	87.0717
ignorance factor, *P*	0.04
no. of observns, $I > 3.00\sigma(I)$	3728
no. of variables	433
data:param	8.610
shift:error	0.026
R	0.0521
R_w	0.0674
highest peak in final diff Fourier map	0.711 e/Å^3
max ρ in final diff Fourier map	2787.165 e/Å^3
error in observn of unit weight	0.8872

Table II. Selected Bond Distances (Å) for 8a[a]

Pt–P1	2.366(4)	P1–C5	1.83(2)	O2–C4	1.59(4)
Pt–P2	2.205(5)	P2–C23	1.82(2)	C1–C2	1.50(3)
Pt–C1	2.11(2)	O1–C3	1.24(2)	C2–C3	1.52(3)
Pt–O1	2.12(1)	O2–C3	1.35(3)		

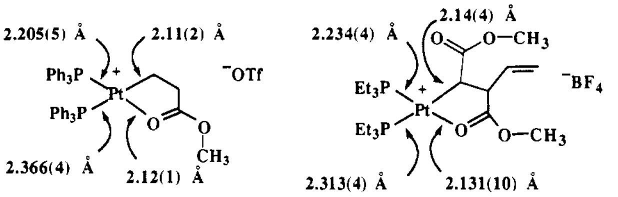
[a] Numbers in parentheses indicate the standard deviation in the least significant digit.

significantly different Pt–P bond lengths. The phosphorus *trans* to the oxygen has a bond length of 2.205(5) Å while that *trans* to the carbon of the η^1 ligand is 2.366(4) Å. This bond length difference is indicative of the stronger *trans* influence of the sp^3 carbon relative to the carbonyl oxygen.[11a] To our knowledge, this is one of the greatest Pt–P bond length differences yet observed in a platinum(II) complex.

Table III. Selected Bond Angles (deg) for 8a[a]

P1–Pt–P2	97.1(2)	C3–O2–C4	115.0(2)
P1–Pt–O1	89.3(3)	Pt–C1–C2	109.0(1)
P1–Pt–C1	171.8(6)	C1–C2–C3	110.0(2)
P2–Pt–O1	173.5(3)	O1–C3–O2	118.0(2)
P2–Pt–C1	91.1(5)	O1–C3–C2	125.0(2)
Pt–O1–C3	111.0(1)	O2–C3–C2	117.0(2)

[a] Numbers in parentheses indicate the standard deviation in the least significant digit.



8a **9**

Figure 3. Structures and crystal data for complexes **8a** and **9**. Data for **9** are from Attig and Brock.[11a]

Only one similar structure, **9**, was found during a Cambridge Crystallographic Database search, and it contains two features in addition to those in complex **8a**: a noncomplexed ester and a vinyl moiety appended to the basic oxacyclic core.[11a] The structure and significant bond lengths of **8a** and **9** are shown in Figure 3 for comparison.

Comparison of the bond lengths of complexes **8a** and **9** reveals that the Pt–C and Pt–O bond lengths of both compounds are nearly the same within experimental error. The Pt–P distances are significantly different, however. The two Pt–P bond lengths of **9** show much less disparity, although the greater *trans* influence of the sp^3 carbon compared to the carbonyl is still evident. The greater similarity of Pt–P lengths in **9** is likely due to the greater basicity of the triethylphosphine ligands relative to the triphenylphosphines of complex **8a**.

Mechanism. In order to establish the mechanism of this novel process, the reaction of 2.1 equiv of methyl acrylate (**7a**) and [(2-propenyl)(PPh$_3$)$_2$Pt][OTf] (**1a**) was followed by ^{1}H NMR spectroscopy in CD$_2$Cl$_2$ at room temperature. As the reaction proceeded, vinyl resonances of the free acrylate **7a** (δ 5.84 (dd), 6.13 (dd), 6.42 (dd)) began to decrease in intensity while the resonances of the product (**8a**) appeared. There were also new resonances: a singlet at δ 1.88, a multiplet at δ 5.32, and a doublet at δ 5.86 ($^3J_{HH}$ = 15.7 Hz). Additionally, the reaction required 2 equiv of acrylate in order to completely consume the starting platinum(II) triflate complex. Reaction of 1 equiv of acrylate ester only led to 50% conversion. The byproduct was isolated by extraction with pentane (which concomitantly precipitated the platinum product from solution) and filtration. The byproduct was then identified as methyl 4-methyl-2,4-pentadienoate (**10a**) on the basis of mass spectral as well as ^{1}H and ^{13}C{^{1}H} NMR data. The spectral data were also compared to those of Heck-type products independently prepared[13] by Stille and Heck via the well-known Heck reaction.

The Heck reaction is very predictable and has been utilized extensively in organic synthesis:[14] aryl or vinyl halides[13c] are reacted with unsaturated carbonyl compounds under palladium(0)-catalyzed conditions to afford

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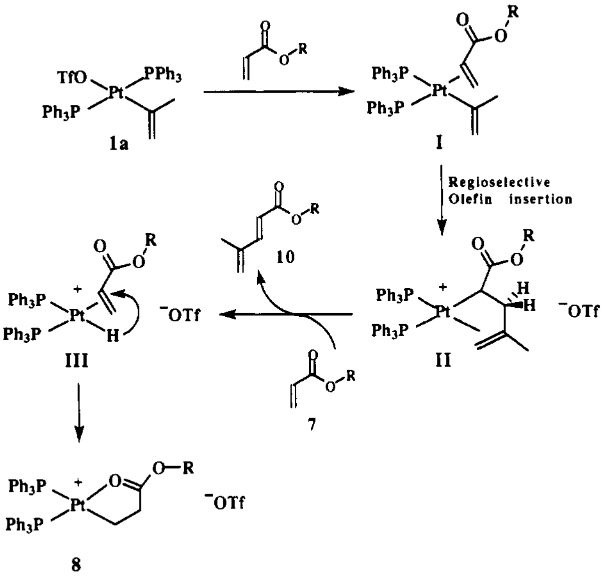
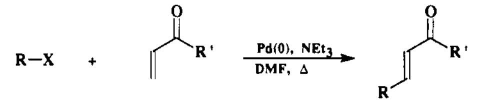


Figure 4. Proposed mechanism for the formation of complex 8 and Heck product 10.

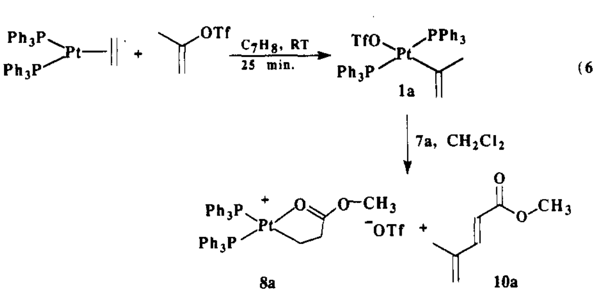
conjugated carbonyl compounds. This reaction proceeds with a wide variety of palladium catalysts and also works well with vinyl triflates.[13a,b] The products possess predominantly *trans* stereochemistry and almost complete regioselectivity in the carbon–carbon bond formation between the β-carbon of the carbonyl compound and the carbon to which the original halide or triflate was bonded. A generalized representation of the Heck reaction is shown in eq 5.



(5)

R = vinyl or aryl
X = OTf or halide

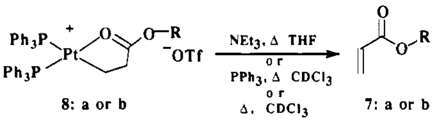
In the present reaction, platinum complex **1a** is prepared from a 2-propenyl triflate and $(PPh_3)_2Pt(C_2H_4)$, which is then reacted with the acrylate esters. We have, in essence, reacted the esters with the platinum analog of a possible intermediate in the palladium-catalyzed Heck reaction and generated the dienoates (**10a** and **10b**) from 2-propenyl triflate and methyl and ethyl acrylates (eq 6).



(6)

A likely mechanism for the reaction of the platinum complex **1a** and acrylate esters is shown in Figure 4. Although the proposed intermediates were not observed by ^1H or ^{31}P NMR spectroscopy, previous studies from this and other laboratories support their existence.[7,15] The initial step probably involves the coordination of the acrylate double bond to the open site previously occupied by the triflate anion. As in other similar reactions, this is likely followed by phosphine dissociation and rearrangement to the *cis* complex **I**. Insertion of the acrylate double bond between the metal center and the 2-propenyl moiety would then afford complex **II**, from which β-hydride elimination and coordination of a second acrylate would give hydride complex **III** and the Heck product **10**. Evidence for the intermediacy of hydride complex **III** includes the reaction of bis(triethylphosphine)platinum(II) hydride with ethyl acrylate to produce the triethylphosphine analog of **8b**.[16] The hydrogen then adds to the coordinated acrylate along with oxygen lone-pair coordination to afford the chelated product, **8**. It is interesting to note that this reaction did not occur in less polar solvents such as benzene and was very slow in $CDCl_3$. The more polar CH_2Cl_2 undoubtedly aids in the dissociation of the σ-bonded triflate to leave a vacant coordination site. The reaction also did not occur over the course of several days when the bromide analog of **1a** was used.

In order to further establish analogies between the current reaction and the palladium-catalyzed Heck reaction, the methyl acrylate complex **8a** was heated to 90 °C for 1.5 h in $CDCl_3$, heated in the presence of excess PPh_3, and also heated using NEt_3 in THF-d_8 solvent at 80 °C. In the first case, only a slight amount of acrylate was liberated and a complex reaction mixture resulted. In the latter two cases, however, **8a** was deprotonated α to the carbonyl carbon to liberate free methyl acrylate (**7a**) more cleanly and unidentified platinum species (eq 7).



(7)

This could have occurred via direct deprotonation with NEt_3 or displacement of the chelated oxygen by NEt_3 or PPh_3 followed by β-hydride elimination. Chelate displacement is facile, and the chelated oxygen can be displaced by reagents such as CO (vide infra). Although the kinetic parameters of these acrylate-liberating processes were not established, the reactions show that the acrylate complexes are possible models for an intermediate in a Heck catalytic cycle; the acrylate was regenerated, leaving a "PtL_n" fragment. The coordinatively unsaturated platinum fragments could be analogous to those active palladium species in the catalytic Heck reaction. Although numerous attempts have been made to carry out the platinum-coupling reaction catalytically, none have been successful.

Acrylate complexes **8a** and **8b** themselves are reactive, as is shown in eq 8. Reaction of **8a** with CO gas at room temperature results in CO insertion into the Pt–alkyl bond as well as displacement of the coordinated acrylate carbonyl, providing complex **11** in 91% isolated yield. The structure of **11** was assigned on the basis of number of criteria: (a) three different CO carbons in the $^{13}C\{^1H\}$ NMR spectrum at 172, 176, and 227 ppm; (b) three distinct CO stretches at 2108, 1730, and 1658 cm^{-1} in the infrared spectrum; (c) correct elemental analysis; and (d) the lack of significant Pt–H coupling in the ^1H NMR spectrum.

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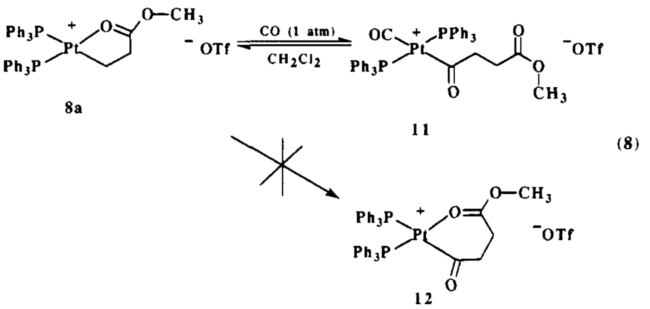

(8)

Although we expected to see some of complex **12** formed, none was observed. This was true even when **11** was dried in vacuum for extended periods of time and is likely due to geometric constraints of the ring system in **12**. Complex **11** is, however, unstable, and recrystallization followed by drying under high vacuum led to a mixture of **11** and **8a** which could be converted quantitatively back to **11** by bubbling CO through a solution of the mixture for 25 min. Subsequent bubbling of N_2 (e.g. 20 min) regenerated a mixture of **11** and **8a**. A $^{13}C\{^1H\}$ spectrum of **8a** after CO bubbling once again showed three carbonyl resonances. Carbon monoxide insertion into palladium– and platinum–alkyl bonds is well precedented[17,18] and is undoubtedly operative in the olefin/carbon monoxide copolymerization reaction catalyzed by palladium species.[19] In a study of CO insertion into the metal–methyl bond by van Leeuwen and co-workers, the carbonyl of a palladium acyl complex "deinserted" upon removal of CO pressure.[18a]

In summary, we have exploited the highly labile triflate of (σ-vinyl)platinum complex **1a** to provide a reactive site for unsaturated organic molecules. Electron-deficient cyano compounds coordinate through the nitrogen atom, alkynols react by rearrangement to the alkoxycarbene complexes, and acrylate esters afford Heck-type coupling products while forming "chelated" Pt(II) complexes in good yield. The chelated species also react with CO to give insertion products similar to those postulated in palladium-catalyzed carbon monoxide/ethylene copolymerization reactions. Further investigations on the reactions of (σ-vinyl)platinum(II) triflates with unsaturated compounds are currently underway.

Experimental Section

General Procedures. All melting points were obtained on a Mel-Temp capillary melting point apparatus and are uncorrected; IR spectra were recorded neat or as thin films in CCl_4 on a Mattson Polaris FTIR spectrometer with 4-cm^{-1} resolution. NMR spectra were recorded on either a Varian Unity 300 or XL-300 spectrometer. ^1H NMR spectra were recorded at 300 MHz, and all chemical shifts are reported relative to internal TMS (0.00 ppm) or the residual protons of the deuterated solvent (7.25 ppm, $CDCl_3$; 5.32 ppm, CD_2Cl_2). ^{13}C NMR spectra were recorded at 75 MHz, and all chemical shifts are reported in ppm relative to the carbon of the deuterated solvent (77.0 ppm, $CDCl_3$; 53.8 ppm, CD_2Cl_2). ^{31}P NMR spectra were recorded at 121 MHz, and all chemical shifts are reported in ppm relative to external 85% H_3PO_4 at 0.00 ppm. Mass spectra were recorded on either a Finigan MAT 95 high-resolution GC/mass spectrometer or a VG Micromass 7050E double-focusing high-resolution mass spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. Solvents were purified according to established procedures[20] or were high-purity HPLC grade solvents used as received. Methyl acrylate, ethyl acrylate, acrylonitrile, ethyl cyanoacetate, 3-butyn-1-ol, and (±)-4-pentyn-2-ol were purchased from Aldrich Chemical Co. and used as received. Starting platinum complex **1a** was synthesized according to a known procedure.[10]

Preparation of [*trans*-Pt(=$\overline{C(CH_2)_3O}$)(2-propenyl)(PPh_3)$_2$][OTf] (4a). A 25-mL round-bottomed flask equipped with a magnetic stir bar was charged with ca. 3 mL of CH_2Cl_2, and [*trans*-(2-propenyl)(PPh_3)$_2$Pt][OTf] (**1a**) (0.1002 g, 0.110 mmol) was added. 3-Butyn-1-ol (**3a**) (30 μL, 0.0163 g, 0.40 mmol) was then added via syringe and the solution stirred overnight at room temperature. Addition of ca. 2 mL of toluene followed by 10 mL of Et_2O and cooling to −18 °C gave 0.0943 g (87%) of product as an off-white microcrystalline solid with $^1/_2$ mol of CH_2Cl_2 trapped in the lattice: mp 169–170 °C dec; IR (CCl_4 film, cm^{-1}) 3051 w, 2916 w, 1587 m, 1480 m, 1435 s, 1275 vs, 1143 m, 1033 s, 696 m, 636 s; ^1H NMR δ ($CDCl_3$) 0.82 (m, overlapping, 2H), 0.87 (m, overlapping, CH_3 of vinyl, 3H), 2.29 (t, $^3J_{HH}$ = 16 Hz, 2H), 4.02 (t, $^3J_{HH}$ = 16 Hz, 2H), 4.40 (br s, $^3J_{PtH}$ = 28 Hz, *cis*-vinyl, 1H), 5.30 (br s, $^3J_{PtH}$ = 48 Hz, *trans*-vinyl, 1H), 740–7.70 (aromatics, 30H); ^{31}P NMR δ ($CDCl_3$) 15.7 (s, $^1J_{PtP}$ = 3012 Hz); $^{13}C\{^1H\}$ NMR δ ($CDCl_3$) 18.5 (s, $-CH_2-$), 29.7 (s, $^2J_{PtC}$ = 17 Hz, $-CH_3$), 57.4 (s, $^3J_{PtC}$ = 75 Hz, $-CH_2-$), 88.6 (s, J_{PtC} = 46 Hz, $-CH_2-$), 121.0 (q, $^1J_{CF}$ = 321 Hz, CF_3), 122.7 (t, J_{PC} = 5 Hz, α-vinyl), 128.6 (t, J_{PC} = 29.1 Hz), 128.8 (t, J_{PC} = 11 Hz), 131.6 (s, *para*), 134.3 (t, J_{PC} = 12 Hz), 155.2 (t, J_{PC} = 21 Hz, β-vinyl), 307.7 (t, $^1J_{PC}$ = 22 Hz, carbene). Anal. Calcd for $C_{44}H_{41}F_3O_4SP_2Pt\cdot{}^1/_2CH_2Cl_2$: C, 52.28; H, 4.14. Found: C, 52.34; H, 4.19.

Preparation of [*trans*-Pt(=$\overline{C(CH_2)_2CH(CH_3)O}$)(2-propenyl)($PPh_3$)$_2$][OTf] (4b). This compound was prepared in a manner identical to that for **4a** with [(2-propenyl)(PPh_3)$_2$Pt]-[OTf] (**1a**) (0.0651 g, 0.065 mmol) and (±)-4-pentyn-2-ol (**3b**) (40 μL, 0.42 mmol), yielding 0.0520 g (73%) of a white microcrystalline product with $^1/_2$ mol of H_2O trapped in the lattice: mp 179–180 °C dec; IR (CCl_4 film, cm^{-1}) 3054 w, 2917 w, 1586 w, 1435 s, 1275 vs, 1143 s, 1033 s, 696 m, 636 s; ^1H NMR δ ($CDCl_3$) 0.22 (m, 1H), 0.80 (d, $^3J_{HH}$ = 6.3 Hz, CH_3CH-, 3H), 0.83 (s, $^3J_{PtH}$ = 19 Hz, CH_3 of vinyl, 3H), 1.29 (m, 1H), 1.92 (m, 1H), 2.84 (m, 1H), 4.06 (m, 1H), 4.36 (br s, $^3J_{PtH}$ = 28 Hz, *cis*-vinyl), 5.23 (br s, $^3J_{PtH}$ = 51 Hz, *trans*-vinyl), 7.40–7.70 (aromatics, 30H); ^{31}P NMR δ ($CDCl_3$) 17.1 (s, $^1J_{PtP}$ = 3031 Hz); $^{13}C\{^1H\}$ NMR δ ($CDCl_3$) 19.2 (s, CH_3 of carbene), 26.3 (s, J_{PtC} = 12 Hz, $-CH_2-$), 29.5 (t, J_{PC} = 1.2 Hz, J_{PtC} = 20 Hz, CH_3 of vinyl), 58.1 (s, J_{PtC} = 72 Hz, $-CH_2-$), 100.2 (s, $^3J_{PtC}$ = 44 Hz, $-OCH(CH_3)-$), 121.0 (q, $^1J_{CF}$ = 321 Hz), 122.3 (t, J_{PC} = 5 Hz, α-vinyl), 128.6 (J_{PC} = 28.9 Hz), 128.7 (t, J_{PC} = 5.5 Hz), 131.6 (s, *para*), 134.4 (t, J_{PC} = 12.2 Hz), 155.8 (t, J_{PC} = 23.5 Hz, β-vinyl, 305.4 (t, J_{PC} = 16.4 Hz, carbene). Anal. Calcd for $C_{45}H_{44}F_3SO_4P_2Pt\cdot{}^1/_2H_2O$: C, 53.89; H, 4.42. Found: C, 53.84; H, 4.34.

Preparation of [(acrylonitrile)(2-propenyl)(PPh_3)$_2$Pt]-[OTf] (6a). **6a** was prepared in a 25-mL round-bottom flask equipped with a stir bar and charged with ca. 3 mL of CH_2Cl_2. Complex **1a** (0.0977 g, 0.011 mmol) was dissolved in the solvent and acrylonitrile (20 μL, 0.03 mmol) added via syringe. The solution was stirred at room temperature for 12 h, and pentane was added until the solution was slightly cloudy. The flask was then placed in a freezer at −18 °C for 12 h, and the flaky white microcrystals were collected by vacuum filtration on a Hirsch funnel, affording 0.0899 g (87%) of product: mp 169–171 °C dec; IR (CCl_4 film, cm^{-1}) 3056 m, 2264 (CN) m, 1585 m, 1479 m, 1435 s, 1267 vs, 1153 s, 1099 vs, 1032 vs, 693 s, 638 s; ^1H NMR δ (CD_2Cl_2) 0.92 (s, $^3J_{PtH}$ = 41 Hz, 3H), 4.60 ($^3J_{PtH}$ = 60 Hz, 1H), 4.8–5.4

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(overlapping multiplets, 3H), 5.92 (d, J_{HH} = 12 Hz, 1H), 7.4–7.7 (m, aromatics, 30H); ^{31}P NMR (CD_2Cl_2) δ 20.6 (s, $^1J_{PtP}$ = 3161 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 28.8 (t, J_{PC} = 4.7 Hz, $-CH_3$), 104.3 (s, α-vinyl of acrylonitrile), 116.8 (t, $^2J_{PC}$ = 4.7 Hz, α-vinyl of propene), 120.9 (s, CN), 121 (q, $^1J_{CF}$ = 321 Hz), 127.6 (t, $^1J_{PC}$ = 28 Hz, *ipso*), 128.8 (t, J_{PC} = 5.4 Hz), 131.7 (s), 134.3 (t, J_{PC} = 6.2 Hz), 137.9 (t, J_{PC} = 9.2 Hz), 143.5 (β-vinyl of acrylonitrile). Anal. Calcd for $C_{43}H_{38}F_3SO_3NP_2Pt$: C, 53.64; H, 3.98. Found: C, 53.50; H, 3.99.

Preparation of [(ethyl cyanoacetate)(2-propenyl)(PPh_3)$_2$Pt][OTf] (6b). This nitrile complex was prepared in the same manner as the acrylonitrile complex **6a** with complex **1a** (0.1002 g, 0.11 mmol) and ethyl cyanoacetate (200 μL, 0.94 mmol) in ca. 3 mL of CH_2Cl_2 at room temperature. Pentane was added until the solution was slightly cloudy and the flask placed in the freezer at −18 °C for 12 h. The flaky white needles were collected by vacuum filtration on a Hirsch funnel and washed with pentane, affording 0.0869 g (77%) of product: mp 135–136 °C dec; IR (CCl_4 film, cm^{-1}) 3059 w, 2924 w, 2248 w, 1750 s, 1482 m, 1436 s, 1264 vs, 1100 s, 1031 s, 696 m, 638 m; ^{1}H NMR δ (CD_2Cl_2) 0.78 (s, $^3J_{PtH}$ = 33 Hz, 3H), 1.00 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 3.02 (s, $-CH_2CN$, 2H), 3.87 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 4.48 (s, $^3J_{PtH}$ = 60 Hz, *cis*-vinyl, 1H), 5.10 (s, $^3J_{PtH}$ = 111 Hz, *trans*-vinyl, 1H), 7.25–7.65 (m, aromatics, 30H); ^{31}P NMR (CD_2Cl_2) δ 20.5 (s, $^1J_{PtP}$ = 3162 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 13.7 ($-CH_2CH_3$), 25.2 ($-CH_2CN$), 28.8 ($=CCH_3$), 62.8 ($-OCH_2CH_3$), 116.9 (α-vinyl), 119.4 (CN), 120.9 (q, $^1J_{CF}$ = 321 Hz), 127.6 (t, $^1J_{PC}$ = 28 Hz, *ipso*), 128.7 (t, J_{PC} = 5 Hz), 131.5 (s), 134.4 (t, J_{PC} = 6 Hz), 137.5 (t, J_{PC} = 9 Hz, β-vinyl), 160.8 (s, $-CO_2-$). Anal. Calcd for $C_{45}H_{42}F_3SO_5NP_2Pt$: C, 52.84; H, 4.14. Found: C, 52.49; H, 4.12.

Preparation of $[(PPh_3)_2\overline{PtCH_2CH_2C(O}){OCH_3}][OTf]$ (8a). A 25-mL round-bottom flask was equipped with a magnetic stir bar and charged with ca. 3 mL of CH_2Cl_2, [(2-propenyl)(PPh_3)$_2$Pt][OTf] (**1a**) (0.1496 g, 0.164 mmol), and methyl acrylate (50 μL, 0.56 mmol). The solution was stirred at room temperature for 6 h, and 2 mL of toluene and 5 mL of Et_2O were added. This cloudy mixture was placed in the freezer at −18 °C, and the resulting white, microcrystalline solid was collected by vacuum filtration on a Hirsch funnel, yielding 0.0991 g (63%): mp 152–153 °C dec; IR (CCl_4 film, cm^{-1}) 3057 w, 1602 vs (C=O), 1437 m, 1274 vs, 1141 s, 1034 s, 696 s, 637 s; ^{1}H NMR δ (CD_2Cl_2) 1.36 (m, $PtCH_2CH_2-$, 2H), 3.13 (m, $PtCH_2CH_2-$, 2H), 3.26 (s, 3H), 7.2–7.6 (m, aromatics, 30H); ^{31}P NMR δ (CD_2Cl_2) 12.0 (d, $^1J_{PtP}$ = 4877 Hz, $^2J_{PP}$ = 14 Hz), 30.9 (d, $^1J_{PtP}$ = 1915 Hz, $^2J_{PP}$ = 14 Hz); $^{13}C\{^1H\}$ NMR δ (CD_2Cl_2) 21.6 (dd, $^2J_{PC}$ = 80 Hz, *trans*-P, $^2J_{PC}$ = 4.1 Hz, *cis*-P, $^1J_{PtC}$ = 487 Hz), 37.5 (t, $^3J_{PC}$ = 5 Hz, $^2J_{PtC}$ = 34 Hz), 56.2 (s, $-OCH_3$), 128.9 (m, J_{PC} = 9.7 Hz), 131.2 (s), 132.0 (s), 134.4 (m, J_{PC} = 6.9 Hz), 199.5 (m, $-CO_2-$). Anal. Calcd for $C_{41}H_{37}F_3P_2SO_5Pt$: C, 51.27; H, 3.95. Found: C, 51.36; H, 3.99.

Preparation of $[(PPh_3)_2\overline{PtCH_2CH_2C(O})OCH_2CH_3][OTf]$ (8b). This was prepared in a manner identical to that for **8a** with complex **1a** (0.1224 g, 0.11 mmol) and ethyl acrylate (60 μL, 0.55 mmol), in ca. 3 mL of CH_2Cl_2. Isolation by filtration afforded 0.0789 g (58%) of **8b** as an off-white microcrystalline solid: mp 148–149 °C dec; IR (CCl_4 film, cm^{-1}) 3056 w, 1586 s, 1436 s, 1261 vs, 1149 s, 1032 s, 693 s, 637 s; ^{1}H NMR δ (CD_2Cl_2) 0.98 (t, $^3J_{HH}$ = 7.1 Hz, CH_3, 3H), 1.36 (m, $PtCH_2CH_2-$, 2H), 3.02 (m, $PtCH_2CH_2-$, 2H), 3.61 (q, $^3J_{HH}$ = 7.1 Hz, $-OCH_2CH_3$, 2H), 7.20–7.60 (aromatics, 30H); ^{31}P NMR δ (CD_2Cl_2) 12.16 (d, $^2J_{PP}$ = 14 Hz, $^1J_{PtP}$ = 4855 Hz), 30.8 (d, $^2J_{PP}$ = 14 Hz, $^1J_{PtP}$ = 1909 Hz); $^{13}C\{^1H\}$ NMR δ (CD_2Cl_2) 13.8 (s, CH_3), 21.5 (dd, $^2J_{PC}$ = 80 Hz, *trans*-P, $^2J_{PC}$ = 4.6 Hz, *cis*-P, $^1J_{PtC}$ = 562 Hz, $-PtCH_2-$), 37.7 (d, $^2J_{PC}$ = 5.3 Hz, $PtCH_2CH_2-$), 66.6 (s, OCH_2-), 121.4 (q, $^1J_{CF}$ = 317 Hz, CF_3), 128.8 (m, J_{PC} = 12 Hz), 131.2 (s), 131.9 (d, J_{PC} = 3.0 Hz), 134.3 (m, J_{PC} = 7.3 Hz), 199.0 (d, $^2J_{PC}$ = 13 Hz); FAB HRMS for [M − OTf]$^+$ ($C_{41}H_{39}P_2O_2Pt$) calcd 820.207 353, found 820.208 615.

NMR Observation of the Reaction of [(2-propenyl)(PPh_3)$_2$Pt][OTf] (1a) and Methyl Acrylate (7a). Complex **1a** (0.0083 g, 0.009 mmol) was placed in a 5-mm NMR tube with 0.6 mL of CD_2Cl_2. Methyl acrylate (1.6 μL, 0.018 mmol) was added via syringe. The reaction was then monitored by ^{1}H NMR at ambient temperature (23 °C) over a period of 6 h.

Single-Crystal X-ray Diffraction Analysis of 8a. A clear prism of **8a** was obtained by vapor diffusion of pentane into a CH_2Cl_2/toluene solution. The crystal was glued to a glass fiber and mounted for data collection on a CAD4 diffractometer. Cell constants (Table I) were obtained from 25 reflections with 20.0 < 2θ < 30.0°. The space group was determined from systematic absences (*hkl*, *h* + *k* = 2*n*; 0*kl*, *k* = 2*n*; *h*0*h* = 2*n*; *hk*0, *h* + *k* = 2*n*; *h*00, *h* = 2*n*; 0*k*0, *k* = 2*n*; 00*l*, *l* = 2*n*) and subsequent least-squares refinement. Standard reflections showed no decay during data collection.

Lorentz and Polarization corrections, and an empirical absorption correction based upon a series of ψ scans were applied to the data. The structure was solved by the standard heavy-atom techniques with the SDP/VAX package. Non-hydrogen atoms were refined with anisotropic thermal parameters, except for triflate groups which were refined isotropically. There were two independent triflate anions which were disordered due to crystallographically imposed two-fold symmetry. Scattering factors, and δf′ and δf″ values were taken from the literature.[21]

Preparation of [(CO)(η^1-(CO)(methyl propanoate))(PPh_3)$_2$Pt][OTf] (11). Complex **8a** (0.1257 g, 0.132 mmol) was placed in a 50-mL round-bottom flask equipped with a stir bar and charged with 10 mL of CH_2Cl_2. Dry CO was bubbled through the solution for 4 h at atmospheric pressure. Pentane was then added until the solution was slightly cloudy and the flask placed in the freezer at −18 °C for 48 h. The off-white microcrystalline solid was collected by vacuum filtration and washed with pentane, affording 0.1191 g (91%) with $^2/_3$ mol of CH_2Cl_2 trapped in the lattice: mp 100–102 °C dec with gas evolution; IR (CCl_4 film, cm^{-1}) 3061 m, 2108 s, 1730 s, 1658 s, 1436 s, 1265 vs, 1152 vs, 1034 vs, 695 s, 638 s; ^{1}H NMR δ ($CDCl_3$) 1.22 (t, $^3J_{HH}$ = 7.1 Hz, 2H), 1.87 (t, $^3J_{HH}$ = 7.1 Hz, 2H), 3.41 (s, $-OCH_3$, 3H), 7.55–7.80 (aromatics, 30H); ^{31}P NMR δ ($CDCl_3$) 13.0 (s, $^1J_{PtP}$ = 2989 Hz); $^{13}C\{^1H\}$ NMR δ ($CDCl_3$) 27.7 (s), 50.3 (t, $^3J_{PC}$ = 6.7 Hz), 51.4 (s, $-OCH_3$), 121.0 (q, $^1J_{CF}$ = 321 Hz, $-CF_3$), 127.0 (t, J_{PC} = 29.5 Hz, *ipso*), 129.7 (t, J_{PC} = 6.7 Hz), 132.8 (s), 134.0 (t, J_{PC} = 6.7 Hz), 172.3 (s, $-CO_2CH_3$), 176.3 (t, J_{PC} = 11 Hz), 227.2 (t, J_{PC} = 6.7 Hz). Anal. Calcd for $C_{43}H_{37}F_3P_2SO_7Pt{\cdot}{}^2/_3CH_2Cl_2$: C, 49.09; H, 3.62. Found: C, 49.18; H, 3.66.

Deprotonation of Complex 8a. An NMR tube was charged with 0.6 mL of THF-d_8, complex **8a** (0.0051 g, 0.0053 mmol), and NEt_3 (2 μL, 0.014 mmol). An ^{1}H NMR spectrum was obtained after 1 h and showed that no reaction had occurred. The tube was then heated at 80 °C for 1 h and another ^{1}H spectrum obtained showing the liberation of free methyl acrylate. Similar experiments were performed in $CDCl_3$ with **8a** (0.0050 g, 0.052 mmol) and excess PPh_3 (0.010 g, 0.038 mmol) as well as with 0.010 g of **8a** heated in the absence of any other reactant.

Methyl 4-Methyl-2,4-pentadienoate (10a). This coupling product was isolated by removal of solvent from the preparation of acrylate complex **8a**. Pentane and Et_2O were added to induce crystallization, and the solid product was removed by filtration through 1 g of Florisil. The solvent was then removed, and IR, ^{1}H NMR, and $^{13}C\{^1H\}$ NMR spectra of the clear, colorless oil were obtained: IR (neat, NaCl, cm^{-1}) 3067 w, 2978 m, 1720 vs, 1632 m, 1608 m, 1312 s, 1273 vs, 1171 vs, 1020 m, 983 m, 911 w, 865 m; ^{1}H NMR δ ($CDCl_3$) 1.88 (s, $CH_2{=}C(CH_3)-$, 3H), 3.77 (s, $-OCH_3$, 3H), 5.32 (m, $CH_2{=}C(CH_3)-$, 2H), 5.86 (d, $^3J_{HH}$ = 15.7 Hz, $-CH{=}CHCO_2-$), 7.35 (d, $^3J_{HH}$ = 15.7 Hz, $-CH{=}CHCO_2-$, 1H); $^{13}C\{^1H\}$ NMR δ ($CDCl_3$) 17.8 ($CH_2{=}C(CH_3)-$), 51.5 ($-OCH_3$), 118.3 ($-HC{=}CHCO_2-$), 124.4 ($H_2C{=}C(CH_3)-$), 140.5 ($CH_2{=}C(CH_3)-$), 147.3 ($-CH{=}CHCO_2-$), 167.6 ($-CO_2-$); mass spectrum (EI) *m/z* 126 ([M]$^+$, 92%), 111 ([M − (CH_3)]$^+$, 54%), 95 ([M − (OCH_3)]$^+$, 100%), 67 ([M − (CO_2CH_3)]$^+$, 50%); EI HRMS for $C_7H_{10}O_2$ ([M]$^+$) calcd 126.068 08; found 126.068 98.

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[21] Hahn, T., Ed. *International Tables for Crystallography*; D. Reidel Publishing Co.: Boston, MA, 1983; Vol. A, Table 20.

Ethyl 4-Methyl-2,4-pentadienoate (10b). This compound was isolated in the same manner as **10a**: IR (neat, NaCl, $\mathrm{cm^{-1}}$) 2979 m, 1717 vs, 1634 m, 1607 w, 1270 vs, 1175 s, 1039 m, 982 w, 734 w; ^{1}H NMR δ ($\mathrm{CDCl_3}$) 1.31 (t, $^3J_{\mathrm{HH}} = 7.2$ Hz, $-\mathrm{OCH_2C}\mathit{H}_3$, 3H), 1.89 (s, $\mathrm{CH_2{=}C(C}\mathit{H}_3)-$, 3H), 4.22 (q, $^3J_{\mathrm{HH}} = 7.2$ Hz, $-\mathrm{OC}\mathit{H}_2$-$\mathrm{CH_3}$, 2H), 5.33–5.37 (m, $\mathrm{C}\mathit{H}_2\mathrm{{=}C(CH_3)}-$, 2H), 5.88 (d, $^3J_{\mathrm{HH}} = 15.7$ Hz, $-\mathrm{CH{=}C}\mathit{H}\mathrm{CO_2}-$, 1H), 7.36 (d, $^3J_{\mathrm{HH}} = 15.7$ Hz, $-\mathrm{C}\mathit{H}\mathrm{{=}CHCO_2}-$, 1H); ^{13}C{^{1}H} δ ($\mathrm{CDCl_3}$) 14.3 ($-\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 18.0 ($\mathrm{CH_2{=}C(}\mathit{C}\mathrm{H_3)}-$), 60.3 ($-\mathrm{OCH_2}-$), 118.8 ($-\mathrm{CH{=}}\mathit{C}\mathrm{HCO_2}-$), 124.2 ($\mathit{C}\mathrm{H_2{=}C}-$), 140.5 ($\mathrm{CH_2{=}}\mathit{C}\mathrm{(CH_3)}-$), 147.0($-\mathit{C}\mathrm{H{=}CHCO_2}-$), 167.2 ($-\mathrm{CO_2}-$); EI HRMS for $\mathrm{C_8H_{12}O_2}$ ($[\mathrm{M}]^+$) calcd 140.083 72; found 140.083 66.

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Supplementary Material Available: Tables of crystal data, bond distances and angles, least-squares planes, general displacement parameters, and bond distance and angle calculations for **8a** (13 pages). Ordering information is given on any current masthead page.

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