uate student) and thank the Johnson Matthey Research Center for a loan of RuCl$_3$.

Registry No. 1, 94658-85-2; 2, 96482-50-7; 3, 12321-08-3; 4, 96482-51-8; 5, 96482-52-9; 1-octene, 111-66-0; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; styrene, 100-42-5; *trans*-stilbene, 103-30-0; 1-hexyne, 693-02-7; 4-octyne, 1942-45-6; diphenylacetylene, 501-65-5; anthracene, 120-12-7; diethyl ketone, 96-22-0; cyclohexanone, 108-94-1; diisopropyl ketone, 565-80-0; dibenzyl ketone, 102-04-5; acetophenone, 98-86-2; benzophenone, 119-61-9; benzaldehyde, 100-52-7; pentanal, 110-62-3; octane, 111-65-9; pentane, 109-66-0; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2; ethylbenzene, 100-41-4; 1,2-diphenylethane, 103-29-7; hexane, 110-54-3; tetrahydroanthracene, 30551-09-8; octahydroanthracene, 1079-71-6; 3-pentanol, 584-02-1; cyclohexanol, 108-93-0; 2,4-dimethyl-3-pentanol, 5381-92-0; 1-phenylethanol, 98-85-1; diphenylmethanol, 119-61-9; benzyl alcohol, 100-51-6; benzyl benzoate, 120-51-4; 1-pentanol, 71-41-0; *n*-pentyl *n*-pentanoate, 540-07-8; tetracyclone, 479-33-4.

Cyclobutaneone Formation via In Situ Generated Vinylketene Complexes of Chromium

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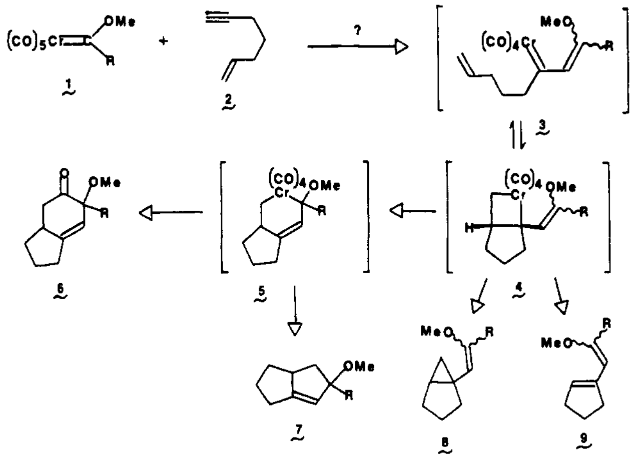
Summary: The reaction of (methoxymethylmethylene)pentacarbonylchromium with 6-hepten-1-yne in acetonitrile proceeds to give two isomeric bicyclo[3.2.0]heptan-6-ones that are substituted in the angular position α to the carbonyl with either an *E* (**10**) or *Z* (**11**) 2-methoxypropenyl group. The reaction with the corresponding tungsten complex fails. The reaction in THF gives a complex mixture of products, the two major of which are the *E* isomer **10** and a trisubstituted furan. There are two reasonable mechanisms to account for the formation of the bicycloheptanones. A methanol-trapping experiment provides evidence for a pathway involving initial reaction of the carbene complex with the acetylene functionality to give a vinylcarbene complex intermediate followed by carbon monoxide insertion to give a vinylketene complex which is then trapped intramolecularly by the olefin to give the bicycloheptanones.

It is well established that chromium Fischer carbene complexes such as 1 will react readily with unactivated acetylenes.[1] Although the heteroatom stabilized chromium carbene complexes such as 1 are unreactive with unactivated olefins,[2] group 6 carbene complexes (probably in high oxidation states) have been strongly implicated in the olefin metathesis reaction which is general for a variety of olefins.[3]

We envisioned a process outlined in Scheme I in which the reaction of an unactivated olefin with a low-valet group 6 carbene complex may be made more favorable. The reaction of complex 1 with an enyne such as 2 would be expected to proceed first with the acetylene functionality to give the intermediate vinylcarbene complex 3[4] in which the intramolecular reaction with an olefin is not only favored entropically but also by the anticipated increased reactivity of this nonstabilized chromium carbene complex.[4,5] According to the accepted mechanism for olefin metathesis,[3] the olefin should add to give the chromacyclobutane derivative 4 which can undergo scission to regenerate either 3 or the new olefin 9. This type of intramolecular metathesis has recently been observed for tungsten complexes.[6] Metallacyclobutane intermediates (W, Cr) have also been demonstrated to undergo reductive elimination to give cyclopropanes from both inter-[2,4,5] and intramolecular[7] reactions of carbene complexes with olefins. The presence of the vinyl group in intermediate 4 may allow for a 1,3-migration of chromium to give the isomeric η^1-allyl species 5. Resonable fates for this intermediate would be reductive elimination to give the bicyclooctene derivative 7 or carbon monoxide insertion and reductive elimination to give the cyclohexenone derivative 6, which would be analogous to the product we have obtained from the reaction of 1a with 1,6-heptadiyne.[8a]

Scheme I



This analysis proved to be only partly correct. The reaction of 1 with enyne 2 does generate intermediates that lead to intramolecular reaction with the unactivated olefin; however, none of the anticipated products indicated in Scheme I could be observed. Instead, the reaction of the methyl complex 1a with enyne 2 in acetonitrile produces the two bicycloheptanones 10 and 11 in 45% yield. The olefin geometry in each case was assigned by NOE difference ^{1}H NMR spectroscopy. Hydrolysis of the mixture of 10 and 11 gave only the angularly substituted dione 12.

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(1) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 0000.

(2) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1972**, *105*, 1356.

(3) Banks, R. L. In "Catalysis"; The Royal Society of Chemistry: London, 1982; Vol. 4, p 100.

(4) For a mechanistic discussion of this reaction see ref 1a and: Casey, C. P. In "Reactive Intermediates"; Wiley: New York, 1981; Vol. 2, p 135.

(5) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.

(6) Katz, J. K.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737.

(7) Casey, C. P.; Vollendorf, N. ww.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3754. (b) Toledano, C. A.; Rudler, H.; Daran, J.-C.; Jeannine, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 574.

(8) (a) Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P. C. *J. Am. Chem. Soc.* **1985**, *101*, 1060. (b) Wulff, W. D.; McCallum, J. S., unpublished results. (c) Yamashita, A.; Scahill, T. A. *Tetrahedron Lett.* **1982**, 3765.

(9) The spectral data for all new compounds can be found in the supplemental material. Unless otherwise specified all reactions were carried out under an argon atmosphere at 0.0044 M in carbene complex with 1.2 equiv of the enyne. Essentially the same yields of 10 and 11 can be obtained at higher concentrations (47% at 0.05 M) which is in contrast to the concentration dependence observed for the reaction of 1a with 1,6-heptadiyne.[8a]

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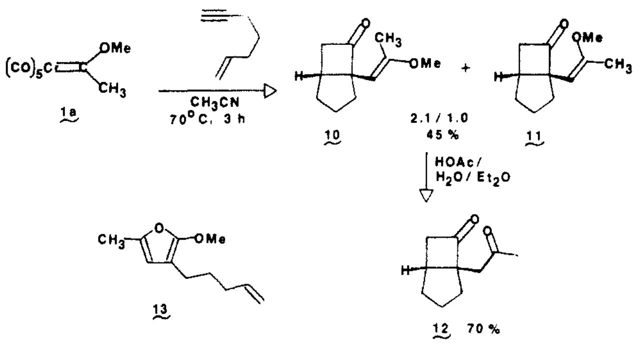
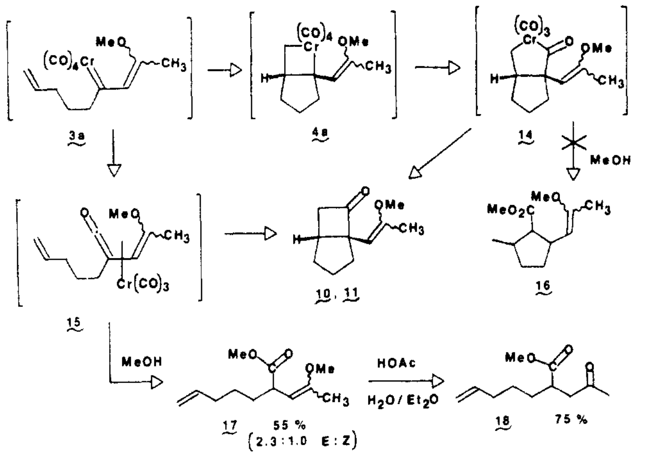
Scheme II



Scheme III



The reaction of complex **1a** and enyne **2** in THF gives a complicated mixture of products. The two major products were identified as the furan **13** (10%) and the cyclobutanone **10** (13%), and several other compounds were formed in smaller amounts which have not yet been identified.[10] It is interesting to note that none of the isomeric cyclobutanone **11** was detected in this reaction by capillary GC. This suggests that furan formation can occur only from the *Z*-olefin isomer of the vinylcarbene complex intermediate **3**, and we have independent evidence to support this suggestion from other work directed at the mechanism of furan formation.[8b] Tungsten carbene complexes have recently been reported to react with certain enynes to give methathesis products of the type **9**.[5] We have examined the reaction of enyne **2** with the pentacarbonyltungsten complex corresponding to **1a** and were unable to obtain more than trace amounts of materials that could be eluted by GLC or TLC (Scheme II).

Cyclobutanones have not been previously observed from the reaction of a carbene complex and an unactivated olefin.[11] Two possible mechanisms to account for the formation of **10** and **11** are presented in Scheme III. Although, the formation of a metallacyclobutane from a carbene complex and an olefin is precedented, the insertion of carbon monoxide into a metallacyclobutane is unknown for group 6 metals.[12] Reductive elimination from **14** would, however, provide for a straightforward accounting of the formation of the cyclobutanones **10** and **11**. An alternative mechanism involves a carbon monoxide insertion into the carbene carbon of the vinylcarbene complex **3a** to give the vinylketene complex **15**. This type of carbon monoxide insertion has been previously invoked in other reactions of chromium carbene complexes and acetylenes.[4,13] An intramolecular 2 + 2 cycloaddition of the olefin with the vinyl ketene[11,14,15] would then account for the cyclobutanones **10** and **11**.

It should be possible to distinguish between the two mechanisms presented in Scheme III by a methanol-trapping experiment.[16] Interception of the acyl complex **14** would give the carbomethoxycyclopentane derivative **16** and provide evidence for the carbon monoxide insertion into the chromacyclobutane **4a**. The formation of acyclic methyl ester **17**, on the other hand, would provide evidence for the intermediacy of the vinylketene complex **15**. The reaction of complex **1a** with enyne **2** in a 7:3 acetonitrile/methanol mixture produced only the acyclic methyl ester **17** as a 2.3/1.0 mixture of *E* and *Z* isomers, which can be converted to the single keto ester **18**. It cannot be determined at this time whether this cycloaddition is mediated by the metal or occurs after the free vinylketene is decomplexed from the metal since both the complexed and uncomplexed vinylketene could be intercepted by methanol.

The key element revealed from the reaction of complex **1a** with enyne **2** is that the ketene functionality in the intermediate vinylketene complex **15** can be intercepted by an olefin to give the cyclobutanones **10** and **11**. This is suggestive that the ketene may be intercepted with other unsaturated carbon-based functional groups as well. Four new carbon-carbon bonds are made during the formation of the bicycloheptanones **10** and **11** which are attractive as potential synthetic intermediates by virtue of the angular vinyl group α to the carbonyl, which should allow for various ring expansion reactions or upon hydrolysis further elaborations via the dione **12**. Vinylcyclobutanones are versatile intermediates for the synthesis of five-, six-, and eight-membered rings,[15,17] and examples include vinyl-substituted bicyclo[3.2.0]heptanones.[18,19] The only previously known example of an angular vinyl-substituted bicyclo[3.2.0]heptan-6-one has recently been employed in the synthesis of poitediol and 4-epipoitediol.[20] We intend

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[10] The cyclobutanone **10** is not a primary product of this reaction in THF. One of the primary products, along with the furan **13**, is an unstable organometallic complex which has so far eluded isolation and which decomposes to give several compounds including **10**, but not **9**.

[11] The only known example from the reaction of a carbene complex involves an intermolecular reaction with a vinylpyrrolidone under 2200 psi of carbon monoxide: Dorrer, B.; Fischer, E. O. *Chem. Ber.* **1974**, *107*, 2683.

[12] A few examples are known for other transition metals: (a) Theopold, K. H.; Bergman, R. G. *Organometallics* **1982**, *1*, 1571. (b) Roundhill, D. M.; Lawson, D. W.; Wilksinson, G. *J. Chem. Soc. A* **1968**, 845.

[13] Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 954.

[14] (a) Brady, W. T. In "The Chemistry of Ketenes, Allenes and Related Compounds"; Patai, S., Ed.; Wiley: New York, 1980; Part 1; p 279. (b) "Cycloaddition Reactions of Heterocumulenes"; Ulrich, H., Ed.; Academic Press: New York, 1967.

[15] Jackson, D. A.; Rey, M.; Dreiding, A. A. *Helv. Chim. Acta* **1983**, *66*, 2330 and references therein.

[16] Vinyl ketene complexes of chromium have previously been intercepted from the reactions of chromium carbene complexes and acetylenes by alcohols and amines in intramolecular[1a,8b] and intermolecular reactions.[8c]

[17] (a) Lyle, T. A.; Mereyala, H. B.; Pascual, A.; Frei, B. *Helv. Chim. Acta* **1984**, *67*, 774. (b) Bhupathy, M.; Cohen, T. *J. Am. Chem. Soc.* **1983**, *105*, 6978. (c) Cohen, T.; Bhupathy, M.; Matz, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 520. (d) Gadwood, R. C.; Lett, R. M. *J. Org. Chem.* **1982**, *47*, 2268. (e) Danheiser, R. L.; Martinez-Oavila, C.; Sard, H. *Tetrahedron* **1981**, *37*, 3943. (f) Matz, J. R.; Cohen, T. *Tetrahedron Lett.* **1981**, *22*, 2459. (g) Lee-Ruff, E.; Hopkinson, A. C.; Dao, L. H. *Can. J. Chem.* **1981**, *59*, 1675. (h) Wilson, S. R.; Mao, D. T. *J. Chem. Soc., Chem. Commun.* **1978**, 479.

[18] (a) Paquette, L. A.; Andrews, D. R.; Springer, J. P. *J. Org. Chem.* **1983**, *48*, 1147. (b) Danheiser, R. L.; Gee, S. K.; Sard, H. *J. Am. Chem. Soc.* **1982**, *104*, 7670. (c) Trahanovsky, W. S.; Surber, B. W.; Wilkes, M. C.; Preckel, M. M. *J. Am. Chem. Soc.* **1982**, *104*, 6779. (d) Huston, R.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* **1982**, *65*, 1563, 451.

[19] Gadwood, R. C.; Lett, R. M.; Wissinger, J. F. *J. Am. Chem. Soc.* **1984**, *106*, 3869.

to investigate the scope and stereoselectivity of these reactions involving the intramolecular trapping[21] of vinylketene complexes of chromium.

Acknowledgment. This work was supported by a grant from donors of the Petroleum Research Fund, administered by the American Chemical Society. The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program and by the NCI via the University of Chicago Research Center (CA 14599).

Registry No. **1a**, 20540-69-6; **10**, 96761-03-4; **11**, 96844-10-9; **12**, 96761-04-5; **13**, 96761-08-9; (*E*)-**17**, 96761-05-6; (*Z*)-**17**, 96761-06-7; **18**, 96761-07-8; 6-hepten-1-yne, 65939-59-5.

Supplementary Material Available: Spectral and physical data for all new compounds (2 pages). Ordering information is given on any current masthead page.

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(20) Paquette, L. R.; Colapret, J. A.; Andrews, D. R. *J. Org. Chem.* **1985**, *50*, 201.

(21) The scope of intramolecular [2 + 2] cycloadditions of olefins with simple ketenes has recently been examined: (a) Marko, I.; Ronsmans, N.; Hesbian-Frisque, A. M.; Dumas, S.; Ghosez, L.; Ernst, B.; Greuter, H. *J. Am. Chem. Soc.* **1985**, *107*, 2192. (b) Snider, B. B.; Hui, R. A. H. F.; Kulkarni, V. S. *J. Am. Chem. Soc.* **1985**, *107*, 2194.

Preparation and Properties of Platinum Ketene Complexes. Facile C–C Bond Cleavage of Coordinated Ketene

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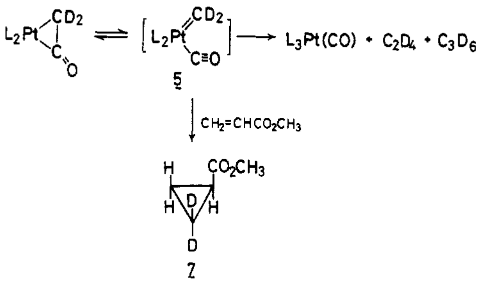
Summary: η^2-(C,C) ketene complexes $Pt(CH_2{=}C{=}O)L_2$ (L = PPh_3 and Cl) and $PtCl_2(CH_2{=}C{=}O)(PMe_2Ph)_2$, which were isolated from the reaction of PtL_4 with CH_2Br_2 and carbon monoxide in the presence of Zn or direct ligation of PtL_4 with ketene, thermally decomposed to afford a variety of hydrocarbons by a novel pathway involving C–C bond cleavage of the bound ketenes and underwent reduction with H_2 to yield acetaldehyde, ethanol, and hydrocarbons.

Scheme I

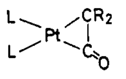


Transition-metal ketene complexes[1] have drawn considerable attention as models for the possible intermediates implicated in the elementary carbon–carbon coupling step[2] in surface-catalyzed[3] or homogeneous carbon monoxide reduction.[4] Although the formation of ketene complexes by coupling reactions of CO with carbene ligands has precedent,[2,5] their reactivity relevant to their actual roles in homogeneous CO reduction remain unexplored. We report herein the preparation of unsubstituted ketene complexes of Pt and describe the facile C–C bond cleavage of ketene ligands and the pronounced effects of ligands on their decomposition modes. Also, their reactivities toward hydrogen are investigated as a model for the conversion of syngas to C_2-oxygenated products.[4d,5]

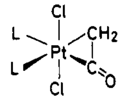
A THF suspension (–30 °C) of $Pt(PPh_3)_4$ (1.18 mmol, 0.15 M) was treated with CH_2Br_2 (11.8 mmol) in the presence of Zn powder (11.8 mmol), exposed to 3 atm of CO, and warmed to 20 °C (10 h). The resulting light brown suspension was passed through a short column of neutral alumina (Woelm N Super I) at –5 °C. Addition of ether to the brown eluent resulted in precipitation of the light brown, crystalline product $Pt(CH_2{=}C{=}O)(PPh_3)_2$, **1** (23%).[6] Coveniently, **1** is also accessible by the direct treatment of ketene with $Pt(C_2H_4)(PPh_3)_2$ in toluene (47%).[7]

$$Pt(PPh_3)_4 + CO_2Br_2 \xrightarrow[\text{Zn, THF}]{\text{CO}} \underset{\mathbf{1}}{(Ph_3P)_2Pt(CH_2{=}C{=}O)} + ZnBr_2$$

$PtCl_2(CH_2{=}C{=}O)$ (**3**) was readily isolated as deep red crystals by direct reaction of $[PtCl_2(C_2H_4)]_2$ with ketene.[8]



1, L = PPh₃ ; R = H
2, L = P Ph₃ ; R = D
3, L = Cl ; R = H



4, L = PMe₂Ph

Further treatment of an acetone solution of **3** with 2 equiv of dimethylphenylphosphine led to the formation of $PtCl_2(CH_2{=}C{=}O)(PMe_2Ph)_2$ (**4**), isolated as light brown crystals (48%).[9] The coordination mode of the ketene

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(1) (a) Moore, E. .; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068. Ho, S. C. H.; Straus, D. A.; Armantraut, J.; Schaefer, W. P.; Grubbs, R. H. *Ibid.* **1984**, *106*, 2210. (b) A number of substituted ketene complexes have been prepared. See: Fachnetti, G.; Brian, C.; Floriani, C.; Chies-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1978**, *100*, 1921. Herrman, W. A.; Plank, J.; Ziegler, M.; Weidenhammer, K. *Ibid.* **1979**, *101*, 3133. Mitsudo, T.; Watanabe, Y.; Takegami, Y. *J. Chem. Soc. Chem. Cummun.* **1979**, 265. Casey, C. P.; O'Connor, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 2919. And references therein.

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(3) Blyholder, G.; Emmet, P. H. *J. Phys. Chem.* **1960**, *64*, 470. Ichikawa, M.; Sekigawa, K.; Shikakura, K.; Kawai, M. *J. Mol. Catal.* **1981**, *11*, 167.

(4) (a) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (b) Keim, W. "Catalysis in C_1 Chemistry"; D. Reidel Publishing Co.: Dordrecht, 1983; p 5. (c) Lin, Y. C.; Calabrese, J. c.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679. (d) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Reingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4783.

(5) (a) Herrman, W. A.; Plank, J. *Angew Chem.* **1978**, 555. (b) Miyashita, A.; Grubbs, R. H. *Tetrahedron Lett.* **1981**, 1255. (c) Barger P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178.

(6) **1**: IR (KBr) 2995 (m, ν_{CH}), 2850 (m, ν_{CH}), 1725 cm^{-1} (s, ν_{CO}); ^{1}H NMR (acetone-d_6) δ 2.23 (m, 2 H, CH_2, J_{PtH} = 131 Hz, J_{PH} = 7 Hz), 7.1 (m, 30 H, Ph); ^{13}C NMR (gated decoupled) (toluene-d_8) δ 74.7 (t, CH_2, J_{PtC} = 904 Hz, J_{CH} = 159 Hz), 213.8 (C=O). Anal. Calcd for $C_{38}H_{32}OP_2Pt$: C, 59.91; H, 4.23. Found: C, 59.87; H, 4.34.

(7) Ketene-d_2 was obtained by pyrolysis of acetone-d_6 (isotopic purity 98%). Fieser and Fieser "Reagents for Organic Synthesis", Vol. 1, p 528. Andreades, S.; Carlson, H. D. *Org.* Synth. **1965**, *45*, 50. $Pt(CD_2{=}C{=}O)(PPh_3)_2$ (**2**): IR (KBr) 2240 (m, ν_{CD}), 2125 (sh, ν_{CD}), 1726 cm^{-1} (s, ν_{CO}); ^{1}H NMR (acetone-d_6) δ 7.1 (m, Ph); ^{13}C{^{1}H} NMR (toluene-d_8) δ 214.2 (C=O).

(8) An acetone solution of Zeise's dimer $[PtCl_2(C_2H_4)]_2$ was treated with $CH_2{=}C{=}O$ (20 equiv), initially at –60 °C, warming to 20 °C (15 h). The resulting red solution was passed through a short column of neutral alumina. Addition of ether to the red eluent led to the precipitation of deep red crystals of **3**, which were recrystallized from acetone (54%). **3**: IR (KBr) 2980 (m, ν_{CH}), 2910 (m, ν_{CH}), 1720 cm^{-1} (s, ν_{CO}); ^{1}H NMR (acetone-d_6) δ 1.64 (CH_2, J_{PtH} = 299 Hz); ^{13}C {^{1}H} NMR δ 25.8 (CH_2, J_{PtC} = 1010 Hz), 225.2 (C=O, J_{PtC} = 857 Hz). Anal. Calcd for $C_2H_2OCl_2Pt$: C, 7.79; H, 0.65; Cl, 23.01. Found: C, 7.83; H, 0.77; Cl, 23.35.

0276-7333/85/2304-1463$01.50/0