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

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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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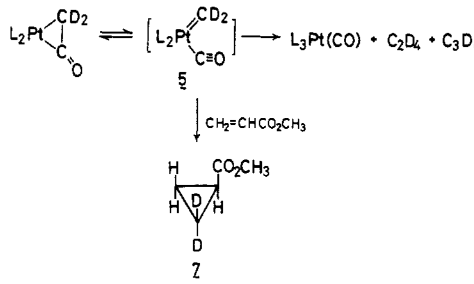
Summary: η^2-(C,C) ketene complexes $Pt(CH_2{=}C{=}O)L_2$ (L = PPh_3 and Cl) and $PtCl_2(CH_2{=}C{=}O)(PMe_2Ph)_2$, which were isolated from the reaction of PtL_4 with CH_2Br_2 and carbon monoxide in the presence of Zn or direct ligation of PtL_4 with ketene, thermally decomposed to afford a variety 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.

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]

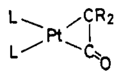
Scheme I

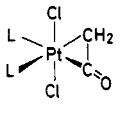


A THF suspension (−30 °C) of $Pt(PPh_3)_4$ (1.18 mmol, 0.15 M) was treated with CH_2Br_2 (11.8 mmol) in the presence of Zn powder (11.8 mmol), exposed to 3 atm of CO, and warmed to 20 °C (10 h). The resulting light brown suspension was passed through a short column of neutral alumina (Woelm N Super I) 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]

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

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


1, L = PPh_3 ; R = H
2, L = PPh_3 ; R = D
3, L = Cl ; R = H


4, L = PMe_2Ph

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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(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.

Table I. Thermal Decomposition of Pt Ketene Complexes 1, 3, and 4[a]

complexes	temp, °C	products,[b] %						
		CH_4	C_2H_4	C_3H_6	C_4H_8	CO	CH_2CO	*f*[c]
3	110		14	5	7	11	15	5
3	210		15	6	8	68	16	5
4	180	17	8	16	3	56	4	23
1	80		15	14	4	8	2	48
1	200	3	18	12	5	72	1	95

[a] Pyrolysis of the solid was performed under vacuum, and the products were collected on a cold finger cooled with liquid nitrogen. The temperature was raised from 20 °C to the specific point at a rate of 5 °C/min. [b] All products were identified by GC-MS (EI, 20 eV) and GC-IR using a short column of Durapak (octane on Porasil C) treated with trimethylsilyl ether. [c] $f = \sum^4_{m=1} m\text{-}(CH_2)_m/CH_2C{=}O$.

ligands was determined by means of IR and NMR spectroscopy.[1] The data are fully consistent with an η^2-(C,C) ketene structure for 1–4; the magnitude of $^1J_{PtC}$ or $^2J_{PtH}$ in NMR spectra of 1 and 3 reflects the s character of the carbon hybrid orbital involved in the Pt–C bonding, corroborating the platinacyclopropane structure.[10]

The ketene complexes thermally decompose to yield various hydrocarbons. Upon being heated at 55 °C in acetone, 2 decomposed to give C_2D_4 (17%), C_3D_6 (16%), and C_4D_8 (7%). From the decomposition residue, $Pt(CO)(PPh_3)_3$ was isolated in 36% yield.[11] This result may be ascribed to a C–C bond cleavage reaction of the ketene ligand of 2, followed by the formation of the kinetically viable metal–carbene–CO intermediate 5, the carbene fragment of which presumably oligomerizes to form olefins (Scheme I).[12] This observation is in accord with recent studies on the bridging ketene complex of Os which is in partially reversible equilibrium with the methylene complex.[4d,13] This rearrangement, which probably proceeds through metal–carbene species 5, is consistent with the formation of cyclopropane derivative 7 (36%) in carbene trapping experiments of 2 with Michael acceptors such as methyl acrylate.[14]

The ketene complexes 1, 3, and 4 readily decompose to yield hydrocarbons and CO as summarized in Table I. $Pt(CH_2{=}C{=}O)(PPh_3)_2$ (1) almost exclusively affords hydrocarbons, resulting in a large *f* value, whereas $PtCl_2(CH_2{=}C{=}O)$ (3) yields more ketenes. It was found that those 4 which have electron-donating phosphine ligands[15] gave larger *f* values affording less ketene compared with 3. The decomposition mode of the ketene complexes involving a C–C bond scission of the bound ketenes seems to be largely affected by the nature of the ligands coordinated to the metal center.[15] However, thermolysis of 1 in the presence of H_2 has led to the formation of C_2-oxygenated products, irrespective of its dominant decomposition route.

The ketene ligands of complexes 1–4 were found to be reduced by H_2 under mild condition. Hydrogenation of 1 by 3 atm of H_2 (26 °C) gave CH_3CHO (36%) and C_2H_5OH (20%), together with hydrocarbons [CH_4 (20%), C_2H_6 (2%), and C_3H_8 (5%)], while 3 afforded C_2H_5OH (55%), CH_3CHO (21%), and CH_3OH (2%) in addition to CH_4 (3%) and C_3H_8 (9%).

$$L_2Pt(CH_2{=}C{=}O) \xrightarrow[\text{acetone}]{H_2} C_2H_5OH + CH_3CHO + C_nH_{2n+2}$$

$$L_2Pt(CH_2{=}C{=}O) \xrightarrow[\text{THF}]{LiAlH_4} C_2H_5OH$$

Reduction of 1, 3, or 4 with $LiAlH_4$ in THF produced C_2H_5OH in 93, 87, or 92% yield, respectively. These observation may indicate that the ketene complexes can be substantially converted to C_2-alcohol and aldehyde along with hydrocarbons under mild conditions. Such hydrogenations appear to be important because of the potential relevance of ketene intermediates on catalyst surfaces during CO reduction chemistry.

Acknowledgment. We gratefully acknowledge the financial support of the Ministry of Education (Grant 580555) and the experimental assistance of Mr. S. Ikezu.

Registry No. 1, 96728-28-8; 2, 96705-37-2; 3, 96705-38-3; 4, 96705-39-4; 7, 90115-89-2; $Pt(PPh_3)_4$, 14221-01-3; $Pt(C_2H_4)(PPh_3)_2$, 12120-15-9; $[PtCl_2(C_2H_4)]_2$, 12073-36-8; $Pt(CO)(PPh_3)_3$, 15376-99-5; CH_2Br_2, 74-95-3; CH_2CO, 463-51-4; norcarane, 51592-70-2; methyl acrylate, 96-33-3; ketene-d_2, 4789-21-3; cyclohexene, 110-83-8.

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(9) 4: IR (KBr) 2990 (m, ν_{CH}), 2870 (m, ν_{CO}), 1722 (s, ν_{CO}), 325 (w, ν_{PtCl}); ^1H NMR (toluene-d_8) δ 1.62–1.70 (m, 14 H, CH_2, PMe) 7.2–7.4 (m, 10 H, Ph). Anal. Calcd for $C_{18}H_{24}OCl_2P_2Pt$: C, 36.99; H, 4.14; Cl, 12.13. Found: C, 37.28; H, 4.50; Cl, 11.82. Only one Pt–Cl stretching vibration, which is consistent with the trans-halogen structure, is observed. See: Binns, S. E.; Cragg, R. H.; Gillard, R. D.; Heaton, B. T.; Pilbrow, M. E. *J. Chem. Soc. A* **1969**, 227.

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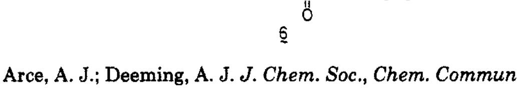
(11) Malatesta, L.; Cariello, C. *J. Chem. Soc.* **1958**, 2323. Chini, P.; Logoni, G. *J. Chem. Soc. A* **1970**, 1542.

(12) An alternative decomposition process involving platinacyclobutanone complex 6 is conceivable, although no cyclopropanone was detected on pyrolysis of 2. However, the experimental result that thermolysis of 2 in the presence of ca. 2 equiv of $CH_2{=}C{=}O$ yielded C_2D_4 and C_3D_6 as the major products along with cyclopropanone-d_2 (4%) and $C_2H_2D_2$ (2%) may exclude this possibility.



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(14) The carbene fragment of 2 could be also trapped with cyclohexene to yield norcarane (17%). Norcarane and 7 were isolated by preparative GLC and identified by ^1H NMR and mass spectroscopy.

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Stable Titanacyclopentanes: Isolation, Characterization, and Reactions of 5,5-Bis(pentamethylcyclopentadienyl)-5-titanaspiro[2.4]heptanes Derived from $(\eta^5\text{-}C_5Me_5)_2Ti(CH_2{=}CH_2)$ and Methylenecyclopropanes

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Summary: 5,5-Bis(pentamethylcyclopentadienyl)-5-titanaspiro[2.4]heptanes prepared by the oxidative coupling of $(\eta^5\text{-}C_5Me_5)_2Ti(CH_2{=}CH_2)$ with methylenecyclopropanes have been isolated and characterized by spectroscopic and X-ray analyses. Divergent thermal reactions involving novel skeletal rearrangements and reductive eliminations giving cycloalkanes have been observed, which are highly dependent on the molecular structures of the metallacycles.

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