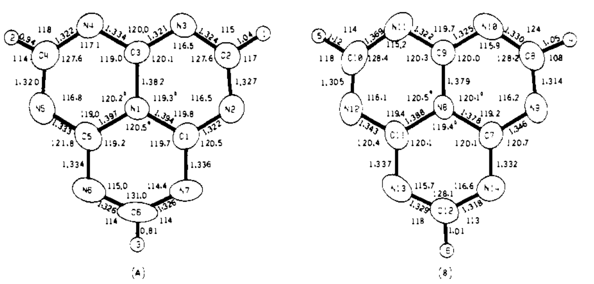

Figure 1. Bond lengths and bond angles for the two crystallographically independent molecules, A and B, of tri-*s*-triazine (**1**). The separate esd values are given in the supplementary material. For the bond lengths and angles not involving H, the esd values are in the range 0.003–0.005 Å and 0.2–0.3°, respectively.

havior of tri-*s*-triazine (**1**) to *s*-triazine[3,28] is exemplified by the decomposition of both in water. The chemical shift value of 8.3 for the protons in tri-*s*-triazine is greater than any previously observed for unsubstituted azacycl[3.3.3]azines,[16c] greater also than that, δ 7.3, for N—CH=N—Ar model, *N,N*-dimethyl-*N'*-phenylformamidine,[29] and smaller than the δ 9.2 value for ^{1}H in "aromatic" *s*-triazine.[30] The ^{15}N NMR chemical shift of the peripheral nitrogens in **1**, ~237 ppm downfield from ammonia,[31] is less than that for (^{15}N)-*s*-triazine, 282.9.[32] The central C–N bonds are shortened from the usual 1.47-Å single-bond distance to an observed 1.39-Å average value. The deshielded central ^{15}N resonance at ~186 ppm downfield from NH_3 prompts examination of the ring-current effect on the central N in other representative azacycl[3.3.3]azines. Application of the abbreviated synthesis to such cyclazines is in progress.

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Registry No. 1, 204-34-2; 2, 504-08-5; 3, 82679-23-0; methyl *N*-cyanomethanimidate, 51688-22-3.

Supplementary Material Available: Complete crystallographic data, including tables listing atomic positional and thermal parameters, bond angles, torsional angles, intermolecular contact distances, weighted least-squares planes, and observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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Preparation and Reaction of Metal Ketene Complexes of Zr and Ti

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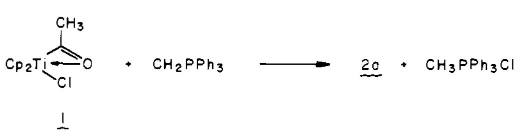
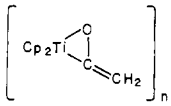
Transition-metal ketene complexes have been proposed as intermediates in catalytic[1a] and stoichiometric[1b] reductions of carbon monoxide and as models for the isoelectronic ligand, carbon dioxide.[2] Complexes that contain highly stabilized ketene fragments, especially diphenylketene, have generally (but see ref 3) been prepared by direct reaction of the ketene with a coordinately unsaturated metal complex[2,4] or by carbonylation of metal alkylidenes.[5]

We have found a general route to unsubstituted and alkyl-substituted ketene complexes of titanium and zirconium.[6] In an attempt to prepare titanocene enolate complexes, the η^2-acetyl **1**[7a] was treated with CH_2PPh_3 in dichloromethane–ether at −50 °C (eq 1). Yellow **1** reacted instantly to give a red solution from

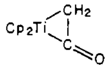


(1)

which red microcrystalline **2a** soon precipitated. Methyltriphenylphosphonium chloride was isolated from the supernatant. Reaction of **1** with $NaN(SiMe_3)_2$ in ether also gives **2a**. The



2a,b



3

product is a moderately air-sensitive solid that is stable at room temperature for several days under an inert atmosphere and is sparingly soluble in a variety of solvents but decomposes rapidly in methylene chloride. In benzene, red **2a** isomerizes to yellow **2b**, reaching equilibrium in a matter of minutes at room temperature. The ratio of **2a**:**2b** at equilibrium is ca. 1:10. The yellow isomer crystallizes from benzene solution. Several lines of evidence suggest that **2a** and **2b** have the basic η^2(C,O) ketene structure shown. The ^{1}H NMR spectra exhibit inequivalent methylene protons for each isomer with chemical shifts and coupling constants in the range typical of terminal olefins.[8] An η^2(C,C) ketene, **3**, should show a single methylene resonance. The proposed structure is similar to that observed for diphenylketene complexes of Ti,

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(3) (a) The dimeric ketene complex $(Cp_2ZrOCCPh_2)_2$ has recently been prepared by carbonylation of $Cp_2Zr(CHPh_2)R$ (R = CH_3 or CH_2SiMe_3): Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, 462. The enolic hydrogen in $Cp_2Zr(COCHPh_2)R$ should be quite acidic. In view of this and the carbanionic nature of group 4 transition-metal-bound alkyl groups, it is probable that this complex is produced by a mechanism similar to that discussed below. (b) Messerle, L. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1979.

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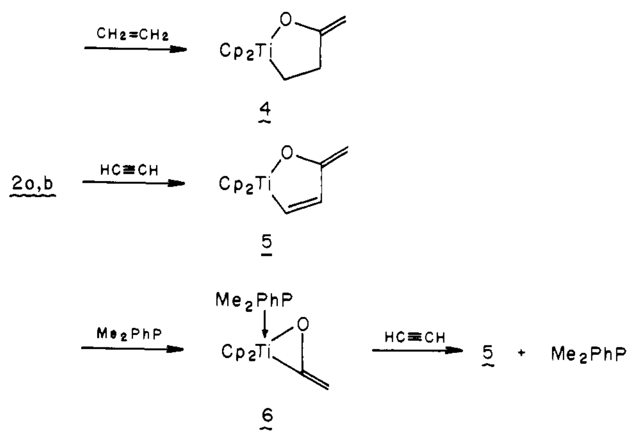
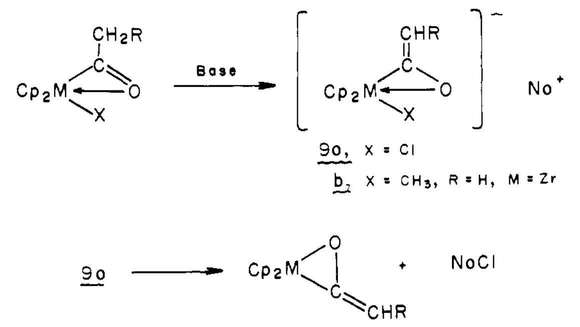
(8) ^{1}H NMR (C_6D_6): **2a** δ 3.36 (s, 1 H), 4.19 (s, 1 H), 5.99 (s, 10 H); **2b** δ 3.88 (d, *J* = 1.5 Hz, 1 H), 4.85 (d, *J* = 1.5 Hz, 1 H), 5.66 (s, 10 H). IR (KBr) **2a** 1610 cm^{-1}; **2b** 1610 cm^{-1}.

Scheme I

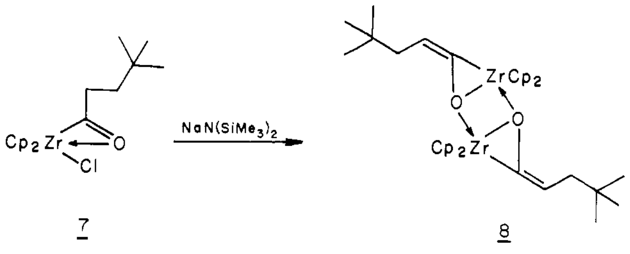


Scheme II



V,[2] and Zr.[3a] Furthermore, both isomers are converted cleanly to the starting acyl **1** on treatment with 1 equiv of HCl gas in toluene at -50 °C. Complex **2a** reacts readily at room temperature with ethylene (ca. 1 atm, C_6D_6) to give purple **4** (Scheme I) and with acetylene to form green **5**.[9,10] The same products are formed from **2b**, although much more slowly. Complex **2a** reacts rapidly with Me_2PPh to form adduct **6**, which is sparingly soluble in ether but highly soluble in benzene.[11] This yellow complex reacts rapidly with acetylene to produce **5**. Preparation of ^{13}C-enriched **2a** and **2b**[12] shows similar ^{13}C NMR shifts (220 and 197 ppm, respectively) for these isomers in the range between that of titanium acyl complexes[13] (ca. 300 ppm) and enolates[14] (ca. 170 ppm). It is likely that **2a** and **2b** exist in oligomeric forms ($n > 1$) and differ in their mode of aggregation. Attempts to obtain diffractable crystals are in progress.

The generality of the dehydrohalogenation is illustrated by the reaction of the zirconium acyl **7**[7b] with $NaN(SiMe_3)_2$ in toluene at room temperature to give the remarkably stable dimer **8**. Although ketene **8** affords **7** on reaction with HCl, it is inert toward a variety of reagents, including ethylene and acetylene. The ^1H and ^{13}C NMR spectra[15] of **8** are similar with those of **2a** and **2b**. The neopentyl group is assumed to occupy the sterically less crowded exo position. Monitoring the formation of **8** by NMR reveals no evidence of isomeric structures or intermediates. The importance of dimerization as a factor in the low reactivity of **8** has been demonstrated by preparation of highly soluble, monomeric decamethylzirconocene derivatives that undergo a number of facile reactions.[16]



The dehydrohalogenation of these chloroacyl complexes may proceed in a stepwise or concerted manner (Scheme II). The feasibility of the anionic intermediate **9a** and the acidic nature of the α protons in these group 4 acyl complexes is established by the deprotonation of $Cp_2Zr(COCH_3)CH_3$[17] with $NaN(SiMe_3)_2$. The reaction in ether is rapid at -30 °C and the white salt **9b**·Et_2O precipitates in high yield.[18] Alkylation of this anion with methyl iodide in tetrahydrofuran produces $Cp_2Zr(COCH_2CH_3)CH_3$[19] as the sole product upon mixing at room temperature.

We have demonstrated that this route can be used to generate a variety of ketene complexes that show a range of reactivities. Their use as models for catalytic intermediates as well as reagents for organometallic and organic synthesis is under further study.

Acknowledgment. We gratefully acknowledge the financial support of the Department of Energy and the helpful suggestions of T. R. Howard.

Registry No. 1, 66320-88-5; **1**-^{13}C, 82808-25-1; **2a**, 82808-16-0; **2a**-^{13}C, 82808-24-0; **4**, 82808-17-1; **5**, 82808-18-2; **6**, 82808-19-3; **7**, 82808-20-6; **8**, 82808-21-7; **9b**, 82808-22-8; $Cp_2Zr(COCH_2CH_3)CH_3$, 82808-23-9; $Cp_2Zr(COCH_3)CH_3$, 60970-97-0; $CH_2{=}CH_2$, 74-85-1; $HC{\equiv}CH$, 74-86-2; Me_2PhP, 672-66-2; CH_2PPh_3, 3487-44-3; $NaN(SiMe_3)_2$, 1070-89-9.

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(9) **4**: ^1H NMR (C_6D_6) δ 1.92 (t, J = 8.2 Hz, 2 H), 3.63 (t, J = 8.2 Hz, 2 H), 3.86 (s, br, 2 H), 5.83 (s, 10 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 52.5, 53.0, 78.2, 115.3, 169.9; IR (C_6D_6) 1628 cm^{-1}. Acidolysis (HCl gas, C_6D_6) gives 2-butanone in 50% yield (NMR, GC). **5**: ^1H NMR (C_6D_6) δ 4.00 (s, 1 H), 4.04 (s, br, 1 H), 5.84 (s, 10 H), 6.15 (d, J = 8.8 Hz, 1 H), 6.97 (d, J = 8.8 Hz, 1 H).

(10) (a) $(Cp_2TiOCCPh_2)_2$ adds Ph_2CCO to give $Cp_2TiOC(CPh_2)OC(CPh_2)$; ref 2. However, $CpMn(CO)_2OCCPh_2$, an η^2(C,C)-bound ketene complex, reacts with ethylene to give $CpMn(CO)_2(C_2H_4)$ and free Ph_2CCO; ref 4a. (b) Metal–olefin complexes react with a variety of carbon–carbon and carbon–heteroatom multiple bonds to form metallacyclopentanes: McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558. Cohen, S. E. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1982. (c) A zirconium aldehyde complex and a tantalum ketone complex have been found to react with olefins to form metallaoxocyclopentanes: Roddick, D. M.; Bercaw, J. E., personal communication. Mayer, J. M. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1983.

(11) $Cp_2Ti(OCCH_2){\cdot}P(CH_3)_2Ph$ (**6**): ^1H NMR (C_6D_6) δ 1.11 (s, br, 6 H), 3.99 (s, 1 H), 5.26 (s, 10 H), 5.36 (s, 1 H), 7.08 (m, 2 H), 7.40 (m, 3 H). Solutions of this complex slowly decompose at room temperature.

(12) ^{13}C-enriched **1** was prepared by stirring a toluene solution of Cp_2TiCH_3Cl under 40 psi of carbon monoxide (99% ^{13}C-enriched, Monsanto Research Corp., Mound Labs) at 50 °C for 12 h. The product was collected by filtration and washed with hexane. Ketene complex **2a**-^{13}C was obtained by treatment of **1**-^{13}C with $NaN(SiMe_3)_2$ in ether at -30 °C. The red solid was washed with ether. **2b**-^{13}C is prepared by stirring a suspension of **2a**-^{13}C in benzene at room temperature and collecting the yellow precipitate that forms. ^1H NMR (C_6D_6): **2a**-^{13}C δ 3.40 (s, br, 1 H), 4.18 (d, $^2J_{HC}$ = 10.7 Hz, 1 H), 5.99 (s, 10 H); **2b**-^{13}C δ 3.87 (dd, J_{HH} = 1.5 Hz, $^2J_{HC}$ = 1.0 Hz, 1 H), 4.84 (dd, J_{HH} = 1.5 Hz, $^2J_{HC}$ = 11.2 Hz, 1 H), 5.66 (s, 10 H). ^{13}C NMR (C_6D_6) **2a**-^{13}C δ 220.4 (solubility too low to measure coupling in gated spectrum); **2b** δ 197.3 (dd, $^2J_{CH}$ = 11.4, 1.2 Hz).

(13) Erker, G.; Rosenfeldt, F. *Angew. Chem., Int. Ed. Engl.* **1978**, 605.

(14) Stille, J. R.; Grubbs, R. H., to be submitted for publication.

(15) Dimer **8**: ^1H NMR (C_6D_6) δ 1.17 (s, 9 H), 2.29 (d, J = 7.3 Hz, 2 H), 5.68 (t, J = 7.3 Hz, 1 H), 5.88 (s, 10 Hz); ^{13}C NMR (C_6D_6) δ 30.0 (q, $^1J_{CH}$ = 124 Hz), 31.4 (s), 44.6 (d, $^1J_{CH}$ = 127 Hz), 99.9 (dt, $^1J_{CH}$ = 146 Hz, $^2J_{CH}$ = 6 Hz), 109.0 (d, $^1J_{CH}$ = 172 Hz), 187.8 (dt, $^2J_{CH}$ = 8 Hz, $^3J_{CH}$ = 8 Hz); IR (KBr) 1620 cm^{-1}. Molecular weight by cryoscopy in benzene 652, calcd 667.

(16) The complex $(\eta^5\text{-}C_5Me_5)_2Zr(OCCH_2){\cdot}$pyr has been isolated and found to exhibit reactivity similar with that of **2a**. The chemistry of this and a number of related complexes is currently under investigation: Moore, E. J.; Straus, D. A.; Bercaw, J. E.; Grubbs. R. H.

(17) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946.

(18) $Cp_2Zr(COCH_2)CH_3Na{\cdot}Et_2O$: ^1H NMR (THF-d_8) δ -0.68 (s, 3 H), 1.10 (t, J = 7 Hz, 6 H), 3.37 (q, J = 7 Hz, 4 H), 3.64 (d, J = 2 Hz, 1 H), 4.55 (d, J = 2 Hz, 1 H), 5.43 (s, 10 H); IR (Nujol) 1575 cm^{-1}. The Et_2O may be exchanged with THF to give $Cp_2Zr(COCH_2)CH_3Na{\cdot}2THF$; ^{13}C NMR (THF-d_8) δ 8.8 (q, $^1J_{CH}$ = 115 Hz), 74.3 (t, $^1J_{CH}$ = 146 Hz), 105.2 (d, $^1J_{CH}$ = 170 Hz), 199.8 (t, $^2J_{CH}$ = 9 Hz).

(19) $Cp_2Zr(COCH_2CH_3)CH_3$: ^1H NMR (C_6D_6) δ 0.53 (s, 3 H), 1.05 (t, J = 7 Hz, 3H), 2.55 (q, J = 7 Hz, 2 H), 5.32 (s, 10 H); IR (KBr) 1530 cm^{-1}. Anal. Calcd for $C_{14}H_{18}OZr$: C, 57.29; H, 6.18. Found: C, 57.09; H, 6.16.