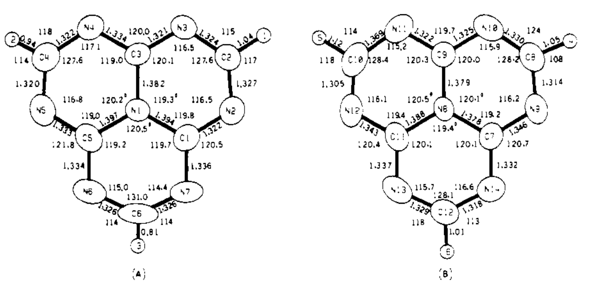

**Figure 1.** Bond lengths and bond angles for the two crystallographically independent molecules, A and B, of tri-*s*-triazine (**1**). The separate esd values are given in the supplementary material. For the bond lengths and angles not involving H, the esd values are in the range 0.003–0.005 Å and 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, $\delta$ 7.3, for N—CH═N—Ar model, *N,N*-dimethyl-*N′*-phenylformamidine,[29] and smaller than the $\delta$ 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.

**Acknowledgment.** This work was supported by Research Grant No. CHE-81-21796 from the National Science Foundation.

**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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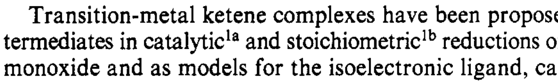
Transition-metal ketene complexes have been proposed as intermediates in catalytic[1a] and stoichiometric[1b] reductions of carbon monoxide and as models for the isoelectronic ligand, carbon dioxide.[2] Complexes that contain highly stabilized ketene fragments, especially diphenylketene, have generally (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 $\eta^2$-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



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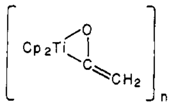
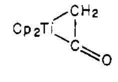
(1)

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 $\eta^2$(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 $\eta^2$(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** $\delta$ 3.36 (s, 1 H), 4.19 (s, 1 H), 5.99 (s, 10 H); **2b** $\delta$ 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$^{-1}$.

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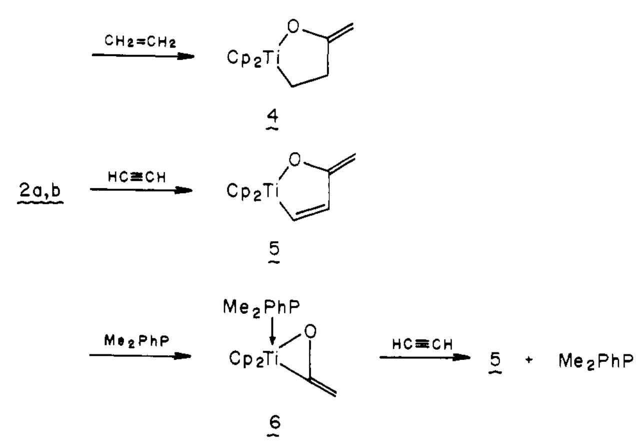
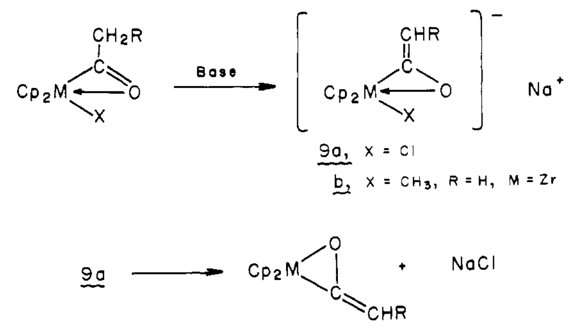
Scheme I

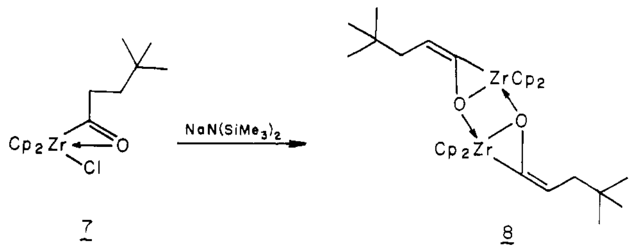


Scheme II



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≡CH, 74-86-2; $Me_2PhP$, 672-66-2; $CH_2PPPh_3$, 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 $\eta^2$(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.