

Dr. P. Ochsner, Givaudan SA, for a generous sample of (+)-longifolene. (a)

References and Notes

- (1) For recent reviews, see P. de Mayo, *Acc. Chem. Res.*, **4**, 41 (1971); (b) H. Meier in "Houben-Weyl, Methoden der Organischen Chemie," Vol 4/5b, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1975, p 924.
- (2) We know only of the related photoaddition-hydrolysis sequence of alkenylamino- and alkenyloxy-2-cyclohexenones: Y. Tamura, Y. Kita, H. Ishibashi, and M. Ikeda, *Tetrahedron Lett.*, 1977 (1972); *J. Chem. Soc., Chem. Commun.*, 101 (1973).
- (3) For the structure elucidation of (+)-longifolene (11), a constituent of the essential oil of many *Pinus* species, see (a) G. Ourisson, *Bull. Soc. Chim. Fr.*, 895 (1955), and references cited therein; (b) J.-C. Thierry and R. Weiss, *Tetrahedron Lett.*, 2663 (1969).
- (4) For successful total syntheses of longifolene, see (a) E. J. Corey, M. Ohno, R. B. Mitra, and P. Vatakcherry, *J. Am. Chem. Soc.*, **86**, 478 (1964); (b) J. E. McMurry and S. J. Isser, *Ibid.*, **94**, 7132 (1972); (c) R. A. Volkmann, G. C. Andrews, and W. S. Johnson, *Ibid.*, **97**, 4777, (1975). Unsuccessful attempts are cited in ref 4b; see also G. Brieger, *J. Am. Chem. Soc.*, **85**, 3783 (1963).
- (5) For longifolene as a subject for synthetic planning and strategy, see ref 4a and E. J. Corey, W. J. Howe, H. W. Orf, D. A. Pensak, and G. Petersson, *J. Am. Chem. Soc.*, **97**, 6116 (1975).
- (6) The acid chloride 2 was prepared from the carboxylic acid 1 (SOCl₂, reflux, 1 h, 90%) which is accessible from cyclopentadiene in 52% overall yield: S. Branner-Jørgensen and A. Berg, *Acta. Chem. Scand.* **20**, 2192 (1966).
- (7) IR, ¹H NMR, and mass spectra are in full agreement with the assigned structure.
- (8) S. Hünig and W. Lendle, *Chem. Ber.*, **93**, 909 (1960).
- (9) The spectral data did not permit the rigorous exclusion of the presence of the corresponding exocyclic enol esters; however, this point appears to be of little relevance as far as the subsequent photoaddition to 5 is concerned. It can thus be expected that light-induced isomerization of the exocyclic (*E*)- and (*Z*)-enol esters, followed by spontaneous 1,5-acyl migration of the latter, gives an equilibrium concentration of 4; for a close analogy, see E. Wachsen and K. Hartke, *Chem. Ber.*, **108**, 683 (1975). 4 should then be selectively trapped by photoaddition (4 → 5) owing to the endocyclic nature of the conjugated olefinic bond which is also favorably placed with respect to the isolated double bond.¹⁰
- (10) For a review on photoadditions of alicyclic conjugated enones to olefins, see P. E. Eaton, *Acc. Chem. Res.*, **1**, 50 (1968).
- (11) The ¹³C NMR spectrum agrees fully with the assigned structure.
- (12) Although the conversion of 12 into 10 can be envisaged by approaches involving a fragmentation step,^{4b} the preparation and selective functionalization of 6, as described below, provides a more direct route to longifolene.
- (13) The longifolene framework is numbered here as in *Chemical Abstracts*.
- (14) J.-M. Conia and J.-C. Limasset, *Bull. Soc. Chim. Fr.*, 1936 (1967).
- (15) J. M. Denis, C. Girard, and J. M. Conia, *Synthesis*, 549 (1972).
- (16) (a) C. W. Woodworth, V. Buss, and P. v. R. Schleyer, *Chem. Commun.*, 569 (1968). (b) C. Gröger and H. Musso, *Angew. Chem.*, **88**, 415 (1976); *Angew. Chem. Int. Ed. Engl.*, **15**, 373 (1976).
- (17) We thank Mr. K. Bättig for carrying out these comparison studies.
- (18) Reported by one of us (W.O.) at the Chemische Gesellschaft Zürich on Dec 7, 1977.

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Metal Carbene Chemistry. Formation and Reactions of (η^5 -C₅H₅)Fe(CO)_n(CH₂)⁺ (*n* = 1, 2) in the Gas Phase by Ion Cyclotron Resonance Spectroscopy

Sir:

It is often possible to prepare and characterize species in the gas phase whose exceptional reactivity leads only to a fleeting existence in solution, where their presence is more often inferred than demonstrated. Transition metal carbenes are an important class of intermediates for which this is the case.¹⁻³ We wish to report studies, using the techniques of ion cyclotron resonance spectroscopy,⁴ of the formation and reactions of several of these interesting species in the gas phase.⁵

Jolly and Pettit² report the attempted preparation of (η^5 -C₅H₅)Fe(CO)₂(CH₂)⁺BF₄⁻ by cleavage of the ether (η^5 -C₅H₅)Fe(CO)₂(CH₂OCH₃) with HBF₄. While the cationic complex could not be isolated, its presence was postulated to

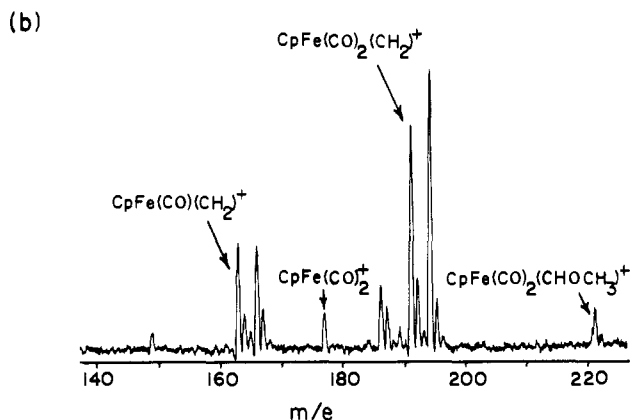
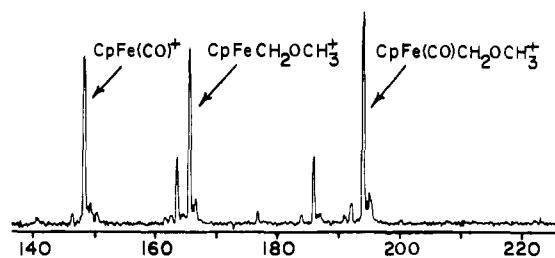
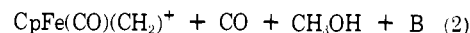
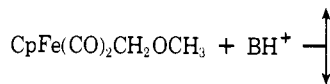


Figure 1. (a) Partial mass spectrum of CpFe(CO)₂CH₂OCH₃ observed in the drift mode at 10⁻⁷ Torr with 70-eV electron energy. (b) Spectrum of products observed after 30-ms reaction time in a mixture of CpFe(CO)₂CH₂OCH₃ (10⁻⁷ Torr) and CH₄ (10⁻⁶ Torr) ionized by a 10-ms 70-eV electron beam pulse. Several ionic species pertinent to the discussion in the text are identified.

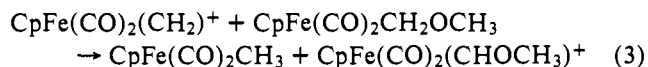
account for methylene transfer to produce norcarane from cyclohexene and *cis*- and *trans*-1,2-dimethylcyclopropane from *cis*- and *trans*-2-butene, respectively. This system struck us as ideally suited for acidic ionization by proton transfer in the gas phase to produce the isolated CpFe(CO)₂(CH₂)⁺ ion.

The electron impact mass spectrum of CpFe(CO)₂CH₂OCH₃⁶ (over the range of 12 to 70 eV) shows major fragment ions CpFe(CO)CH₂OCH₃⁺ and CpFe(CO)₂CH₂OCH₃⁺, arising from sequential loss of CO; the parent ion is not observed. The ions CpFe(CO)₂(CH₂)⁺, CpFe(CO)(CH₂)⁺, and CpFe(CO)₂(CHOCH₃)⁺ are present, but in very low abundance.

The ions CpFe(CO)₂(CH₂)⁺ and CpFe(CO)(CH₂)⁺ show dramatic increase in abundance when the acids BH⁺ = NH₄⁺, C₂H₅⁺, CH₅⁺, and H₃⁺⁷ are used as protonation agents (reactions 1 and 2). The spectra shown in Figure 1 contrast the

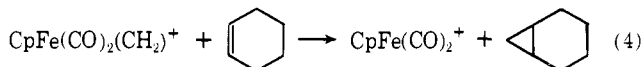


abundant ionic species observed with 70-eV electron impact (Figure 1a) and with the addition of CH₄ (Figure 1b, reaction time 30 ms⁸). Not unexpectedly, as the exothermicity of reaction 1 increases over the series BH⁺ = NH₄⁺, C₂H₅⁺, CH₅⁺, H₃⁺,⁴ there is a concomitant increase in the abundance of CpFe(CO)(CH₂)⁺ relative to CpFe(CO)₂(CH₂)⁺. Double resonance⁹ identifies the carbene CpFe(CO)₂(CHOCH₃)⁺ being produced at longer times or higher pressures, mainly from CpFe(CO)₂(CH₂)⁺, reaction 3.¹⁰

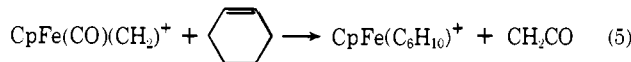


These results illustrate the ease with which metal carbene complexes can be generated in the gas phase.¹¹ The following describes some interesting observations on the reactivity of these species.¹²

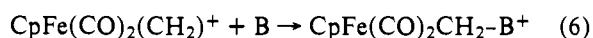
Addition of cyclohexene results in the production of $\text{CpFe}(\text{CO})_2^+$ from $\text{CpFe}(\text{CO})_2(\text{CH}_2)^+$. By analogy to the



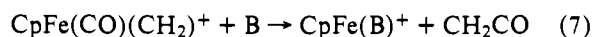
solution chemistry, this is attributed to reaction 4.¹³ The ion $\text{CpFe}(\text{CO})(\text{CH}_2)^+$ does *not* react with cyclohexene to yield $\text{CpFe}(\text{CO})^+$. Rather, reaction 5 is observed, in which cyclohexene displaces ketene from the metal center.



A consistent pattern of reactivity is observed in the interaction of $\text{CpFe}(\text{CO})_n(\text{CH}_2)^+$ ($n = 1, 2$) with the n -donor bases $\text{B} = \text{NH}_3, \text{CH}_3\text{CN},$ and CD_3CDO . Each of these bases adds to $\text{CpFe}(\text{CO})_2(\text{CH}_2)^+$ to give $\text{CpFe}(\text{CO})_2\text{CH}_2\text{-B}^+$,¹⁴ reaction 6.¹⁵



No ligand displacement reactions are observed with $\text{CpFe}(\text{CO})_2(\text{CH}_2)^+$. In contrast to this behavior, these bases react with $\text{CpFe}(\text{CO})(\text{CH}_2)^+$ by displacement of ketene, reaction 7.



Thermoneutral exchange of carbon monoxide was monitored using ¹³CO. The ions $\text{CpFe}(\text{CO})^+$ and $\text{CpFe}(\text{CO})_2^+$ readily exchange CO. Neither $\text{CpFe}(\text{CO})_2(\text{CH}_2)^+$ nor $\text{CpFe}(\text{CO})(\text{CH}_2)^+$ exchange CO, and processes analogous to reactions 6 and 7 are not observed.

The following conclusions emerge from the above results. (1) The reactions of $\text{CpFe}(\text{CO})_2(\text{CH}_2)^+$ in the gas phase, specifically methylene transfer to cyclohexene, hydride abstraction to yield $\text{CpFe}(\text{CO})_2\text{CH}_3$, and addition of n -donor bases to the methylene carbon, are entirely in accord with the postulated solution reactions of this species^{2,3} and consistent with its formulation as a metal carbene. (2) The novel complex $\text{CpFe}(\text{CO})(\text{CH}_2)^+$ does not exhibit the carbene chemistry of the dicarbonyl species. Reaction of both cyclohexene and n -donor bases results in displacement of CH_2CO from the metal center, strongly suggesting the formulation of this species as a metal ketene complex. The question arises as to whether ketene is present as a structural moiety in the complex $\text{CpFe}(\text{CO})(\text{CH}_2)^+$ or whether it is formed in the intermediate which results from binding a π - or n -donor base to the coordinately unsaturated metal center. In the latter case, the equivalence of the two coordinated CO ligands in the reaction of ¹³CO with $\text{CpFe}(\text{CO})(\text{CH}_2)^+$ would allow for incorporation of labeled ligand in the complex. Failure to observe this is evidence for the formulation of the complex as $\text{CpFe}(\text{CH}_2\text{CO})^+$, I, a metal ketene complex, rather than the metal carbene, II.¹⁶



The extension of the present work to other systems is in progress. We are particularly interested in identifying the molecular properties which lead to differing reaction pathways (methylene addition to form cyclopropanes vs. olefin metathesis) and obtaining quantitative metal-carbene bond energies.¹⁷

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References and Notes

- F. D. Mango and I. Dvoretzky, *J. Am. Chem. Soc.*, **88**, 1654 (1966); M. R. Collier, B. M. Kingston, and M. F. Lappert, *Chem. Commun.*, 1498 (1970); N. J. Cooper and M. L. H. Green, *J. Chem. Soc.*, 761 (1974); C. P. Casey, T. J. Burkhardt, C. A. Bunnell, and J. C. Calabrese, *J. Am. Chem. Soc.*, **99**, 2127 (1977), and references therein; C. P. Casey, L. D. Albin, and T. J. Burkhardt, *ibid.*, **99**, 2533 (1977), and references therein; P. G. Gassman and T. H. Johnson, *ibid.*, **98**, 6055 (1976), and references therein; P. G. Gassman and T. H. Johnson, *ibid.*, **98**, 6057 (1976); P. G. Gassman and T. H. Johnson, *ibid.*, **99**, 622 (1977).
- P. W. Jolly and R. Pettit, *J. Am. Chem. Soc.*, **88**, 5044 (1966).
- M. L. H. Green, M. Ishaq, and R. N. Whiteley, *J. Chem. Soc. A*, 1508 (1967).
- J. L. Beauchamp, *Ann. Rev. Phys. Chem.*, **22**, 527 (1971).
- For related studies of transition metal complexes, see M. S. Foster and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 4808 (1975); M. S. Foster and J. L. Beauchamp, *ibid.*, **97**, 4814 (1975); R. R. Corderman and J. L. Beauchamp, *Inorg. Chem.*, **15**, 665 (1976); R. R. Corderman and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 3998 (1976); R. R. Corderman and J. L. Beauchamp, *ibid.*, **98**, 5700 (1976); R. R. Corderman and J. L. Beauchamp, *Inorg. Chem.*, **16**, 3135 (1977); R. R. Corderman and J. L. Beauchamp, *ibid.*, **17**, 68 (1978).
- $\text{CpFe}(\text{CO})_2\text{CH}_2\text{OCH}_3$ was prepared similarly to the method of Green et al.³ and chromatographed on alumina, eluting with petroleum ether-THF (19:1). The only impurity detected in the mass spectrum is a small amount of ferrocene, the molecular ion of which is evident at m/e 186 in Figure 1a.
- High temperature (100 °C) hydrogenation of several carbene ligands is reported by C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, **99**, 1651 (1977). The acid H_3^+ from electron impact ionization of H_2 was typically used to produce $\text{CpFe}(\text{CO})_2(\text{CH}_2)^+$ and $\text{CpFe}(\text{CO})(\text{CH}_2)^+$. No reaction of H_2 with these species was observed, even though the formation of CH_4 is very likely to be an exothermic process.
- T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instr.*, **43**, 509 (1972).
- All of the reactions described in the text are identified by double-resonance techniques, described in ref 4 and 8. In this case, a decrease in the abundance of $\text{CpFe}(\text{CO})_2(\text{CHOCH}_3)^+$ is seen on irradiating $\text{CpFe}(\text{CO})_2(\text{CH}_2)^+$. Neutrals are not detected.
- $\text{CpFe}(\text{CO})_2\text{CH}_3$ was isolated as a product from the reaction of HBF_4 and $\text{CpFe}(\text{CO})_2\text{CH}_2\text{OCH}_3$ in solution,² but there is no indication of the hydride source.
- In ICR experiments ions can be detected in trapped ion experiments several seconds after they are formed. The lifetime of the carbenes generated in this study toward unimolecular dissociation is in excess of this time scale. The carbenes produced are highly reactive in bimolecular encounters. It is this exceptional reactivity that precludes their observation in solution.
- In ion cyclotron resonance experiments, ions are detected in a time short compared with the time between collisions and reaction processes are not perturbed by the observing oscillator. Reactions identified are exothermic or thermoneutral processes which proceed without activation energies and have significant rate constants with thermal energy ions; endothermic processes are observed only when ions are accelerated with an irradiating oscillator. This is described more completely in ref 4.
- Because of the complexity of the reaction scheme, an accurate reaction rate constant was not determined for the methylene transfer process 4. However, we estimate a rate constant of $\sim 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; reaction occurs on approximately one out of ten collisions.
- Addition of a base has been seen with other carbenes. See, for example, A. Sanders, L. Cohen, W. P. Giering, D. Kennedy, and C. V. Magatti, *J. Am. Chem. Soc.*, **95**, 5430 (1973), and F. R. Kreissl and W. Heid, *J. Organomet. Chem.*, **88**, C10 (1975).
- Double resonance indicates in the case of NH_3 that the product $\text{CpFe}(\text{CO})_2\text{CH}_2\text{NH}_3^+$ also results directly from reaction of NH_4^+ with $\text{CpFe}(\text{CO})_2\text{CH}_2\text{OCH}_3$. This can be formulated as a nucleophilic displacement reaction in which NH_3 displaces CH_3OH following proton transfer from NH_4^+ to the complex. For discussion of related processes, see D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *J. Am. Chem. Soc.*, **92**, 7484 (1970).
- To our knowledge no unsubstituted metal ketene complexes have been reported. A diphenylketene complex of platinum, $(\text{Ph}_2\text{P})_2\text{Pt}(\text{Ph}_2\text{CCO})$, has been prepared, where the ketene is coordinated at the $\text{C}=\text{C}$ bond: K. Schorpp and W. Beck, *Z. Naturforsch. B*, **28**, 738 (1973). The complex $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ gives $[\text{Rh}(\text{CO})(\text{CPh}_2)\text{Cl}]_n$ upon refluxing with diphenylketene, suggesting an initial coordination through the $\text{C}=\text{C}$ bond: P. Hong, N. Nishih, K. Sonogashira, and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, 993 (1972).
- For example, reaction 4 bounds $D(\text{CpFe}(\text{CO})_2^+ - \text{CH}_2) \leq 91 \text{ kcal/mol}$.

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