for Mass Spectrometry for mass spectra and the Southern California Regional NMR Facility for the 500-MHz NMR spectra (NSF Grant No. CHE79-16324). W.R. is a recipient of a Fulbright Fellowship. We also acknowledge Beverly Scher, who under an NSF–URP grant the summer of 1980 carried out several initial experiments on this project.

Registry No. (*Z*)-**3** (R = Bu), 83043-56-5; (*Z*)-**3** (R = *t*-Bu), 83043-68-9; (*Z*)-**3** (R = Ph), 83043-69-0; (E)-(R^*,R^*)-**4** (R = SOPh), 83043-57-6; (E)-(R^*,S^*)-**4** (R = SOPh), 83043-64-5; **4** (R = Bu), 83043-65-6; **4** (R = *t*-Bu), 83043-66-7; **4** (R = Ph), 83043-67-8; (*E*)-**5**, 17974-59-3; (*Z*)-**6a**, 83060-53-1; (*Z*)-**6b**, 83043-58-7; **7a**, 83043-59-8; **8**, 83043-60-1; **9**, 83043-61-2; **10a**, 83043-62-3; **10b**, 83113-64-8; **10c**, 83043-63-4.

Supplementary Material Available: Selected spectral data (^{1}H NMR, ^{13}C NMR, IR, and/or UV) for **4** (R = SOPh, *n*-Bu, *t*-Bu, Ph, H), **6a**, **6b**, **7a**, **7b**, **7c**, **8**, **9**, **10a**, **10b**, and **10c** (6 pages). Ordering information is given on any current masthead page.

Chlorophyll *a* Sensitized Trans–Cis Photoisomerization of *all-trans*-β-Carotene

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Carotenoids are widely distributed in nature,[1,2] and protection of the various organisms against photodestruction seems to be a general function of the carotenoids.[3,4] In photosynthetic organisms, the carotenoids also serve as accessory pigments in the light-harvesting process.[5-7] The excited triplet states of carotenoids are important intermediates in the protective reactions, and consequently the triplet states of carotenoids have been the subject of numerous investigations. Recently the excited triplet states of *all-trans*-β-carotene and other polyenes have been studied by time-resolved resonance Raman spectroscopy by us[8-11] and by Dallinger et al.[12,13] Although the experimental results of the two groups are similar, the interpretations suggested are different, implying either substantial twisting around double bonds[8,9] or essentially no changes in geometry[13] upon electronic excitation. Theoretical calculations[14-16] and extrapolation of the results obtained with shorter polyenes[17] support the former suggestion, while the apparent stability of *all-trans*-β-carotene toward trans–cis isomerization under conditions where the triplet state is produced[13,18-25] supports the latter. Prompted by these conflicting reports and by the possible importance of *cis*-carotenoids in photosynthetic organisms,[26-29] we have initiated a study of the triplet state chemistry of *all-trans*-β-carotene (all-trans) and related compounds.

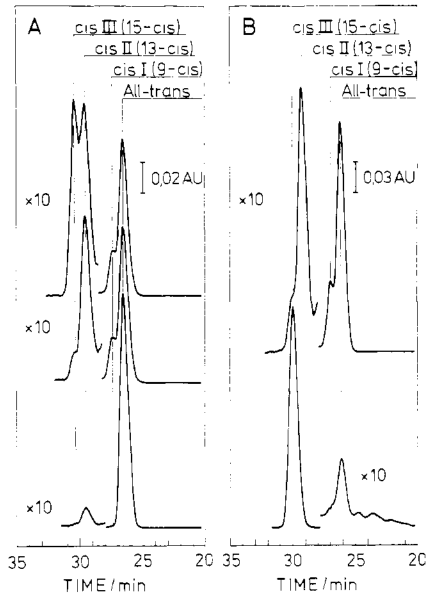

Figure 1. Chromatograms of β-carotene before and after Chl *a* sensitized photoisomerization. The Ar-saturated solutions all contained 2×10^{-5} M Chl *a*. Analysis wavelength 440 nm, other conditions specified in text. (A) Lower trace, 10^{-3} M all-trans before illumination; middle trace, the same solution after illumination for 15 min with λ >610 nm; upper trace, illuminated solution mixed with authentic 15-*cis*-β-carotene. Samples diluted ten times with acetone before HPLC. (B) Lower trace, 10^{-3} M 15-cis before illumination; upper trace, 10^{-3} M 15-cis after illumination for 15 min with λ >610 nm. Samples diluted five times with acetone before HPLC.

Table I. Spectral Data of Photoisomers[a]

	absorbance max, nm	$\epsilon_{max}/\epsilon_{341}$
all-trans	482, *455*, ~434 sh	20.69 ± 0.32
cis I (9-cis)	476, *450*, ~430 sh, 341	9.40 ± 0.58
cis II (13-cis)	474, *448*, ~430 sh, 341	2.16 ± 0.05
cis III (15-cis)	475, *452*, ~430 sh, 341	1.62 ± 0.18
15-cis[b]	475, *452*, ~430 sh, 341	1.65

[a] Solvent, 88% acetone/12% H_2O; maximum is in italics; sh, shoulder. Spectra were taken in a flow-cell after HPLC. [b] Sample of authentic 15,15′-*cis*-β-carotene.

Illumination with red light (λ >610 nm, 25-mm H_2O filter, 89 mW/cm^2) of a 10^{-3} M solution of all-trans[30] in Ar-saturated

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(1) O., Isler, Ed. "Carotenoids"; Birkhäuser Verlag: Basel, 1971.

(2) Goodwin, T. W. "The Biochemistry of the Carotenoids"; Chapman and Hall: London, 1980.

(3) Krinsky, N. I. *Philos. Trans. R. Soc. London, Ser. B* **1978**, *B284*, 581-590.

(4) Krinsky, N. I. *Pure Appl. Chem.* **1979**, *51*, 649-660.

(5) Cogdell, R. J. *Philos. Trans. R. Soc. London, Ser. B* **1978**, *B284*, 569-579.

(6) Goedheer, J. C. *Biochim. Biophys. Acta* **1959**, *35*, 1-8.

(7) Goedheer, J. C. *Biochim. Biophys. Acta* **1969**, *172*, 252-265.

(8) Jensen, N.-H.; Wilbrandt, R.; Pagsberg, P. B.; Sillesen, A. H.; Hansen, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 7441-7444.

(9) Wilbrandt, R.; Jensen, N.-H. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 508-511.

(10) Wilbrandt, R.; Jensen, N.-H. *J. Am. Chem. Soc.* **1981**, *103*, 1036-1041.

(11) Atkinson, G. H.; Pallix, J. B.; Freedman, T. B.; Gilmore, D. A.; Wilbrandt, R. *J. Am. Chem. Soc.* **1981**, *103*, 5069-5072.

(12) Dallinger, R. F.; Guanci, J. J.; Woodruff, W. H.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1355-1357.

(13) Dallinger, R. F.; Farquharson, S.; Woodruff, W. H.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1981**, *103*, 7433-7440.

(14) Baird, N. C.; West, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 4427-4432.

(15) Warshel, A.; Karplus, M. *J. Am. Chem. Soc.* **1974**, *96*, 5677-5689.

(16) Ohmine, I.; Morokuma, K. *J. Chem. Phys.* **1980**, *73*, 1907-1917.

(17) Saltiel, J.; Charlton, J. L. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 25-89.

(18) Claes, H.; Nakayama, T. O. M. *Nature (London)* **1959**, *183*, 1053.

(19) Claes, H. *Biochem. Biophys. Res. Commun.* **1960**, *3*, 585-590.

(20) Claes, H. *Z. Naturforschg., Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1961**, *16B*, 445-454.

(21) Mathis, P.; Kleo, J. *Photochem. Photobiol.* **1973**, *18*, 343-346.

(22) Foote, C. S.; Chang, Y. C.; Denny, R. W. *J. Am. Chem. Soc.* **1970**, *92*, 5218-5219.

(23) Krinsky, N. I. "The Survival of Vegetative Microbes"; Gray, T. G. R., Postgate, J. R.; Eds.; Cambridge University Press: Cambridge, 1976, pp 209-239.

(24) Farmilo, A.; Wilkinson, F. *Photochem. Photobiol.* **1973**, *18*, 447-450.

(25) Rodgers, M. A. J.; Bates, A. L. *Photochem. Photobiol.* **1980**, *31*, 533-537.

(26) Boucher, F.; Van der Rest, M.; Gingras, G. *Biochim. Biophys. Acta* **1977**, *461*, 339-357.

(27) Lutz, M.; Agalidis, I.; Hervo, G.; Cogdell, R. J.; Reiss-Husson, F. *Biochim. Biophys. Acta* **1978**, *503*, 287-303.

(28) Agalidis, I.; Lutz, M.; Reiss-Husson, F. *Biochim. Biophys. Acta* **1980**, *589*, 264-274.

(29) Koyama, Y.; Kito, M.; Takii, T.; Saiki, K.; Tsukida, K.; Yamashita, J. *Biochem. Biophys. Acta* **1982**, *680*, 109-118.

(30) *all-trans-*β-Carotene (Sigma, type IV) was recrystallized four times from $CHCl_3/CH_3OH$. Chlorophyll *a* was extracted from spinach and purified by preparative reverse-phase HPLC. In some experiments Chl *a* obtained from Sigma was used. 15,15′-*cis*-β-carotene was supplied by Roche A/S. The sample used here contained ~2% all-trans.

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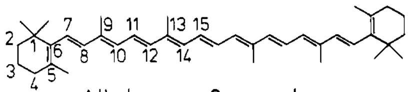
Table II. Distribution of Isomers (%)[a,b]

sample	all-trans	cis I (9-cis)	cis II (13-cis)	cis III (15-cis)
all-trans[c]	99.0–99.2	0	0.8–0.9	~0.1
all-trans (15, 30, 45 min)	69.3	20.4	8.5	1.8
all-trans (air sat.)	90.0	4.7	4.3	1.1
all-trans (O_2 sat.)	89.9	4.6	4.3	1.2
all-trans (without Chl *a*, λ >400 nm)	98.6	0	1.2	0.2
2×10^{-4} M all-trans (5, 15 min)	79.9	14.8	4.4	1.0
1×10^{-4} M all-trans (5 min)	82.4	13.1	3.8	0.8
1×10^{-4} M all-trans[d] (γ radiolysis)	82.9	11.9	3.9	1.3
15-cis	68.2	20.8	8.7	2.3
15-cis (O_2 sat.)	89.0	4.2	4.6	2.2

[a] Substrate, 10^{-3} M; solvent, 50% benzene/50% acetone; sensitizer, 2×10^{-5} M Chl *a*; λ >610 nm; Ar saturated; photolysis time, 15 min unless otherwise noted. Typical uncertainties on yields are ±0.5%. [b] HPLC analysis at 440 nm. Isomer distributions were calculated from corrected peak heights by assuming $\epsilon_{440}{}^{\text{trans}} = \epsilon_{440}{}^{\text{9-cis}} = \epsilon_{440}{}^{\text{13-cis}}$ and $\epsilon_{440}{}^{\text{trans}}/\epsilon_{440}{}^{\text{15-cis}} = 1.33 \pm 0.06$. The latter value was obtained from detector response as a function of the concentration of the isomers. [c] All-*trans*-β-carotene without photolysis. [d] Solvent, benzene; sensitizer, 2×10^{-2} M naphthalene; dose, 400 krad; Ar saturated.



All-trans-β-carotene

50% benzene/50% acetone (v/v) containing 2×10^{-5} M chlorophyll *a* (Chl *a*) and subsequent analysis of the samples by UV/vis absorption spectroscopy after proper dilution with acetone reveal only minor changes: blue-shift of $\lambda_{\max}$ from 455 to 453 nm along with a 3.5% decrease in maximum absorbance and a slight increase in absorbance around 340 nm. The absorbance at 440 nm was nearly unchanged. Analysis of the solutions by reversed-phase HPLC (4.6 × 250 mm Nucleosil $5C_{18}$; 88% acetone/12% H_2O, 1 mL/min) showed the formation of three new compounds, all of which had a higher retention than all-trans. Typical chromatograms are shown in Figure 1. Absorption spectra of the new fractions (blue-shifted $\lambda_{\max}$ and "cis-peak" around 340 nm) are typical for mono-cis isomers,[1,31-33] and on the basis of the increasing strength of the so-called cis peak at 341 nm in the sequence cis I–cis II–cis III (Figure 1 and Table I) we have assigned 9-cis, 13-cis, and 15-cis structures to these fractions.[33] The assignment of 15,15′-*cis*-β-carotene (15-cis) to cis III was confirmed by cochromatography of the illuminated sample with authentic[30] 15-cis, as shown in Figure 1.

Table II summarizes the isomer distribution after illumination or γ irradiation under various conditions. The values given in Table II represent the stationary states except in the case of the air- and oxygen-saturated solutions where the cis I (9-cis) isomer still increased slowly beyond 15 min of illumination. Complete mass balance with respect to all-trans and the cis isomers as well as Chl *a* was observed in the absence of oxygen. In the presence of oxygen, however, slow irreversible degradation (ca. 4% after 15 min) of the total amount of β-carotene (10^{-3} M) was observed during continuous illumination.

The amounts of the three isomers produced by sensitized photolysis of all-trans were all initially linearly dependent upon the illumination dose, indicating that they all are primary products originating from all-trans and not formed from each other by secondary isomerization. Illumination of Ar-saturated solutions of all-trans and 15-cis with red light (λ >610 nm) did not give detectable isomerization in the absence of Chl *a*. Even white light (λ >400 nm) had only a slight effect on all-trans under similar conditions as shown in Table II. The photoisomerization is thus dependent upon the presence of Chl *a*, and the mechanism involved must be transfer of triplet energy from Chl *a* to β-carotene[21] and subsequent isomerization of triplet β-carotene. Quenching of excited singlet Chl *a* (electron-transfer mechanism) by β-carotene is unimportant at the concentrations used in this study,[34] and quenching of triplet Chl *a* by β-carotene in an electron-transfer process is unlikely when the redox potentials are taken into consideration.[35-37]

Table III. Apparent Relative Quantum Yields of Photoisomerization[a]

	trans → 9-cis	trans → 13-cis	trans → 15-cis	15-cis → trans
Ar sat.	0.013	0.088	0.028	1.00
O_2 sat.	≤0.001	0.010	0.004	0.39

[a] HPLC analysis at 440 nm. Substrate, 10^{-3} M carotene; solvent, 50% benzene/50% acetone; sensitizer, 2×10^{-5} M Chl *a*; λ >610 nm (RG 610). All yields are ±10%.

In the presence of air or oxygen the isomerization of all-trans was partly inhibited as revealed by the quantum yields (vide infra) as well as the degree of isomerization (Table II). Lowering the concentration of all-trans gave photostationary mixtures with a smaller degree of isomerization as shown by the results obtained with 10^{-4} and 2×10^{-4} M all-trans (Table II).

Illumination of 15-cis in the absence or presence of oxygen but under otherwise similar conditions as with all-trans led to a very rapid isomerization, although oxygen also had an inhibitory effect in this case. The photostationary mixtures obtained from 15-cis are essentially identical with those obtained from all-trans with respect to isomer distribution (Figure 1 and Table II). The time dependence (under continuous illumination) of the isomerization of 15-cis, however, showed that all-trans is the primary product. The other isomers were formed only after a considerable amount of all-trans had accumulated. This observation is in agreement with the classical result obtained by Foote and co-workers[22] on the photoisomerization of 15-cis by singlet oxygen with methylene blue as sensitizer. These workers, however, did not obtain the photostationary state. γ irradiation of all-trans in Ar-saturated benzene containing 2×10^{-2} M naphthalene as a sensitizer also led to isomerization (Table II), and the isomer distribution is similar to the one obtained by photolysis. As the formation of carotene triplet states by radiolysis of benzene solutions is well-known,[38] this result suggests that the triplet donor energy and eventual ionic processes in the radiolysis are of minor importance, at least under the present conditions.

The apparent relative quantum yields of Chl *a* sensitized photoisomerization (λ >610 nm) of 10^{-3} M β-carotene (all-trans and 15-cis) were determined, and the results are tabulated in Table III. The kinetic scheme of the systems studied here are probably complex, especially in the presence of oxygen. However, the following points should be noticed: (i) the triplet isomerization of 15-cis is an order of magnitude more efficient than the triplet isomerization of all-trans; (ii) the triplet isomerizations are all partly inhibited by oxygen; (iii) there is good correspondence between the quantum yield ratios $\Phi_{\text{trans}\rightarrow 15}/\Phi_{15\rightarrow\text{trans}}$ and the photostationary mass ratios (15-cis)/(all-trans) in both the absence (2.9×10^{-2} vs. 2.6×10^{-2}) and presence (1.0×10^{-2} vs. 1.3×10^{-2}) of oxygen. These observations together with the fact that only one photon–one bond isomerizations are observed are all compatible with a model where the relaxed triplet β-carotene consists of a mixture of several noninterconvertible species, each of them being twisted around either the 9-, 13-, or 15-C=C double bond.

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(31) Moss, G. P.; Weedon, B. C. L. "Chemistry and Biochemistry of Plant Pigments"; Goodwin, T. W., Ed.; Academic Press: London, 1976; Vol. 1, pp 149–224.

(32) Englert, G.; Vecchi, M. *Helv. Chim. Acta* **1980**, *63*, 1711–1718.

(33) Tsukida, K.; Saiki, K.; Sugiura, M. *J. Nutr. Sci. Vitaminol.* **1981**, *27*, 551–561.

(34) Beddard, G. S.; Davidson, R. S.; Trethewey, K. R. *Nature (London)* **1977**, *267*, 373–374.

(35) Seely, G. R. *Photochem. Photobiol.* **1978**, *27*, 639–654.

(36) Mairanovsky, V. G.; Engovatov, A. A.; Ioffe, N. I.; Samokhvalov, G. I. *J. Electronal. Chem.* **1975**, *66*, 123–137.

(37) Park, S.-M. *J. Electrochem. Soc.* **1978**, *125*, 216–222.

(38) Jensen, N.-H.; Wilbrandt, R.; Pagsberg, P. B. *Photochem. Photobiol.* **1980**, *32*, 719–725.

The weight of a particular twisted species however, cannot necessesarily be inferred from the corresponding apparent quantum yield of isomerization, as a low probability of twisted triplet–cis ground-state transition could offset a high relative concentration of the twisted triplet species. Interestingly, recent experiments[39] have shown that the resonance Raman spectra of all-trans and 15-cis are different in the ground states but apparently identical in the triplet states.

In summary, we have in contrast to other reports in the literature[19,20,22,23] demonstrated that *all-trans-β*-carotene undergoes trans–cis isomerization under conditions where the triplet state is the most likely intermediate. This result can be valuable in the interpretation of the resonance Raman spectra of triplet carotenoids. Whether triplet-sensitized isomerizations can explain the existence of *cis*-carotenoids in the reaction centers of photosynthetic bacteria[26-29] is a possibility that deserves further investigation.

Acknowledgment. We are grateful to J. Lundquist, Roche A/S, for providing the sample of 15,15′-*cis*-β-carotene, to Dr. P. Mathis, Saclay, for valuable suggestions, and to Dr. W. Batsberg Pedersen for sharing his HPLC experience and equipment with us. This work was partly supported by a grant from the Danish Natural Science Research Council to N.-H.J.

(39) Wilbrandt, R.; Jensen, N.-H.; Houee-Levin, C.; Sillesen, A. H.; Hansen, K. B. "Raman Spectroscopy"; Lascombe, J., Huong, P. V., Eds.; John Wiley: Chichester, 1982; pp 213–214.

Generation of (η^5-Cyclopentadienyl)dicarbonyliron Carbene Complexes via Protonation of the Corresponding Alkenyl Complexes

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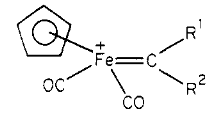
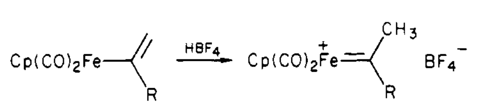
The importance of transition-metal carbene complexes[1] in such processes as alkene metathesis, alkene polymerization,[2] and cyclopropanation reactions is becoming widely recognized. Although these complexes are now known for most of the transition metals, the cationic (η^5-cyclopentadienyl)dicarbonyliron carbene complexes (**1**) and various phosphine derivatives have been particularly well studied. The pioneering work with these compounds was reported by Pettit in 1966[3] and has been followed by further investigations from several other laboratories.[4] The principal motivation for these studies has been that (1) several of these complexes are well-behaved spectroscopically observable species, (2) they can be generated in the absence of the heteroatomic, stabilizing substitutents that are common for many other classes of carbene complexes, and (3) some of the iron complexes are of proven synthetic utility.[5,6]



1

In an earlier paper,[5b] we briefly noted that the vinyliron complex **2** may serve as a simple precursor of the ethylidene complex **3a** by means of a protonation reaction (eq 1), consistent with reports of electrophilic additions to other alkenyl and acetylenic complexes.[7,8] Subsequent to our paper, Cutler also made brief mention of this reaction,[9] and in a very recent study, Casey employed this approach for the isopropylidene complex **3b**.[10] This latter report prompts us to communicate at this time our further findings that demonstrate the generality of this approach to carbene complexes.

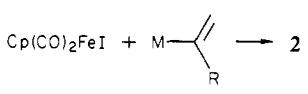


(1)

2a, R = H
b, R = CH$_3$
c, R = Ph

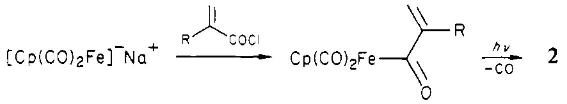
3

The requisite alkenyl complexes **2a–c**[11] are prepared by either of two routes: reaction of alkenyllithium or alkenylmagnesium halides with the iron iodide (eq 2)[12] or acylation of the sodium ferrate with α,β-unsaturated acid chlorides followed by photochemical decarbonylation (eq 3).[13] Typical yields in the first case are 25–40%, whereas the second route proceeds with overall yields of ca. 60–90% but has the disadvantage of requiring two distinct steps.



(2)

M = Li or MgX



(3)

Methylene chloride solutions of the simple vinyl (**2a**) and the isopropenyl (**2b**) complexes react with ether solutions of fluoroboric acid (2 equiv) at −78 °C. After alkenes are added, the mixtures are warmed to 25 °C and quenched with saturated aqueous sodium bicarbonate in order to minimize acid-catalyzed rearrangement of the products. Dimethylcyclopropanes are obtained from 1-decene, isobutylene, styrene, and α-methylstyrene (eq 4).[10,14] To date, the yields of the cyclopropanes are not yet synthetically

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(1) For some recent review of transition-metal carbene complexes see: (a) Casey, C. P. *CHEMTECH* **1979**, 378–383. (b) Brown, F. J. In "Progress in Organic Chemistry"; Lippard, S. J., Ed.; Wiley: New York, 1980; Vol. 27, pp 1–122. (c) Cardin, D. J.; Norton, R. J. In "Organometallic Chemistry"; Abel, E. W., Stone, F. G. A., Senior Reporters; The Chemical Society: London, 1980; Vol. 8, pp 286–292; see also the earlier volumes of this series.

(2) Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 2331–2333.

(3) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044–5045.

(4) For a recent summary of this work see ref 5c, footnote 4.

(5) (a) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473–6475. (b) Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *Ibid.* **1981**, *103*, 1862–1864. (c) O'Connor, E. J.; Helquist, P. *Ibid.* **1982**, *104*, 1869–1874.

(6) (a) Brookhart, M.; Broom, B. H.; Kratzer, H. J.; Nelson, G. O. *J. Am. Chem. Soc.* **1980**, *102*, 7802–7803. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *Ibid.* **1981**, *103*, 979–981.

(7) Precedents for protonation of alkenyl or acetylenic complexes to give carbene complexes may be found in: (a) Bellerby, J. M.; Mays, M. J. *J. Organomet. Chem.* **1976**, *117*, C21–C22. (b) Bell, R. A.; Chisholm, M. H. *Inorg. Chem.* **1977**, *16*, 698–703. (c) Davidson, A.; Selegue, *J. Am. Chem. Soc.* **1978**, *100*, 7763–7765. (d) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471–1485. (e) Adams, R. D.; Davidson, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 7232–7238. (f) Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1471–1483. (g) Marten, D. F. *J. Org. Chem.* **1981**, *46*, 5422–5425.

(8) We note that this approach is not necessarily limited to only protonation but may permit the use of other electrophiles.

(9) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31–C36.

(10) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1980**, 104, 3761.

(11) **2a**: ^{1}H NMR (CDCl$_3$) 6.82 (dd, J = 16.5, 8.5 Hz, 1 H, FeCH=C), 5.70 (d, J = 8.5 Hz, 1 H, C=C*H*H), 5.23 (d, J = 16.5 Hz, 1 H, C=CH*H*), 4.71 (s, 5 H, C$_5$H$_5$). **2b**: ^{1}H NMR (CDCl$_3$) 5.58 (m, 1 H, C=C*H*H), 4.95 (m, 1 H, C=CH*H*), 4.79 (s, 5 H, C$_5$H$_5$), 2.12 (m, 3 H, CH$_3$); ^{13}C NMR (CDCl$_3$) 216.43 (2 CO), 153.67 (Fe*C*=C), 124.89 (C=*C*H$_2$), 85.58 (C$_5$H$_5$), 39.11 (CH$_3$). **2c**: ^{1}H NMR (CDCl$_3$), 7.10 (m, 5 H, Ar H), 5.60 (s, 1 H, C=C*H*H), 5.30 (s, 1 H, C=CH*H*), 4.73 (s, 5 H, C$_5$H$_5$). We note that the isopropenyl complex **2b** is sufficiently stable to permit weighing and other routine operations in the air.

(12) Green, M. L. H.; Ishaq, M.; Mole, T. *Z. Naturforsch., B* **1965**, *20B*, 598.

(13) Quinn, S.; Shaver, A. *Inorg. Chim. Acta* **1980**, *39*, 243–245. Spectral data for the intermediate acyl complexes are typified by Cp(CO)$_2$FeCOC(CH$_3$)=CH$_2$: ^{1}H NMR (CDCl$_3$) 5.34 (m, 1 H, C=C*H*H), 5.26 (m, 1 H, C=CH*H*), 4.86 (s, 5 H, C$_5$H$_5$), 1.75 (dd, J = 1.4, 0.9 Hz, 3 H, CH$_3$); ^{13}C NMR (CDCl$_3$) 255.79 (Fe*C*(O)C), 214.18 (2 CO), 157.77 (*C*(CH$_3$)=C, 118.76 (C=*C*H$_2$), 86.13 (C$_5$H$_5$), 18.56 (CH$_3$). This compound is quite air-stable in that it may be purified by silica gel chromatography in the air.

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