

- (2) G. Stork and W. N. White, *J. Am. Chem. Soc.*, **78**, 4609 (1956); G. Stork and A. F. Kreft, III, *ibid.*, **99**, 3850 (1977).
 (3) R. M. Magid and O. S. Fruchey, *J. Am. Chem. Soc.*, **99**, 8368 (1977).
 (4) G. Stork and A. F. Kreft, III, *J. Am. Chem. Soc.*, **99**, 3851 (1977).
 (5) S. Gottfredsen, J. P. Obrecht, and D. Arigoni, *Chimia*, **31**, 62 (1977).
 (6) (a) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **39**, 2116 (1966); **40**, 2018 (1967). (b) W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **86**, 318 (1967). (c) N. T. Anh, *Chem. Commun.*, 1089 (1968). (d) J. Mathieu, *Bull. Soc. Chim. Fr.*, 807 (1973). (e) R. L. Yates, N. D. Epiotis, and F. Bernardi, *J. Am. Chem. Soc.*, **97**, 6615 (1975). (f) C. L. Liotta, *Tetrahedron Lett.*, 523 (1975).
 (7) The components were readily separated by GLC (1.5 m polypropylene-glycol, 80 °C). Heating above 80 °C led to thermal rearrangement of **4** and **5**.
 (8) Obtained from the corresponding 2-chloro-3-hydroxysuccinic acid with $\text{CH}_2\text{N}_2/\text{BF}_3$. For the preparation and configuration of *erythro*- and *threo*-2-chloro-3-hydroxysuccinic acid, see R. Kuhn and F. Ebel, *Ber. Dtsch. Chem. Ges.*, **58**, 919 (1925); O. Gawron, A. J. Glaid, A. Lo Monte, and S. Gary, *J. Am. Chem. Soc.*, **80**, 5856 (1958).
 (9) Following the procedure of S. W. Pelletier, K. N. Iyer, and C. W. J. Chang, *J. Org. Chem.*, **35**, 3535 (1970).
 (10) W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, 1858 (1926).
 (11) The photosensitized addition of 1,2-dichloroethylene to maleic anhydride has been reported by R. Steinmetz, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, **98**, 3854 (1965). The anodic decarboxylation was carried out according to R. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelein, and T. Whitesides, *Tetrahedron Lett.*, 5117 (1968).
 (12) We thank Dr. E. K. G. Schmidt for a generous gift of [1,2- $^2\text{H}_2$]-1,2-dichloroethylene.
 (13) (a) P. D. Gillespie and I. Ugi, *Angew. Chem.*, **83**, 493 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 503 (1971). (b) W. D. Stohrer and K. R. Schmieder, *Chem. Ber.*, **109**, 285 (1976).
 (14) (a) C. A. Maryanoff, F. Ogura, and K. Mislow, *Tetrahedron Lett.*, 4095 (1975); (b) T. Vergnani, M. Karpf, L. Hoesch, and A. S. Dreiding, *Helv. Chim. Acta*, **58**, 2524 (1975); (c) T. El Gomati, J. Gasteiger, D. Lenoir, and I. Ugi, *Chem. Ber.*, **109**, 826 (1976).

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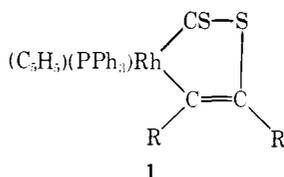
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 Received February 10, 1978

Novel Route to Iron-Carbene Complexes via η^2 -CS₂ Derivatives. 1,3-Dithiolium Species as Precursors for Dithiolene-Iron Complexes and Tetrathiafulvalenes

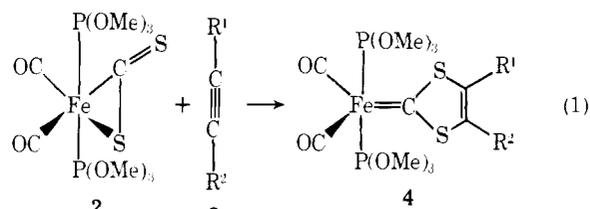
Sir:

Although several routes to carbene-metal complexes have been described which involve modification of a coordinated ligand,¹ none of these methods utilize the cycloaddition of alkynes to a ligand with 1,3-dipolar character. We wish to report here the first examples of carbene complex generation via the addition of activated alkynes to η^2 -CS₂-iron derivatives as well as the use of these intermediate carbenes for the synthesis of dithiolene iron compounds and tetrathiafulvalenes.

Dimethylacetylene dicarboxylate is known to add to a η^2 -CS₂-rhodium complex $\text{Rh}(\text{CS}_2)(\text{PPh}_3)(\text{C}_5\text{H}_5)$ giving the heterocyclic five-membered metalloring derivative **1**.²



By contrast we have found that η^2 -CS₂-iron complexes of type **2**,³ for which a 1,3-dipolar structure has been suggested,⁴ readily react with activated alkynes **3** in benzene at room temperature following a different route: alkynes **3a**, **3b**, or **3c** with complex **2** give air-sensitive adducts **4a**, **4b**, or **4c** which were isolated in 85–95% yields using inert atmosphere column chromatography⁵ (eq 1). The spectroscopic characteristics of complexes **4a–c** were not consistent with what we would have expected for heterometallic compounds, but instead support the carbene structure. The infrared showed two car-



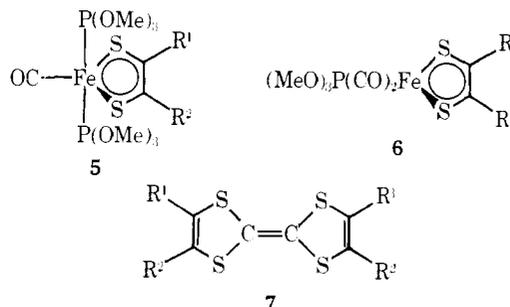
R¹, R²: a (H, CO₂Et); b (*p*-ClC₆H₄, CHO); c (CO₂Me, CO₂Me); d (*p*-O₂NC₆H₄, COCH₃); e (C₆H₅, CHO)

bonyl absorption bands for **4a** (1930, 1870 cm⁻¹), **4b** (1925, 1880 cm⁻¹), and **4c** (1928, 1880 cm⁻¹) at lower frequencies than those of the η^2 -CS₂-iron precursor **2** (2020, 1964 cm⁻¹).⁴ Such a shift is in agreement with the strong electron-donating effect expected for a carbene ligand containing heteroatoms bonded to the carbene carbon atom.⁶ Moreover, ¹³C NMR spectra showed two signals at low field. One triplet corresponds to two equivalent carbonyl ¹³C nuclei coupled with two identical ³¹P nuclei: **4a**, δ (C₆D₆) 219.6 ($2J = 36.0$ Hz); **4b**, δ 222.8 ($2J = 35.9$ Hz); **4c**, δ 220.7 ($2J = 38.1$ Hz). A singlet at lower field⁷ (250.7 (**4a**), 239.6 (**4b**), and 239.4 ppm (**4c**)) corresponds to the range of ¹³C NMR chemical shifts already reported for deshielded, coordinated carbene carbon nuclei.^{1a,8}

¹H and ¹³C NMR data for derivative **4c** rule out the metalloring formulation. Thus the ¹H NMR spectrum presents only one line for the CO₂Me groups (δ 2.65 ppm). Moreover, only three types of ¹³C nuclei originating from alkyne unit were observed in the ¹³C NMR spectrum: δ 52.4 (OCH₃), 145.1 (-C=), 158.8 ppm (-C=O). Equivalence of ¹³C nuclei by pairs indicating the incorporation of the alkyne **3c** in a symmetrical ligand is again in agreement with the 1,3-dithiolium carbene structure.

The trapping of the carbene moiety in complexes **4** under mild conditions is significant since it lends direct support to the suggestion of Hartzler⁹ that cyclic 1,3-dithiolium carbenes are the initial, unstable intermediates in the reactions of free carbon disulfide with activated alkynes. The activation toward cycloaddition afforded by η^2 coordination of carbon disulfide results from the enhancement of nucleophilic character at the uncoordinated sulfur atom and electrophilic character at the coordinated sulfur atom in complexes of type **2**.¹⁰ In contrast, for the rhodium complex $\text{Rh}(\eta^2\text{-CS}_2)(\text{PPh}_3)(\text{C}_5\text{H}_5)$ the metal atom appears to be more electrophilic than the ligated sulfur atom of carbon disulfide.²

Two significant aspects of the behavior of the air-sensitive carbene species **4** are emphasized by their transformation into 1,2-dithiolene-iron complexes and tetrathiafulvalenes. Air-stable, violet compounds **5** were formed when solutions of the corresponding derivatives **4** were allowed to stand in air at room temperature and complexes **5a** (23%), **5b** (22%), or **5c** (35%) could be isolated using Kieselgel thick layer chromatography.¹¹ In addition to complex **5a** a small amount of unstable dithiolene iron derivative **6a** was isolated and characterized.¹²



Dithiolene complexes **5** were more readily obtained without isolation of the carbene intermediate. Thus compounds **5d**

(26%) and **5e** (46%) were isolated by chromatography in air of the reaction mixture of complex **2** with alkynes **3d** and **3e**. Although the mechanism of formation is not clear,¹³ this reaction is a useful method of synthesis for a variety of unsymmetrically disubstituted 1,2-dithiolene-iron complexes containing a functional group.

The trigonal bipyramidal geometry of the dithiolene complexes **4** in solution is supported by ¹H and ³¹P NMR which showed the trans position of identical phosphite ligands¹⁵ and ruled out the square-pyramidal geometry.¹⁶ A dimeric structure has also been ruled out.¹⁷

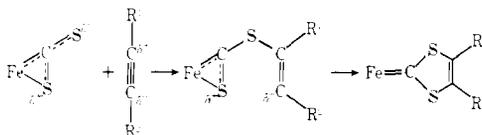
Finally it is worth noting that, after the air oxidation of the carbene complexes **4a** and **4c** besides the dithiolene derivatives **5a** and **5c**, we were able to isolate substituted tetrathiafulvalene derivatives resulting from duplication of 1,3-dithiolium carbenes. Thus the unsymmetrically (**7a**) or the symmetrically (**7c**) substituted tetrathiafulvalenes were obtained in 26 and 28% yields, respectively.¹⁸

The formation of carbene complexes from η²-CS₂-iron complexes is not restricted to derivatives of the phosphite ligand P(OMe)₃. We were also able to characterize similar 1,3-dithiolium-carbene complexes by addition of alkynes to Fe(η²-CS₂)(CO)₂L₂ derivatives when L is PMe₃ or PMe₂Ph. We are currently investigating the influence of the phosphorus ligand on the competitive formation of dithiolene complexes and tetrathiafulvalenes.

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References and Notes

- (1) (a) E. O. Fischer, *Rev. Pure Appl. Chem.*, **30**, 353 (1972); (b) D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *J. Chem. Soc. Rev.*, 99 (1973); (c) J. Tirouflet, P. Dixneuf, and P. Braunstein, *Actual. Chim.*, **5**, 3 (1975); (d) M. F. Lappert, *J. Organomet. Chem.*, **100**, 139 (1975).
- (2) Y. Wakatsuki, H. Yamazaki, and H. Iwasaki, *J. Am. Chem. Soc.*, **95**, 5781 (1973).
- (3) H. Le Bozec, P. Dixneuf, N. J. Taylor, and A. J. Carty, *J. Organomet. Chem.*, **135**, C29 (1977).
- (4) Unpublished work.
- (5) Mass spectra: **4a** (M⁺: found, 533.964; calcd, 533.964), (M - CO)⁺ 506, (M - 2CO)⁺ 478, (M - 2CO, -CS₂C₂(H)(CO₂Et))⁺ 304; **4b** (M⁺: found, 600; calcd, 600) ((M - P(OMe)₃ - 2CO)⁺: found, 419.911; calcd, 419.911); **4c** (M⁺: found, 577.955; calcd, 577.953), (M - CO)⁺ 550, (M - 2CO)⁺ 522, (M - 2CO, -CS₂C₂(CO₂Me)₂)⁺ 304.
- (6) E. O. Fischer, C. G. Kreiter, H. J. Kollmeier, J. Muller, and R. D. Fischer, *J. Organomet. Chem.*, **28**, 237 (1971).
- (7) This signal consists of a singlet for **4a** and **4c**, but with **4b** a triplet was observed corresponding to coupling with two cis ³¹P nuclei (²J_{31P-13C} = 6.7 Hz).
- (8) J. A. Connor, E. M. Jones, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 2419 (1972). A chemical shift of δ 213.0 ppm has been reported for an iron(0)-carbene complex (CO)₄FeC[N(CH₃)CH₂]₂ by D. J. Cardin, B. Cetinkaya, E. Cetinkaya, M. F. Lappert, E. W. Randall, and E. Rosenberg, *ibid.*, 1982 (1973).
- (9) H. D. Hartzler, *J. Am. Chem. Soc.*, **95**, 4379 (1973).
- (10) Formation of complexes **4** may proceed by one-step cycloaddition or as follows:



- (11) Spectroscopic data for **5a** are typical: mass spectrum (M⁺: found, 493.968; calcd, 493.968), (M - CO)⁺ 466, (M - CO, -P(OMe)₃)⁺ 342; IR (Nujol) ν_{C=O} 1965, ν_{C≡O} 1700 cm⁻¹; ¹H NMR (CDCl₃) δ 9.33 (H), 4.27 (q, CH₂), 1.40 (t, CH₃), 3.42 (t, OCH₃) (³J_{P-H} = 11.5 Hz).
- (12) **5a**: IR ν_{C=O} 2030, 1985 cm⁻¹; mass spectrum (M⁺: found, 397.935; calcd, 397.934), (M - CO)⁺ 370, (M - 2CO)⁺ 342.
- (13) Dithiolene complexes of the type M(CO)(PR₃)₂[S₂C₂(CF₃)₂] have been formed by reacting the corresponding phosphorus ligand with [M(CO)₃S₂C₂(CF₃)₂]_x arising from the action of bis(trifluoromethyl)dithietene on metal carbonyls.¹⁴ One possible route to complex **5** is via the dithietene formed by decomposition of the carbene ligand (or tetrathiafulvalene), although this was not observed in the present instance.
- (14) (a) J. Miller and A. L. Balch, *Inorg. Chem.*, **10**, 1410 (1971); (b) G. J. Jones, J. A. McCleverty, and D. G. Orchard, *J. Chem. Soc., Dalton Trans.*, 1109 (1972).

- (15) NMR (CDCl₃) for P(OMe)₃: ¹H triplet at δ ≈ 3.50 ppm (³J_{P-H} ≈ 11.5 Hz). ³¹P NMR for **5d**: δ 175.15 ppm (singlet).
- (16) A square-pyramidal geometry was determined for ruthenium dithiolene derivatives in the solid state: B. I. Bernal, A. Clearfield, E. F. Epstein, J. S. Ricci, A. L. Balch, and J. S. Miller, *J. Chem. Soc., Chem. Commun.*, 39 (1973).
- (17) A dimeric species has been postulated for (Fe(CO)₃S₂C₂[C(F₃)₂]₂)₂.^{14b} A preliminary x-ray study of compound **5d** indicated a monomer: A. J. Carty, personal communication.
- (18) **7a**: mass spectrum (M⁺: found, 347.961; calcd, 347.962); IR 1720 (C=O), 1560 cm⁻¹ (C=C); geometry E or Z undetermined. **7c**: IR 1743 and 1717 (C=O) 1575 cm⁻¹ (C=C).⁹

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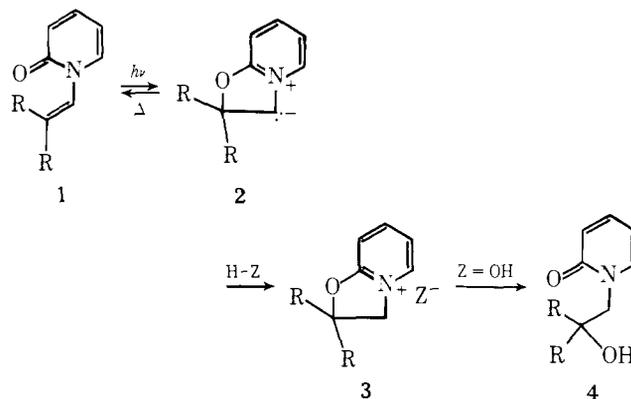
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Kinetic Analysis and Solvent Polarity Effects on the Ylide-Forming Photocyclization Reaction of 1-Vinyl-2-pyridones¹

Sir:

Recently we uncovered a novel photochemical reaction in which 1-vinyl-2-pyridones (**1**) are converted to either oxazolo[3,2-a]pyridinium salts (**3**) or pyrid-2-on-ylethanols (**4**).¹



Accumulated evidence suggested that (a) pyridinium azomethine ylides **2**, generated from singlet 1-vinyl-2-pyridones (**1**^{s1}), are intermediates in this reaction, (b) alcohol products derive from initially formed pyridinium salts when hydroxide is the counterion (Z = OH⁻), and (c) ylides **2** rapidly revert to starting 1-vinyl-2-pyridones. The photochemical step in this process, involving electrocyclicization of the enamide grouping, mimics the analogous reactions followed by isoelectronic systems containing the divinylamine,^{2a} ether,^{2a} and sulfide^{2c} chromophores.

The most significant of several preliminary observations derived from an investigation of the effect of water on the efficiencies of the familiar Dewar pyridone forming reaction (**1** → **5**)³ (also a singlet process)⁴ and competing photocyclization. The efficiency for production of **4** was found to increase at the expense of **5** as water concentration in H₂O-THF solutions is increased, suggesting that partitioning of **1**^{s1} to **5** and **2** (k_{DP}/k_c) is affected by solvent polarity or proton-donating ability. The synthetic and mechanistic importance of potential

