it is unique in operating in the absence of strong Lewis acid metal halides, whose presence may account for why most metatheses are only weakly stereoselective[19,21] and for why some are accompanied by undesirable side reactions.[22]

The observation that acetylenes induce metatheses supports the idea that acetylene polymerization like olefin metathesis involves the addition of metal carbenes to carbon–carbon multiple bonds. The observation that acetylenes quench metatheses too is also in accord with the hypothesis as analyzed in the following paper.[5]

Acknowledgment. We are grateful for the support of the National Science Foundation (CHE-77-22726) and the U.S. Office of Naval Research.

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(21) For additional indications that the stereoselectivity of cyclopentene's metathesis falls with added aluminum compounds and with temperature see: (a) Ivin, K. J.; Laverty, D. T.; Rooney, J. J. *Makromol. Chem.* **1977**, *178*, 1545. (b) Oreshkin, I. A.; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1977**, *26*, 2377; *Eur. Polym. J.* **1977**, *13*, 447.

(22) (a) Hocks, L.; Noels, A.; Hubert, A.; Teyssie, P. *J. Org. Chem.* **1976**, *41*, 1631 references therein. (b) Wolovsky, R.; Moaz, N.; Nir, Z. *Synthesis* **1970**, *2*, 656. (c) Graham, J. R.; Slaugh, L. H. *Tetrahedron Lett.* **1971**, 787. (d) Zowade, T.; Hoecker, H. *Makromol. Chem.* **1973**, *165*, 31. (e) Wang, J. L.; Menapace, H. R. *J. Org. Chem.* **1968**, *33*, 3794. (f) Menapace, H. R.; Maly, N. A.; Wang, J. L.; Wideman, L. G. *Ibid.* **1975**, *40*, 2983. (g) Vialle, J.; Basset, J. M. *React. Kinet. Catal. Lett.* **1975**, *2*, 397.

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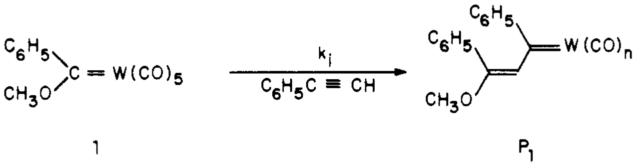
Reactivities of Metal Carbenes toward Alkenes and Alkynes

Sir:

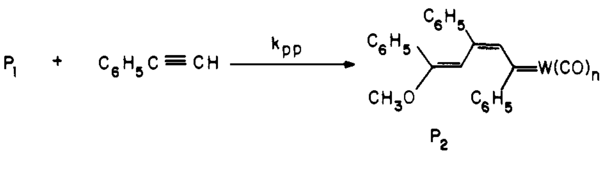
In this paper we report data that show stabilized metal carbenes react much faster with acetylenes than with alkenes, while unstabilized metal carbenes select oppositely. These data were obtained in accounting for acetylenes both inducing an otherwise ineffective metal carbene to initiate olefin metathesis and also quenching the reaction.[1]

We suppose that a metal carbene combines with an acetylene (like phenylacetylene) according to Scheme I of the preceding paper,[1] transforming the initial metal carbene **1** into P_1 (eq 1).



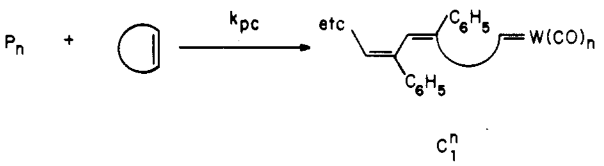
(1)

P_1 then reacts with more of the acetylene according to eq 2; P_2

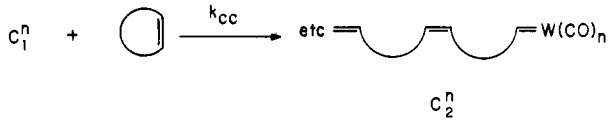


(2)

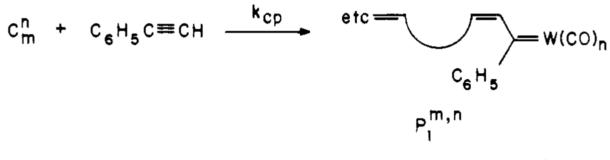
or a higher homologue, P_m, reacts with the olefin, say a cycloalkene, giving C_1 (eq 3); C_1 then propagates the metathesis in the usual way (eq 4). We suppose that eq 5, a plausible analogue of the transformations above, whose action is essentially the reverse of eq 3, accounts for the quenching.



(3)



(4)



(5)

Figure 1, depicting gel-permeation chromatograms of polymers formed from cyclopentene and varying amounts of phenylacetylene, supports these ideas, for the intensity of absorption of 400-nm light (which measures poly(phenylacetylene) units[2] but not polyalkenamers[3]) parallels the intensity of refractive-index changes (which measures the amount of bulk polymer, manily polyalkenamer), implying that poly(phenylacetylene) and polyalkenamer units are attached.

An alternative theory for the quenching, involving either the acetylene or its polymer combining with **1**, destroying its initiating ability, and thereby decreasing the number of polymer chains, might accommodate this observation, but it cannot be correct because, as Figures 1 and 2 show, the molecular weights do not increase with phenylacetylene concentration as they should.[5] However, if eq 5 applies and growing polyphenylacetylenes terminate easily (which seems plausible since polyacetylenes are commonly found to have much lower molecular weight[6,7] than polyalkenamers[4,9]), then capping a growing polyalkenamer with a phenylacetylene will indeed increase the probability of its early termination.

The chromatograms also provide data for quantitative analyses of the equations. They are bimodal (presumably the high molecular weight material is largely polypentenamer[9] and the low molecular weight material poly(phenylacetylene)[6]), and, as summarized in Table I, the ratio of the areas under the high and low

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(1) Katz, T. J.; Lee, S. J.; Nair, M.; Savage, E. B. *J. Am. Chem. Soc.* **1980**, *102*, preceding paper in this issue.

(2) The electronic spectrum is published in Masuda, T.; Sasaki, N.; Higashimura, T. *Macromolecules* **1975**, *8*, 717.

(3) The polypentenamer obtained by using (diphenylcarbene)pentacarbonyltungsten as the initiator (ref 4) exhibits asorption <100 times as intense at 400 nm.

(4) Katz, T. J.; Lee, S. J.; Acton, M. A. *Tetrahedron Lett.* **1976**, 4247.

(5) They decrease also when phenylacetylene (10 mol) is added to (diphenylcarbene)pentacarbonyltungsten (1 mol) and cyclopentene (100 mol) from $\bar{M}_w = 5.3 \times 10^5$, $\bar{M}_n = 3.1 \times 10^5$ to $\bar{M}_w = 4.6 \times 10^4$, $\bar{M}_n = 1.7 \times 10^4$. The reactions were effected at 40 °C for 16 h, and the yields of polypentenamer were 46% and 22%.

(6) $\bar{M}_n$'s for poly(phenylacetylene) made in a number of ways with metal catalysts range from about 1000 to 15 000 and are commonly around 7000.[2,7,8]

(7) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.

(8) Inter alia: (a) Kern, R. J. *J. Polym. Sci., Part A-1* **1969**, *7*, 621. (b) Kushnerev, M. I.; Bantzirev, G. I.; Cherkashin, M. I.; Berlin, A. *Bull. Acad. Sci. USSR* **1971**, *20*, 2161. (c) Simionescu, C. I.; Percec, V.; Dumitrescu, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2497. (d) Biyani, B.; Campagna, A. J.; Daruwalla, D.; Srivastava, C. M.; Ehrlich, P. *J. Macromol. Sci. Chem.* **1975**, *A9*, 327. (e) Nguyen, H. X.; Amdur, S.; Ehrlich, P. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1977**, *18*, 200. (f) Masuda, T.; Thieu, K.-Q.; Higashimura, T. *Polym. J.* **1978**, *10*, 269. (g) Woon, P.S.; Farona, M. F. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1749.

(9) Polyalkenamers have molecular weights that are usually between 10^5 and 10^6 (see ref 4 and 10).

(10) Inter alia: (a) Witte, J.; Hoffmann, M. *Makromol. Chem.* **1978**, *179*, 641. (b) P. Günther et al. *Angew. Makromol. Chem.* **1970**, *14*, 87. (c) Glenz, W.; Holtrup, W.; Küpper, F. W.; Meyer, H. H. *Ibid.* **1974**, *37*, 97. (d) Calderon, N.; Ofstead, E. A.; Judy, A. W. *J. Polym. Sci., Part A* **1967**, *5*, 2209. (e) Arlie, J.-P.; Chauvin, Y.; Commereuc, D.; Soufflet, J.-P. *Makromol. Chem.* **1974**, *175*, 861.

0002-7863/80/1502-7942$01.00/0

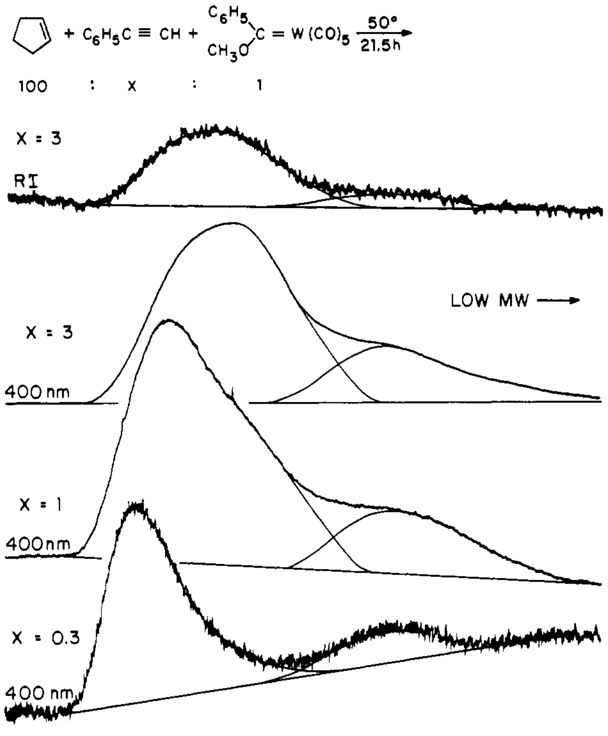

Figure 1. Gel-permeation chromatograms in toluene on μ-styragel columns (exclusion limits 10^6, 10^5, 10^4, 10^3, 500 Å) of the polymer obtained from cyclopentene (100 equiv), phenylacetylene (x equiv), and **1** (1 equiv) after 21.5 h at 50 °C. Analyses were by refractive index (top chromatogram) and by light absorption at 400 nm (bottom three chromatograms).

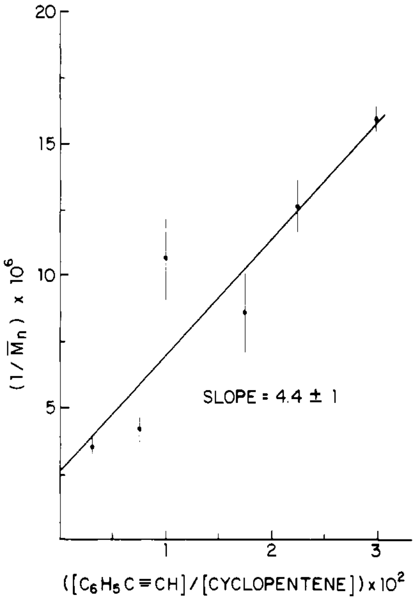

Figure 2. The relationship between the number average molecular weight of the polypentenamer and the ratio of phenylacetylene and cyclopentene combined with **1** at 50 °C. The data are from Table I.

Table I. Summary of Yields and Polymer Distributions Resulting When Cyclopentene (100 equiv), Phenylacetylene (x equiv), and 1 (1 equiv) Are Combined at 50 °C for 21.5 h

x	% yield polypentenamer[a]	$\bar{M}_w \times 10^{-3}$ [b]	$\bar{M}_n \times 10^{-3}$ [b]	% PPA at low mol wt[c]	% yield total PPA[d]
3.0	4.9	178	66	24.42 ± 0.3	27
2.25	4.2	262	83	16.35 ± 0.4	23
1.75	7.0	333	119	16.4 ± 2	24
1.0	15.8	348	100	19.3 ± 2	26
0.75	20.3	594	289	15.0 ± 2	19
0.3	36.7	674	340	17.2 ± 3	17

[a] The ratio of the weight of polymer (isolated by dissolving the product in CH_2Cl_2, precipitating with CH_3OH, and drying under vacuum), diminished by the amount of poly(phenylacetylene), and the weight of cyclopentene. [b] Measured by gel-permeation chromatography by using toluene solutions and Waters Associates' μ-styragel columns. The weights are one-half those of polystyrenes that would exhibit the chromatograms observed (ref 11). The characteristics of the high-weight materials are listed. Those of the low-weight materials were measured as approximately "M_w" = (19.2 ± 2) × 10^3, "M_n" = (8.6 ± 3) × 10^3 (these are the weights of polystyrenes that would exhibit the chromatograms observed). Very low molecular weight fractions may, however, have been excluded because (a) the instrument could not resolve very low molecular weights, (b) they may have been transparent, or (c) they may have been lost during the isolation. [c] PPA = poly(phenylacetylene). The ratio of the area under the low molecular weight peak in Figure 2 and the area under both peaks. For each sample the areas were measured on at least three chromatograms, and averages and standard deviations are listed. [d] Both attached to and free of polyalkenamer. Measured by comparing the absorption at 400 nm with that of pure PPA. When x is small, small amounts of poly(phenylacetylene) of low molecular weight may be lost during the isolation.

molecular weight peaks monitored by the light absorption is independent of the amount of phenylacetylene in the reaction mixture. This accords with our hypothesis since whether a poly(phenylacetylene) chain does or does not have a polyalkenamer attached to it depends on the concentration and reactivity of the cycloalkene, not the acetylene. The area ratio therefore measures this reactivity.

The fraction of the phenylacetylene polymerized (measured by the amount of light absorbed) and the total number of polymer chains (measured by the yields and molecular weights) are also independent of the concentration of phenylacetylene, implying that the rate of initiation, eq 1, is independent of this concentration too.[13,14]

Assuming that termination involves reaction of two P chains, the slope of the line in Figure 2 implies that $k_{cp}/k_{cc} = 0.125 \pm 0.03$ and the slope of the line in Figure 1 of the preceding paper that $k_{pp}/k_{pc} = 170 \pm 55$.[15,16] (If termination were unimolecular in P, the corresponding figures would be 0.178 ± 0.04 and 119 ± 41.)[16,17]

Similar data for cyclooctene are less complete, but preliminary results imply that k_{cp}/k_{cc} is at least 4 times smaller and k_{pp}/k_{pc} at least 100 times larger.

Thus C's, like other electrophiles,[18-20] react faster with alkenes than with the acetylene. But the stabilized metal carbenes P,

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(11) This should be true if gel-permeation chromatography measures end-to-end dimensions of polymers, and the dimensions $(L_0{}^2/M)^{1/2}$ for the polyalkenamers can be estimated as the weighted averages of their components, 1.07 Å for polyethylene and 0.920 Å for *cis*-polybutadiene (ref 12). The value of $(L_0{}^2/M)^{1/2}$ for the polypentenamer divided by $(L_0{}^2/M)^{1/2}$ for the polystyrene is 0.49. (For polyheptenamer the value is 0.46 and for polyoctenamer 0.45.)

(12) (a) Dawkins, J. V. *Eur. Polym. J.* **1970**, *6*, 831. (b) Dawkins, J. V.; Denyer, R.; Maddock, J. W. *Polymer* **1969**, *10*, 154.

(13) This conclusion contrasts with that of the only related study concerning the rates at which ynamies react with **1** and related molecules: Fischer, H.; Dötz, K. H. *Chem. Ber.* **1980**, *113*, 193.

(14) The number of polymer chains is 30% of the lowest number of moles of **1** used in the experiments in Table 1 and 3% of the highest number.

(15) $1/\bar{x}_n = (k_{cp}/k_{cc})([C_6H_5C{\equiv}CH]/[cyclopentene])[R^{1/2}(1 - R)/(2 - R + R^{1/2})]$, where $\bar{x} = M_n/68$ and R is the ratio of the area under the low molecular weight peak in Figure 1 divided by the area under both peaks.

(16) $1/y = (k_{pp}k_{cp}/k_{pc}k_{cc})[(1/y') - 1]\{[C_6H_5C{\equiv}CH]_0/[cyclopentene]_0\} + 1$, where y and y' are the fractional yields of polyalkenamer and polyphenylacetylene, respectively. Subscript zero refers to initial concentrations.

(17) $1/x_n = (k_{cp}/k_{cc})[C_6H_5C{\equiv}CH]R/[cyclopentene]$.

(18) Bromine and acid: Yates, K.; Schmid, G. H.; Regulski, T. W.; Garratt, D. G.; Leung, H.-W.; McDonald, R. *J. Am. Chem. Soc.* **1973**, *95*, 160.

(19) Transition-metal ions: Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163.

(20) Carbenium ions are anomalous: Marcuzzi, F.; Melloni, G. *Tetrahedron Lett.* **1975**, 2771.

unlike the unstabilized C's, discriminate very much more and inversely, which is strange,[21] but accords with 1 (also a stabilized metal carbene) reacting much more quickly with acetylenes than with alkenes.[1,7,22,23]

Acknowledgment. We are grateful to Yuan-Chi Ying for assisting with the experiments with cyclooctene and to the National Science Foundation (CHE-77-22726) and the U.S. Office of Naval Research for support.

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(21) It correlates with nucleophilic reactivity: Dickstein, J. I.; Miller, S. I. In "Chemistry of the Carbon-Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978; Vol. 2, p 813 ff.

(22) Katz, T. J.; Acton, N. *Tetrahedron Lett.* **1976**, 4251.

(23) P's are presumably less stabilized than **1**, which is why they initiate metatheses that **1** does not.

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Unusual Interaction of Iron-Bleomycin with Cyanide

Sir:

The bleomycin (BLM)-Fe(II) complex appears to act by reducing molecular oxygen to a more reactive species in the vicinity of a susceptible DNA bond, resulting in its cleavage.[1] Optical, ^{1}H NMR, and ESR spectroscopies have demonstrated that the BLM-Fe(II) complex forms a complex with either CO, isocyanide, or NO.[2] The activity of BLM, monitored by the production of malondialdehyde, is reversibly inhibited by CO or ethyl isocyanide.[2a] These substances are oxygen antagonists, just as with heme oxygenases. It is known that CN ion binds more strongly to ferric than to ferrous hemes[3] and inhibits the reaction by heme oxygenases.[4] In contrast, cyanide ion enhances the BLM activity against DNA cleavage.[2a]

On the basis of several spectroscopic results, Scheme I has been proposed for the BLM-iron interaction.[5] The reaction of the high-spin BLM-Fe(II) complex with O_2 yields the corresponding Fe(III) complex, which again undergoes reduction by a reducing agent. Recent stopped-flow optical spectroscopy indicated the presence of a short-lived intermediate, an oxygenated BLM-Fe(II) complex.[6] A stable, diamagnetic BLM-Fe(II)-CO adduct complex has been shown by a proton NMR study.[2b]

In connection with the cyanide enhancement of BLM activity, we have investigated the interaction of the BLM-iron complexes with CN ion by optical, ^{1}H NMR, and ESR spectroscopies and found an unusual cyanide interaction of iron-BLM.

The Fe(II) and Fe(III) complexes of bleomycin-A_2 (BLM) were prepared according to the previous procedure.[5] 220-MHz FT ^{1}H NMR (sample concentration 10 mM) and X-band ESR (1 mM) spectra were recorded with Varian HR-220 and JES-FE-3X spectrometers, respectively.

The addition of NaCN to the BLM-Fe(II) and BLM-Fe(III) complexes induced color changes from pink to blue-violet and from yellow-brown to red-brown, respectively. Table I summarizes the visible spectral characteristics of these iron complexes. The results of optical titration at pH 6.9 indicated that the BLM-Fe(II) (or -Fe(III)) complex forms a 1:1 cyanide adduct complex.

Scheme I

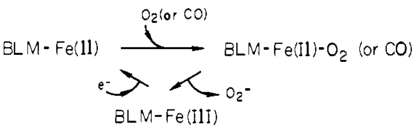

Table I. Effect of Cyanide Ion on Visible Absorption Spectra of Bleomycin-Iron Complexes

complex	λ_{max}, nm (ϵ)
BLM-Fe(II)	476 (380)
BLM-Fe(II) + CN$^-$	385 (1600), 570 (1400), 605 (1300)
BLM-Fe(III)	365 (2000), 384 (1900)
BLM-Fe(III) + CN$^-$	390 (2000), 465 (800)

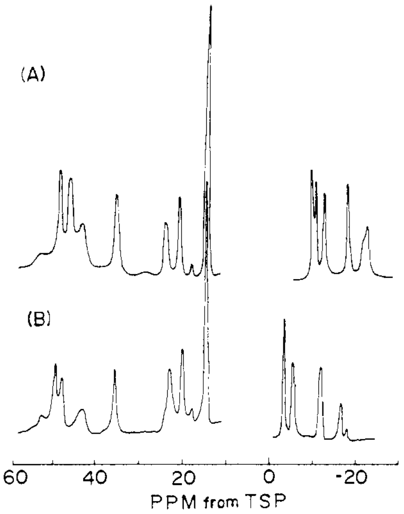

Figure 1. Proton NMR spectra of the BLM-Fe(II) complex (A) and the BLM-Fe(II)-CN complex (B) at pD 7.3 and 25 °C.

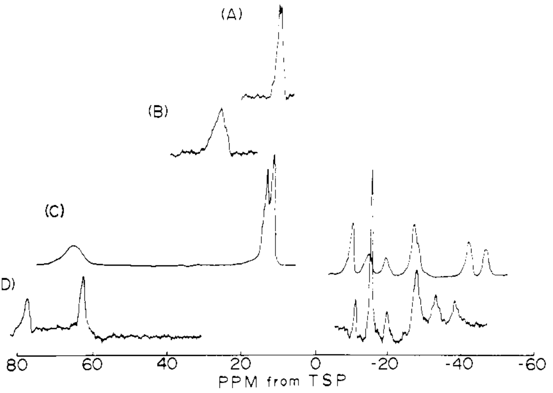

Figure 2. Proton NMR spectra of the BLM-Fe(III) complex (A), the BLM-Fe(III)-CH_3NH_2 complex (B), the BLM-Fe(III)-CN complex (C), and the BLM-Fe(III)-CH_3NH_2-CN complex (D) at pD 7.3 and 25 °C.

Figure 1 shows the 220-MHz FT ^{1}H NMR spectrum of the 1:1:1 BLM-Fe(II)-CN complex together with that of the original BLM-Fe(II) complex. Although the spectra show similar patterns, the magnitude of the proton paramagnetic shifts of the BLM-Fe(II)-CN complex differs somewhat from that of the original BLM-Fe(II) complex and the former signals appear at lower field. In contrast with the absence of proton paramagnetic signals for the corresponding CO (or C_2H_5NC) adduct ($S = 0$), the large paramagnetic shifts of the BLM-Fe(II)-CN adduct suggest the presence of a high-spin ferrous iron ($S = 2$).[7]

Figure 2 illustrates the 220-MHz FT ^{1}H NMR spectra of the

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(1) Sausville, E. A.; Stein, R. W.; Peisach, J.; Horwitz, S. B. *Biochemistry* **1978**, *17*, 2746-54.

(2) (a) Burger, R. M.; Peisach, J.; Blumberg, W. E.; Horwitz, S. B. *J. Biol. Chem.* **1979**, *254*, 10906-12. (b) Oppenheimer, N. J.; Rodriguez, L. O.; Hecht, S. M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 5616-20. (c) Sugiura, Y.; Ishizu, K. *J. Inorg. Biochem.* **1979**, *11*, 171-80.

(3) Keilin, D.; Hartree, E. F. *Biochem. J.* **1955**, *61*, 153-71.

(4) Ohnishi, T.; Hirata, F.; Hayaishi, O. *J. Biol. Chem.* **1977**, *252*, 4643-7.

(5) Sugiura, Y. *J. Am. Chem. Soc.* **1980**, *102*, 5208-5215.

(6) Burger, R. M.; Horwitz, S. B.; Peisach, J.; Wittenberg, J. B. *J. Biol. Chem.* **1979**, *254*, 12299-302.

(7) The Mössbauer parameters of the BLM-Fe(II)-CN adduct are also typical of high-spin Fe(II) and are somewhat different from those of the original BLM-Fe(II) complex. On the other hand, the BLM-Fe(III)-CN adduct has Mössbauer constants characteristic of high-spin Fe(III) (unpublished results).