

**Figure 4.** Histograms of BEDF·Fe<sup>II</sup> cleavage patterns on 517 bp DNA restriction fragment (base pairs 4337–4296 on plasmid pBR322) from high-resolution denaturing gel (Figure 3). Arrows represent amount of cleavage resulting in removal of indicated base. Boxes define binding site location and size based on model described in ref 4.

forming bridges between adjacent N3 or O2 atoms of adenine (A) and thymine (T) on opposite strands of the DNA helix.<sup>4–7</sup> We anticipate there is a point where an oligo-*N*-methylpyrrolicarboxamide will no longer fit the natural twist of the B helix.<sup>6</sup> The recognition of DNA sequences larger than the upper limit permissible with oligo-*N*-methylpyrrolicarboxamides will require linkers compatible with both these DNA binding units and the minor groove of A·T rich sequences of B DNA. The question arises whether the *N*-methylpyrrolicarboxamide ring, a two base pair DNA recognition element, can be replaced by structurally similar moiety. For example, the diamide of fumaric acid might mimic *N*-methylpyrrolicarboxamide with regard to shape and distance between the amide NHs (Figure 1).

We report a new sequence-specific DNA binding molecule, bis(EDTA–distamycin)fumaramide (BEDF)<sup>8</sup> (Figure 2). This crescent-shaped octaamide contains two *N*-methylpyrrole tripeptide units<sup>1–6</sup> coupled at the amino termini via fumaric acid (Figure 2). Attachment of EDTA to the carboxy terminus of each tripeptide allows use of the affinity cleaving method<sup>4–6</sup> to visualize the sequence and size of the DNA recognition site by analysis of DNA cleavage patterns on <sup>32</sup>P-end-labeled DNA restriction fragments by high-resolution denaturing gel electrophoreses.<sup>1–6</sup>

A 517 base pair *Rsa I/Eco RI* restriction fragment (3848–4362 bp) from plasmid pBR322 DNA was labeled separately with <sup>32</sup>P on the 5′- and 3′-ends.<sup>2,3</sup> The DNA restriction fragments were allowed to react with BEDF·Fe<sup>II</sup> (1.5 μM concentration) at dimer/DNA base pair ratios of 0.015 in the presence of dithiothreitol (5 mM) for 2 h (37 °C, pH 7.9).<sup>9</sup> The DNA cleavage sites were visualized by high-resolution gel electrophoreses (Figure 3). From densitometric analysis of the autoradiogram, the DNA cleavage patterns reveals major cleavage sites flanking two sequences 5′-ATTTTTTATA-3′ and 5′-ATAATAAT-3′ (Figure 4).

According to the “*n* + 1 rule”, a functional octaamide in the minor groove should bind nine base pairs. The observation of eight and nine base pair binding in the absence of five base pair binding suggests that BEDF is binding DNA exclusively in the dimeric

mode. This is in contrast to results with a dimer of the same tripeptide coupled with heptanedioic acid, a flexible C-7 hydrocarbon linker.<sup>2</sup> In this case, monomeric binding at one site, 5′-atATAAAT-3′, was competitive with dimeric binding at the 5′-TTTTTATA-3′ site on the same restriction fragment.<sup>2</sup> The fact that we observe eight as well as nine base pair binding site sizes for BEDF may be due to our inability to assign exactly the binding site boundaries based on the asymmetric cleavage pattern model.<sup>4–6</sup> Alternatively, the appearance of an eight base pair binding site may indicate that there are other binding options for the fumaramide linker.

In summary, the dimer of tris-*N*-methylpyrrolicarboxamide connected by a flexible C-7 linker, which had the property of monomeric binding competitive with dimeric binding,<sup>2</sup> was redesigned with a shorter rigid C-4 linker of favorable curvature affording a new molecule, BEDF, that has the property of exclusive dimeric binding which results in the recognition of eight–nine contiguous base pairs of A·T rich double helical DNA.

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### Formation of Acrylic Acid Derivatives from the Reaction of CO<sub>2</sub> with Ethylene Complexes of Molybdenum and Tungsten<sup>†</sup>

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There is at present a great deal of interest in the organometallic chemistry of carbon dioxide, largely aimed at finding new catalytic processes for the conversion of abundant CO<sub>2</sub> into organic chemicals of commercial interest.<sup>2</sup> In the course of our studies on CO<sub>2</sub> chemistry,<sup>3</sup> we have found that the complexes *trans*-M-

<sup>†</sup> Dedicated to Professors Gonzalez Garcia and Gutiérrez Rios on the occasion of their retirement.

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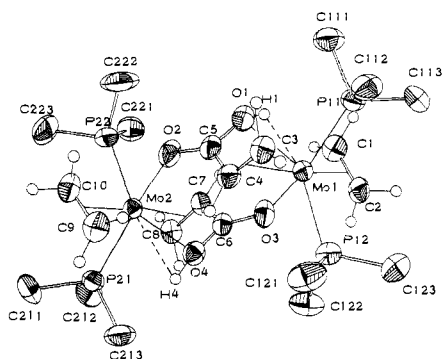
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(8) The NMR, IR, UV, and mass spectral data are consistent with the assigned structure. The synthetic details, similar to methods described in ref 2 and 4, will be published elsewhere.

(9) The cleavage reactions were run with >600 cpm of <sup>32</sup>P end-labeled restriction fragments and made up to a total DNA concentration of 100 μM (bp) with sonicated calf thymus DNA. The samples were equilibrated with the DNA at 37 °C for 2 h and reaction was initiated by the addition of a dithiothreitol solution. The reactions were run at 37 °C for 2 h and terminated by freezing followed by lyophilization and suspension in 4 μL of a pH 8.3 100 mM Tris-borate, 50% formamide solution. These solutions were heat denatured and loaded on a 0.4 mm thick, 40 cm long, 8% polyacrylamide, 1:20 cross-linked, 50% urea gel and electrophoresed at 1500 V. Autoradiography of the gels was carried out at –50 °C on Kodak, X-Omat AR film, and the autoradiograms were scanned at 485 nm. The relative peak area for each site was equated to the relative cleavage efficiency.



**Figure 1.** ORTEP diagram for **1** and atom labeling scheme. Important bond distances and angles: Mo1–O1 = 2.243 (5), Mo1–C3 = 2.244 (6), Mo1–C4 = 2.209 (6), Mo1–O3 = 2.216 (4), C5–O1 = 1.276 (7), C5–O2 = 1.262 (7) Å; P11–Mo1–O3 = 155.0 (1)°, P12–Mo1–O1 = 149.9 (2)°, O1–Mo1–C3 = 72.9 (2)°, O1–Mo1–C4 = 61.0 (2)°. Values for Mo2 entirely similar.

(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> (M = Mo,<sup>4</sup> W<sup>5</sup>) react under very mild conditions with CO<sub>2</sub>, to afford white crystalline materials<sup>6</sup> of analytical composition [M(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(CO<sub>2</sub>)(PMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (M = Mo (**1**), M = W (**2**)) which contain acrylic acid or acrylate ligand (formed by coupling of CO<sub>2</sub> with one of the C<sub>2</sub>H<sub>4</sub> molecules) bridging the two metal atoms.

The electron-rich nature of the metal center in *trans*-Mo-(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> and the availability of a vacant coordination position by facile dissociation of one of the PMe<sub>3</sub> ligands<sup>4</sup> make this complex and the tungsten analogue<sup>5</sup> ideal candidates for CO<sub>2</sub> activation.<sup>7</sup> Interaction of the ethylene complexes with CO<sub>2</sub> (1 atm) affords<sup>8</sup> off-white, fairly air-stable crystals of **1** and **2** in good yields. A strong IR band at ca. 1500 cm<sup>-1</sup> suggests the presence of a carboxylate ligand, also indicated by the appearance of a <sup>13</sup>C resonance at 175–180 ppm. The olefinic carbon atoms derived from the original ethylene molecules yield resonances at 32.8, 38.3, 39.6, and 55.1 ppm (data for **2**). The last resonance becomes a ca. 1:2:1 triplet in the spectrum of **2** ca. 50% enriched in <sup>13</sup>CO<sub>2</sub> (<sup>1</sup>J<sub>CC</sub> = 60 Hz), suggesting that coupling of CO<sub>2</sub> with one of the ethylene molecules has occurred,<sup>9</sup> with formation of acrylic acid or acrylate ligands.<sup>10</sup>

The molecular complexity and bonding mode in **1** and **2** have been determined by X-ray studies. Figure 1 shows an ORTEP view of **1**.<sup>11</sup> The compound is approximately centrosymmetric,<sup>12</sup> with two molecules of acrylic acid bridging the two molybdenum centers coordinated to one metal atom through the C=C and the O–H bonds and to the other through the second oxygen atom. The

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(8) *trans*-W(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> 0.96 g (1.75 mmol), in 80 mL of Et<sub>2</sub>O was reacted with CO<sub>2</sub> (bubbling) for 30 min and the resulting solution (**2** may precipitate at this stage) cooled at –20 °C overnight. A total of 0.50 g (ca. 65%) of **2** was collected from this and subsequent crystallizations of the mother liquor. Molecular weight (cryoscopically, C<sub>6</sub>H<sub>6</sub>, Et<sub>2</sub>O-free sample). Calcd for [W(CH<sub>2</sub>=CHCOOH)(C<sub>2</sub>H<sub>4</sub>)(PMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>: 872. Found: 822. Microanal. Calcd for [W(CH<sub>2</sub>=CHCOOH)(C<sub>2</sub>H<sub>4</sub>)(PMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·1/2 Et<sub>2</sub>O: C, 31.7; H, 6.3. Found: C, 31.6; H, 6.3. **1** is similarly obtained (–15 °C, 1 h) although workup is complicated by extensive decomposition.

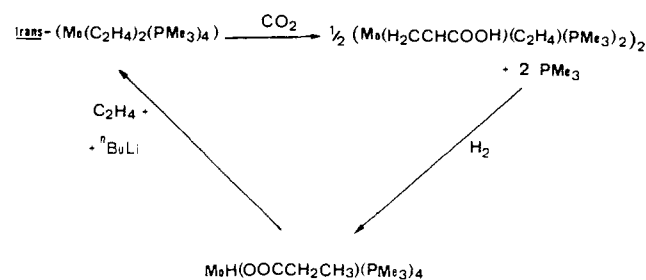
(9) Oxidative coupling of C<sub>2</sub>H<sub>4</sub> and CO<sub>2</sub> induced by Ni(0) has been observed; see: Hoberg, H.; Schaefer, D. *J. Organomet. Chem.* **1983**, *251*, C51.

(10) An absolutely clear distinction between the acrylic acid and the hydride-acrylate formulations (see structures A and B in the text) cannot be made with present data.

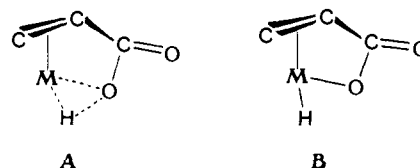
(11) An X-ray determination on **2**, now in progress, reveals that both complexes are isomorphous and isostructural.

(12) Complex **1** crystallizes in the monoclinic space group *P*<sub>21/n</sub> with *a* = 12.117 (8) Å, *b* = 15.072 (5) Å, *c* = 17.700 (5) Å, β = 102.18 (3)°, and *D*<sub>calcd</sub> = 1.46 g cm<sup>-3</sup> for *Z* = 4. Least-squares refinement based on 3500 observed reflections led to a final *R* = 0.032.

### Scheme I

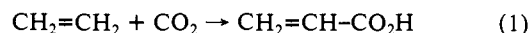


geometry around each molybdenum atom is that of a distorted octahedron. The ethylene molecules approximately eclipse the

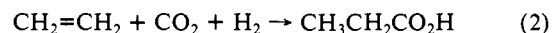


Mo1–P12 and Mo2–P22 bond directions, and the acrylic CH=CH double bonds approximately eclipse the Mo1–P11 and Mo2–P21 vectors. The existence of an agostic-type interaction<sup>10</sup> MoOH, is suggested by the average bond parameters found for H1 and H4 (Fourier difference, coordinates refined): Mo–O–H 73 (7)°; Mo–H 2.2 (1) Å; O–H 0.8 (1) Å. The C4–C5 and C6–C7 bond distances (1.446 (9) Å, average) are identical within experimental error with that found for the analogous bond in the butyl methacrylate (vinyl) complex<sup>13</sup> RuH(CHC(CH<sub>3</sub>)CO<sub>2</sub>C<sub>4</sub>H<sub>9</sub>)(PPh<sub>3</sub>)<sub>3</sub> (1.442 (15) Å), although in our system there is a large deviation from planarity as shown by the C3–C4–C5–O2 and C8–C7–C6–O3 torsion angles of 62.2° and –62.1°, respectively.

The formation of **1** and **2** from the reactions of *trans*-M-(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> with CO<sub>2</sub> corresponds formally to an insertion of CO<sub>2</sub> into one of the ethylene bonds<sup>14</sup> (eq 1). On the other



hand, hydrogenation of **1** (20 °C, 1 atm) in the presence of PMe<sub>3</sub> produces the red hydride-propionate<sup>15</sup> Mo(O<sub>2</sub>CCH<sub>2</sub>CH<sub>3</sub>)(H)(PMe<sub>3</sub>)<sub>4</sub> (**3**), the overall process corresponding formally to ethylene hydrocarboxylation (eq 2). Furthermore, complex **3** can be



reconverted to *trans*-Mo(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> (with subsequent formation of LiO<sub>2</sub>CCH<sub>2</sub>CH<sub>3</sub> and other as yet unidentified products) by reaction with *n*-BuLi under C<sub>2</sub>H<sub>4</sub>, therefore making the process cyclic, as depicted in Scheme I.

In conclusion, the reaction chemistry shown in Scheme I corresponds to the metal-induced transformation of C<sub>2</sub>H<sub>4</sub> and CO<sub>2</sub>, or C<sub>2</sub>H<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>, into acrylic or propionic acid derivatives. This chemistry may be of significance in connection with the industrial use of CO<sub>2</sub> as a one-carbon precursor of organic chemicals, which is at present an important goal of modern chemistry.

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Sir Edward Frankland Fellow of the Royal Society of Chemistry for 1984-1985.

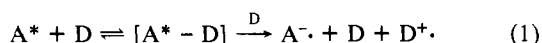
**Supplementary Material Available:** Tables of final fractional coordinates, thermal parameters, bond distances and angles, and observed and calculated structure factors for **1** (42 pages). Ordering information is given on any current masthead page.

## Chemistry of Exciplexes. 19. Exciplex-Promoted Electron Transfer in 1-(Phenylamino)-3-(9-anthryl)propanes

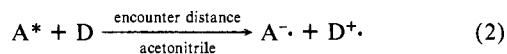
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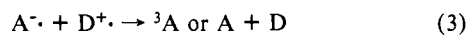
Light-induced electron transfer in multicomponent systems and polychromophoric molecules is a subject of current interest.<sup>4-10</sup> In nonpolar media, a photoexcited molecule may react with a ground-state molecule in a specific orientation yielding an exciplex which may be characterized by its fluorescence.<sup>11</sup> Exciplexes may be deactivated by another ground-state molecule, and it has been suggested that electron transfer may play a role in this deactivation (e.g., reaction 1 where A\* is an excited acceptor and



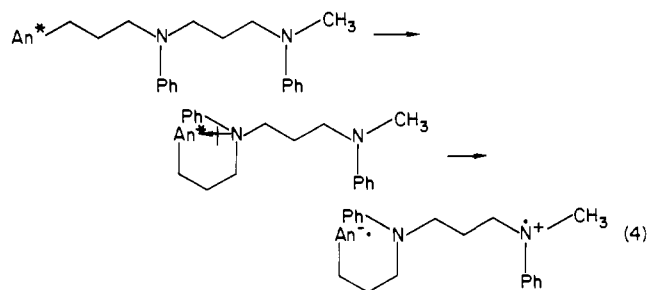
D is a donor).<sup>4-9</sup> However, this suggestion was not supported by any direct experimental evidence. A photoexcited molecule may react with a ground-state molecule to undergo electron transfer at an encounter distance yielding a radical ion pair in polar media (e.g., reaction 2).<sup>11</sup> These radical ions tend to undergo rapid back



electron transfer to revert back to substrates in their ground state or triplet state (e.g., reaction 3).<sup>12,13</sup> In order to convert light



energy into chemical energy in an efficient manner, the rate of back electron transfer must be controlled or retarded. In this investigation, we examined the reactive intermediates generated from photoexcited polychromophoric systems by kinetic spectroscopy. The compounds used were **1-3** containing an anthryl group as the photoexcited acceptor and one or two dialkylanilino groups as the donor(s).<sup>4,14-16</sup> The intermediates derived from these



photoexcited compounds, the anthryl radical anion, dialkylanilino radical cation, and anthryl triplet all exhibit well-defined absorption characteristics.<sup>17-19</sup> This paper demonstrates that an exciplex may undergo electron transfer with another donor molecule in dichloromethane and the lifetimes of ions generated in such a system are substantially longer than the lifetimes of ions from analogous electron transfers in polar media.

Nanosecond transient absorbance measurements were performed with a spectrometer of conventional design, utilizing a frequency tripled Nd-YAG laser.<sup>20</sup> The laser generates a 355-nm, 5-mJ, and 5-ns (fwhm) pulse at 10 Hz which determines the limiting time resolution for the measurements. Similar experiments were performed on a picosecond time scale using a dual beam spectrometer employing multichannel detection. A 600-nm, 2.5-mJ and 2-ps (fwhm) pulse at 10 Hz frequency doubled to yield a 140-μJ pulse at 300 nm. The residual 600-nm light was focused into a cell containing D<sub>2</sub>O to generate the picosecond white light pulse used in the spectroscopic measurements.<sup>21</sup> Solutions containing 5 × 10<sup>-4</sup> M of the samples were circulated through a 1-mm cuvette at a rate sufficient to ensure the excitation of a new sample for each pulse from the laser. The formation and decay of the anilino radical cation as well as that of the anthryl anion were monitored at 470<sup>17</sup> and 700 nm,<sup>18</sup> respectively. The formation of anthryl triplet was monitored at 425 nm.<sup>19</sup> The data were collected and analyzed with a PAR OMA-II detector controlled by a DEC LSI-11/73 computer. The results are tabulated in Table I.

The data from Table I clearly demonstrate that the properties of photoexcited **1** and **2** in acetonitrile, a polar solvent, are practically identical, while those of **3** are in agreement with previous findings.<sup>22-24</sup> All these compounds exhibit extremely rapid rises in absorption of the order of 5-10 ps in the regions where radical ions absorb followed by a rapid decay to form either the ground state or the triplet state of the substrate (270 ps-2.5 ns).<sup>25</sup> However, the properties of photoexcited **1** in dichloromethane differ from those of **2** in that **1** undergoes electron transfer to generate radical ions while **2** does not. Photoexcited **2** exhibits an appreciable exciplex fluorescence (λ<sub>max</sub> 530 nm, φ<sub>f</sub> 0.12, τ<sub>f</sub> 28 ± 1 ns) in deaerated dichloromethane. Although photoexcited **2** also yields a broad and weak absorption at 700 nm, it decays with the same lifetime as that of the exciplex which corresponds to the risetime of the anthryl triplet absorption. The results indicate that the exciplex from **2** undergoes intersystem crossing without passing through the intermediate stage of radical ions. Photoexcited **1** exhibits a very weak exciplex fluorescence (λ<sub>max</sub>

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