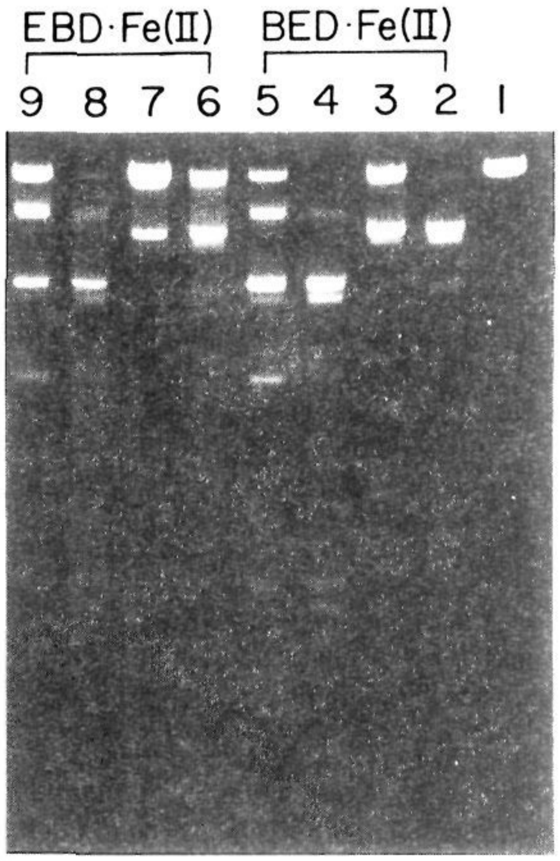

Figure 1. 1% agarose gel/ethidium bromide staining. Lane 1, intact linear pBR-322 DNA (50 μM in base pairs). Lanes 2, 3, 6, and 7 are linearized by *Eco RI* digestion. Lanes 4, 5, 8, and 9 are linearized by *Sal I* digestion. *Lanes* 2 and 4 BED·Fe^{II} at 0.25 μM; lanes 3 and 5 BED·Fe^{II} at 0.06 μM; lanes 6 and 8 EBD·Fe^{II} at 0.25 μM; lanes 7 and 9 EBD·Fe^{II} at 0.06 μM.

Figure 2. Histogram of BED·Fe^{II} and EBD·Fe^{II} cleavage patterns from high-resolution denaturing gels. BED·Fe^{II} (1.0 μM) cleavage reactions on 5′ and 3′ end-labeled 517 bp DNA fragment (100 μM bp). EBD·Fe^{II} (1.0 μM) cleavage reactions on 5′ and 3′ end-labeled 517 bp DNA fragment (100 μM bp). Arrows represent amount of cleavage resulting in removal of indicated base. Solid boxes are the binding site. Assignment is based on the model described in ref 5b,c.

and a minor site contiguous to the five base pair sequence 5′-AATAA-3′ (Figure 2).

The multiple asymmetric cleavage patterns on opposite DNA strands presumably result from a diffusible oxidizing species, such as hydroxyl radical, generated in the minor groove of a right-handed DNA double helix.[5b,c,6,18] Like the tripeptides DE and ED, the dimer EBD can apparently assume two orientations on the DNA.[5,6] The eight base pair (5′-TTTTTATA-3′) and the five base pair (5′-AATAA-3′) binding sites suggest that the hydrocarbon tether allows both dimeric *and* monomeric binding modes. Changes in linker length and/or flexibility might lead to exclusive dimeric binding.

In conclusion, we have found that dimerization of EDTA-distamycin results in molecules capable of double-strand cleavage of DNA (25 °C, pH 7.9) at the eight base pair A + T recognition level and that function effectively at nanomolar concentrations. This work illustrates one approach for the design of double-strand DNA cleaving molecules with defined target sequences and binding site sizes.

Acknowledgment. We are grateful to the National Institutes of Health for grant support (GM-27681).

Registry No. 1, 87802-66-2; **2**, 78486-18-7; **3**, 87802-67-3; BED, 87802-68-4; BED·Fe(II), 87802-64-0; EBD, 87802-70-8; EBD·Fe(II), 87802-65-1; heptanedioic acid di-*N*-hydroxysuccinimide ester, 74648-14-9; heptanedioic acid monoimidazolide ester, 87802-69-5; Fe, 7439-89-6.

Supplementary Material Available: Autoradiograms used for results in Figure 2 (1 page). Ordering information is given on any current masthead page.

Syntheses and X-ray Crystal Structures of Two New Transition-Metal Complexes Having Diphosphene Ligands in Novel Bonding Modes[†]

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A number of recent publications have shown that diphosphenes, RP=PR, can bind in a variety of ways to transition metals. For example, the structures of four complexes in which the diphosphene behaves as a side-on ligand have been published.[1] More recently, the use of large substituents at phosphorus has permitted the isolation of the first end-on bonded complex [*trans*-{[Fe(CO)$_4$]$_2$[PCH(SiMe$_3$)$_2$]$_2$}] (**1**), where each phosphorus atom behaves as a simple two-electron donor.[2]

We now report the syntheses and X-ray crystal structures of two new complexes having diphosphene ligands in previously unobserved bonding modes.[3] The compounds are [Cr(CO)$_5$[PCH(SiMe$_3$)$_2$]$_2$] (**2**), in which only one of the phosphorus atoms behaves as a two-electron donor to a chromium atom, and [Fe(CO)$_4$[μ-Fe(CO)$_4$][P(2,4,6-*t*-Bu$_3$C$_6$H$_2$O)]$_2$] (**3**), where the diphosphene behaves both as a side-on and end-on bonded ligand to two iron atoms. Both **2** and **3** were synthesized by the reaction of the appropriate carbonylmetalate dianion with PCl$_2$[CH(SiMe$_3$)$_2$] or PCl$_2$(2,4,6-*t*-Bu$_3$C$_6$H$_2$O) in ether solution, and the workup was as previously described.[2] The yields (based on phosphorus) were 45% for **2**, orange-yellow crystals, mp 109–114 °C, and 40% for **3**, orange-red crystals, mp 190–191 °C.

The structures of both **2**[4a] and **3**[4b] were determined by single-crystal X-ray diffraction. For the chromium complex, Figure 1, it can be seen that the diphosphene ligand, (Me$_3$Si)$_2$CHP=PCH(SiMe$_3$)$_2$, is bound to chromium through one phosphorus atom only. This is in sharp contrast to the structure of **1** in which each phosphorus atom behaves as a donor to an Fe(CO)$_4$ moiety. We attribute this difference primarily to an increase in crowding, the Cr(CO)$_5$ fragment being larger than Fe(CO)$_4$. The result of the increased steric requirements of Cr(CO)$_5$ can be seen in Figure 1 where both Me$_3$Si groups on C(6) are oriented away from the Cr(CO)$_5$ moiety whereas in **1** the Me$_3$Si groups orient toward the smaller Fe(CO)$_4$. This conformational change effectively prevents coordination to a second Cr(CO)$_5$, and the unique structure observed is the result. The P(1)–P(2) distance, 2.027

[†] No reprints available.

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(3) See also: Cowley, A.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *J. Am. Chem. Soc.*, following paper in this issue.

(4) (a) Mo Kα radiation (λ = 0.71069 Å), T = 293 K; triclinic $P\bar{1}$, a = 9.139 (2) Å, b = 10.851 (1) Å, c = 18.059 (3) Å, α = 76.83 (1)°, β = 80.36 (2)°, γ = 65.01 (1)°; Z = 2; μ = 6.3 cm^{-1}; 2932 unique data, 324 parameters, R = 0.051. (b) Mo Kα radiation (λ = 0.71069 Å), T = 140 K; monoclinic $P2_1/c$, a = 11.243 Å, (3) Å, b = 29.250 (6) Å, c = 15.300 (3) Å, β = 110.67 (1)°; Z = 4; μ = 7.3 cm^{-1}; 6144 unique data, 319 parameters, R = 0.060.

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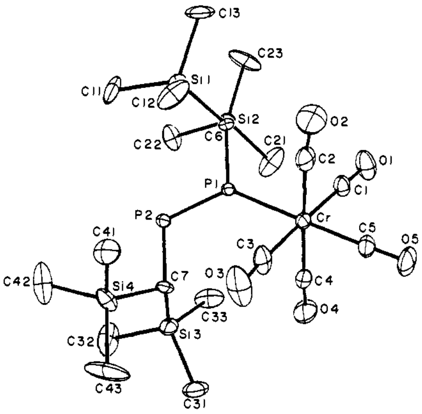

Figure 1. Computer-generated representative diagram for $[Cr(CO)_5[PCH(SiMe_3)_2]_2]$, **2**. Important bond distances (Å) and angles (deg): Cr(1)–P(1) 2.360 (2), P(1)–P(2) 2.027 (3), P(1)–C(6) 1.824 (6), P(2)–C(7) 1.836 (6), Cr(1)P(1)C(6) 120.7 (2), P(2)P(1)C(6) 105.6 (2), P(1)P(2)C(7) 105.9, Cr(1)P(1)P(2) 134.2 (1).

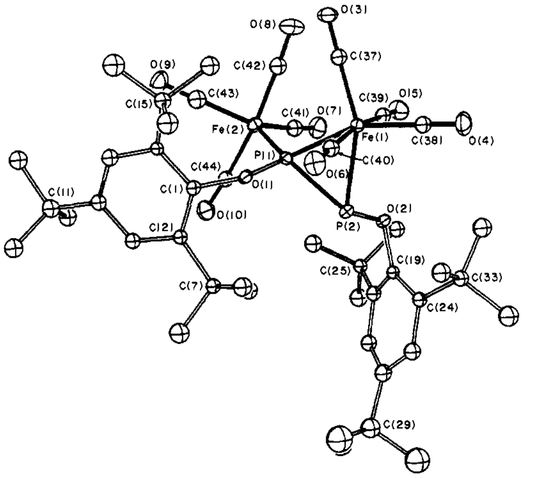

Figure 2. Computer-generated representative diagram for $[Fe(CO)_4[\mu\text{-}Fe(CO)_4][P(2,4,6\text{-}t\text{-}Bu_3C_6H_2O)]_2]$, **3**. Important bond distances (Å) and angles (deg): Fe(1)–P(2) 2.362 (2), Fe(1)–P(1) 2.347 (2), Fe(2)–P(1) 2.226 (2), P(1)–P(2) 2.184 (2), P(2)–O(2) 1.677 (6), P(1)–O(1) 1.681 (6), P(1)Fe(1)P(2) 55.3 (1), Fe(1)P(2)P(1) 62.0 (1), Fe(1)P(1)P(2) 62.7 (1), Fe(1)P(1)Fe(2) 124.9 (1), Fe(2)P(1)O(1) 118.7 (2), P(1)P(2)O(2) 112.7 (2), Fe(1)P(2)O(2) 108.0 (2), P(2)P(1)O(1) 95.1 (2), Fe(1)P(1)O(1) 102.7 (1).

(3) Å, is close to those found[2] in **1** (2.039 (1) Å) and in uncoordinated diphosphenes.[5] The angles C(7)P(2)P(1), 105.9 (2)°, and C(6)P(1)P(2), 105.6(2)°, are similar to the corresponding angles in **1**. The Cr(1)–P(1) distance of 2.360 (2) Å is normal for a trialkyl phosphine $Cr(CO)_5$ complex.

Figure 2 illustrates the structure of $[Fe(CO)_4[\mu\text{-}Fe(CO)_4][P(2,4,6\text{-}t\text{-}Bu_3C_6H_2O)]_2]$ (**3**). The unique feature of this molecule is the behavior of the diphosphene ligand as both a side-on (to Fe(1)) and end-on (to Fe(2)) bonding ligand. The effects of this novel binding scheme are (i), due to side-on bonding of the diphosphene to Fe(1), the P(1)–P(2) distance, 2.184 (2) Å, is considerably longer than the usual P–P double bond,[1,2,5] (ii) the diphosphene ligand remains in a trans configuration, (iii) the O(1)P(1)P(2)O(2) array is at an angle of ca. 94.0° to the Fe(1)P(1)P(2) plane; this allows each P atom to behave as a potential two-electron donor to Fe(2) while π-bonding to Fe(1). In the case of **3**, only one iron is end-on bound due to crowding by the bulky phosphorus substituents (this suggests that less crowded diphosphene complexes[1] should also coordinate additional metals). The P(1)–Fe(1) and P(2)–Fe(1) distances, 2.347 (2) and 2.362 (2) Å, are significantly longer than the P(1)–Fe(2) distance of 2.226 (2) Å. Such differences have been noted elsewhere[1] but are more evident here, perhaps because the aryloxy substituents make the P–P bond a poor side-on π-donor but enhance its π-acceptor properties when behaving as an end-on ligand. For the carbonyls bound to Fe(1), all the CO distances (mean 1.128 (6) Å) are consistently shorter than the CO distances at Fe(2) (mean 1.150 (6) Å) and vice versa for the Fe–C distances, Fe(1)–C(mean) = 1.827 (13) and Fe(2)–C(mean) = 1.787 (16) Å. This suggests that back donation from Fe(2) into CO is greater than for Fe(1) into CO or, in other words, that the side-on diphosphene is a better π-acceptor than the end on.

NMR data are as follows: $^{31}P\{^1H\}$ NMR:[6] **2**, d of d, 480.4, 474.1, 449.4, 443.0 ppm, $^1J_{PP}$ = 510 Hz; **3**, d of d, 237.1, 230.4, 196.8, 190.0 ppm, $^1J_{PP}$ = 532 Hz. ^1H NMR: **2**, 0.269, 0.30 ($SiMe_3$, d), 0.85 (CH, m) ppm; **3** 1.46, 1.65, 1.80 (*t*-Bu, m, m, s), 7.45 (aromatic CH, br s) ppm. IR ν_{CO} (Nujol): **2**, 2060 (sh, m), 1955 (sh, br), 1934 (sh, m) cm^{-1}; **3**, 2095, 2055, 2040, 2030, 2018, 1988, 1972, 1960 cm^{-1}.

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Registry No. **2**, 87841-54-1; **3**, 87830-08-8; $PCl_2[CH(SiMe_3)_2]$, 76505-20-9; $PCl_2(2,4,6\text{-}t\text{-}Bu_3C_6H_2O)$, 796-62-3; $Cr(CO)_5^{2-}$, 71518-79-1; $Fe(CO)_4^{2-}$, 22321-35-3.

Supplementary Material Available: Listing of atom coordinates, thermal parameters, bond distances and angles (5 pages). Ordering information is given on any current masthead page.

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[6] ^{31}P and ^1H NMR data were obtained in $CDCl_3$ solution. The chemical shifts (ppm) are relative to external 85% H_3PO_4 and Me_4Si, respectively.

Reactivity of Diphosphenes and Phosphaarsenes toward Metal Carbonyls

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Recent months have witnessed a flurry of activity in the chemistry of kinetically stabilized compounds featuring double bonds between group 4A and group 5A elements.[1] In group 5A, several diphosphenes (RP=PR),[2] phosphaarsenes (RP=AsR),[3]

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