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First Isolation and Structural Characterization of Bis(Anthracene)Metal Complexes: [Ti(η^6-$C_{14}H_{10}$)(η^4-$C_{14}H_{10}$)(η^2-dmpe)] and [Ti(η^4-$C_{14}H_{10}$)(η^2-$C_{14}H_{10}$)(η^5-C_5Me_5)]$^-$**

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Dedicated to Professor Wolfgang Beck
on the occasion of his 65th birthday

Reagents that function as storable sources of “naked” metal atoms or highly unsaturated organometallic groups offer exciting new possibilities in chemical syntheses owing to their facile reactions with a variety of small molecules and their strongly reducing nature.[1] Of particular significance in this regard are fused-ring arenemetal(0) complexes, which are of substantial interest as possible precursors for the general exploration of zerovalent transition metal chemistry by virtue of the remarkable lability of these arene ligands.[2] Outstanding among these are bis(naphthalene)metal(0) species,[3] for which conventional syntheses were recently reported for the first time.[4] Basolo has presented evidence to suggest that bis(anthracene)metal(0) complexes may be even more labile than their naphthalene counterparts.[5] The only previously known complex of this type, bis(anthracene)chromium(0), was obtained as an inseparable mixture of complex and excess free anthracene by the cocondensation of chromium atoms and anthracene vapor in a metal atom reactor.[6] To our knowledge, no ligand exchange reactions of this compound have been reported to date. The dearth of information on potentially interesting bis(anthracene)metal complexes prompted an investigation of their possible conventional syntheses by the interaction of main group metal anthracenes with transition metal halides. Previously, this approach yielded only mono(anthracene)metal complexes.[7] We now report on the syntheses and molecular structures of the first well-characterized metal complexes containing two coordinated anthracene ligands: [Ti($C_{14}H_{10}$)$_2$(dmpe)] (**1**, dmpe = 1,2-bis(dimethylphosphino)ethane) and [Ti($C_{14}H_{10}$)$_2$(C_5Me_5)]$^-$ (**2**, counterion [K(18-crown-6)(thf)$_2$]$^+$), THF = tetrahydrofuran). They are also of interest as the first structurally characterized Group 4 metal anthracene complexes.[8]

Reduction of [$TiCl_4$(dmpe)] or [$TiCl_3$(C_5Me_5)] by four equivalents of alkali metal anthracene (Na or K) in THF at −55 to −65°C gave deep red-brown or green-black solutions, from which **1** or [K(18-crown-6)(thf)$_2$]-**2** were isolated in 54 % or 28 % yield, respectively, as satisfactorily pure, diamagnetic and deep purple or black microcrystalline substances (see Experimental Section). Reactions of pure **1** (in the presence of an additional equivalent of dmpe) or **2** in THF at −55 to −65°C with normal pressures of carbon monoxide, under the same conditions described for the corresponding alkali metal naphthalene mediated carbonylations,[9,10] provided the known [Ti(CO)$_3$(dmpe)$_2$] (**3**)[11] or [Ti(CO)$_4$(C_5Me_5)]$^-$(**4**)[12] in 57 % or 62 % yields, respectively, of product isolated as the [K(18-crown-6)]$^+$ salt. These syntheses, summarized in Equations 1 and 2, are very similar to previously reported naphthalene anion routes to these carbonyls and lend substantial credence to original suggestions that labile (naphthalene)metal complexes were involved in these and related carbonylation reactions.[13, 14] The anthracene complexes **1** and **2** appear to be substantially more stable in solution and the solid state than corresponding (naphthalene)titanium species, which could not be isolated as pure substances despite numerous attempts.[15] Nevertheless, at least in their reactions with carbon monoxide, **1** and **2** function as effective sources of

$$[\mathrm{TiCl_4(dmpe)}] + 4\,\mathrm{NaC_{14}H_{10}} \xrightarrow[-60\,^\circ\mathrm{C}]{\mathrm{THF}} \mathbf{1} \xrightarrow[\substack{\mathrm{dmpe}\\ -55 \rightarrow 20\,^\circ\mathrm{C}}]{\mathrm{THF,\ CO}} \mathbf{3} \qquad (1)$$

$$[\mathrm{TiCl_3(C_5Me_5)}] + 4\,\mathrm{KC_{14}H_{10}} \xrightarrow[\substack{\text{18-C-6}\\ -60\,^\circ\mathrm{C}}]{\mathrm{THF}} \mathbf{2} \xrightarrow[-65 \rightarrow 20\,^\circ\mathrm{C}]{\mathrm{THF,\ CO}} \mathbf{4} \qquad (2)$$

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the highly unsaturated molecular fragments Ti(dmpe) and $[Ti(\eta^5\text{-}C_5Me_5)]^-$. Their reactions with similar small molecules are under investigation.

NMR solution spectra of **1** and **2** at or near room temperature established that their stoichiometries are identical to those observed in the solid state. HETCOR (i.e., $^1H,^{13}C$-correlated) NMR spectra of **1** permitted identification of four equally intense quaternary ^{13}C signals at $\delta = 127.5$, 133.9, 135.3, and 148.6, which are indicative of two inequivalent ligated anthracenes. ^1H NMR spectra showed four equally intense AA′BB′ multiplets below $\delta = 5.4$, which are assigned to hydrogen atoms on two different bound anthracene rings. These spectra were temperature independent up to about 30°C, when broadening of peaks due to bound anthracenes began to occur. Unique assignments of ^1H or ^{13}C resonances to the different anthracene ligands were not possible in most cases. However, along with other supporting NMR data, the presence of a quaternary ^{13}C signal at $\delta = 148.6$ is good evidence for the presence of one η^4-anthracene group,[16] but the hapticity of the other anthracene ligand in **1** in solution could not be definitely assigned with available data. In contrast, HETCOR NMR solution spectra of **2** at 25°C established that the anthracene ligands are equivalent: the ^1H and ^{13}C NMR spectra showed only five correlated resonances each. The absence of any anthracene ^1H resonances below $\delta = 5.4$ or quaternary ^{13}C resonances above $\delta = 133$ effectively ruled out the possibility that **2** was an 18-electron species with two equivalent η^4-anthracene groups. Indeed, of all previously known fused-ring arene complexes of zerovalent transition metals, $[Ni(\eta^2\text{-naphthalene})(iPr_2PC_2H_4PiPr_2)]$ (**5**)[17] and $[Ni(\eta^2\text{-anthracene})(PEt_3)_2]$ **6**,[7f] have NMR spectral features that appear to most closely match those of **2**. These exhibit arene hydrogen resonances only above $\delta = 5.3$, and both are highly fluxional molecules, which exist predominantly as η^2-arene complexes in solution.[17] Based on the similarity of the NMR spectra of **2**, **5**, and **6**, along with the X-ray results for **2** (vide infra), it is possible that **2** may exist in solution as the 16-electron species $[Ti(\eta^4\text{-}C_{14}H_{10})(\eta^2\text{-}C_{14}H_{10})(\eta^5\text{-}C_5Me_5)]^-$, where each anthracene ligand becomes equivalent by rapid concerted η^2 to η^4 equilibria of bound terminal rings. However, available data do not rule out involvement of the 16 or 14 electron species $[Ti(\eta^6\text{-}C_{14}H_{10})(\eta^5\text{-}C_5Me_5)]^-$ (which would be closely related to $[Ti(\eta^6\text{-}C_{10}H_8)(trmpsi)]$ (**7**, trmpsi = tBuSi$(CH_2PMe_2)_3$)[19]) or $[Ti(\eta^2\text{-}C_{14}H_{10})_2(\eta^5\text{-}C_5Me_5)]^-$, respectively. Clearly additional NMR studies are required to understand the solution behavior and structures of **1** and **2**.

Single crystal X-ray structural characterizations were carried out to provide detailed information on the nature of **1** and **2**.[18] Figures 1 and 2 depict their molecular structures and show that the complex $[Ti(\eta^6\text{-}C_{14}H_{10})(\eta^4\text{-}C_{14}H_{10})(\eta^2\text{-dmpe})]$ (**1**) is formally an 18 electron species, whereas $[Ti(\eta^4\text{-}C_{14}H_{10})(\eta^2\text{-}C_{14}H_{10})(\eta^5\text{-}C_5Me_5)]^-$ (**2**) is a 16-electron complex. All previous structurally characterized (arene)titanium(0) compounds, including compound **7**,[19] $[Ti(\eta^6\text{-arene})_2]$ (**8a**,**b**; arene = benzene, toluene),[20] and $[Ti(\eta^4\text{-}C_{10}H_8)_2(SnMe_3)_2]^{2-}$ (**9**),[21] are also 16-electron compounds. Compounds **1** and **2** represent rare examples of bis(arene)metal species containing identical arenes of different hapticities.[22a]

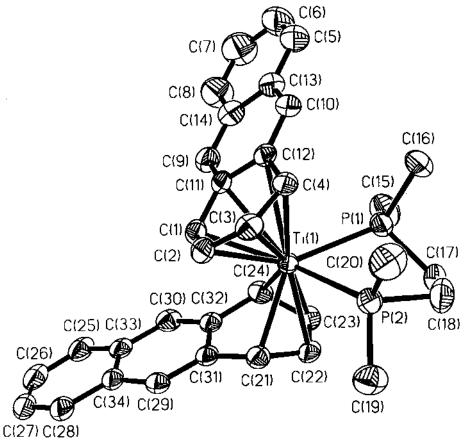

Figure 1. Molecular structure of **1** showing the labeling scheme. Thermal ellipsoids are drawn with 50% probability boundaries, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti–C(1) 2.311(4), Ti–C(2) 2.356(4), Ti–C(3) 2.341(4), Ti–C(4) 2.322(4), Ti–C(11) 2.603(4), Ti–C(12) 2.656(4), Ti–C(21) 2.343(4), Ti–C(22) 2.320(4), Ti–C(23) 2.354(4), Ti–C(24) 2.424(4), Ti–P(1) 2.593(1), Ti–P(2) 2.626(1), C(1)–C(2) 1.399(6), C(2)–C(3) 1.398(6), C(3)–C(4) 1.419(6), C(1)–C(11) 1.447(6), C(11)–C(12) 1.459(5), C(4)–C(12) 1.431(6), C(21)–C(22) 1.433(6), C(22)–C(23) 1.375(6), C(23)–C(24) 1.427(6), C(24)–C(32), 1.463(6), C(21)–C(31) 1.464(5) C(31)–C(32) 1.443(5), C–C$_{avg.}$ for uncoordinated "exonaphthalene" carbons 1.40(3), P–C$_{avg.}$ 1.83(1); P(1)-Ti-P(2) 74.44(1).

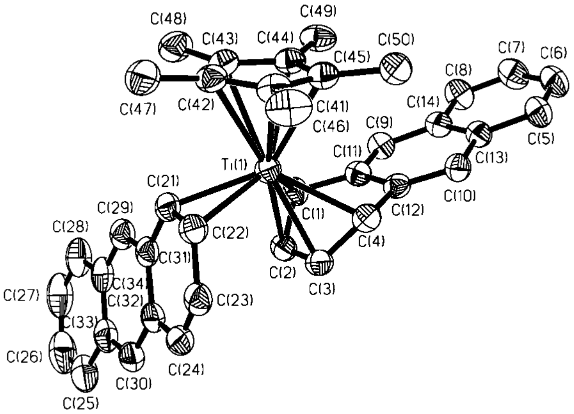

Figure 2. Molecular structure of **2** show the labeling scheme. Thermal ellipsoids are drawn with 50% probability boundaries, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Ti–C(1) 2.306(3), Ti–C(2) 2.295(3), Ti–C(3) 2.305(3), Ti–C(4) 2.322(3), Ti–C(21) 2.264(3), Ti–C(22) 2.273(3), Ti–C(41) 2.444(3), Ti–C(42) 2.509(3), Ti–C(43) 2.451(3), Ti–C(44) 2.399(3), Ti–C(45) 2.407(3), C(1)–C(2) 1.452(4), C(2)–C(3) 1.386(5), C(3)–C(4) 1.430(4), C(1)–C(11) 1.469(4), C(11)–C(12) 1.444(4), C(4)–C(12) 1.473(4), C(21)–C(22) 1.476(4), C(22)–C(23) 1.441(4) C(23)–C(24) 1.352(5), C(24)–C(32) 1.448(5), C(21)–C(31) 1.453(4), C(31)–C(32) 1.450(4), C–C$_{avg.}$ of uncoordinated "exonaphthalene" carbons 1.41(3), ring C–C$_{avg.}$ of C_5Me_5 1.420(7), C–Me$_{avg.}$ of C_5Me_5 1.507(6).

Although several mono(arene)metal(0) compounds are known to contain η^2- or η^4-arene units,[7, 17, 23] **2** appears to be the first well-characterized η^2-arene complex of a low-valent early transition metal.[22b]

Distinctly nonplanar η^4-anthracene groups are present in **1** and **2**. They consist of planar coordinated diene and uncoordinated exonaphthalene components, which have normal dihedral angles of 35.5° and 31.5°, respectively, for η^4-

anthracene complexes.[7e, 7i, 16] Coordinated diene portions of these anthracene groups have C–C distances that exhibit the usual long, short, long pattern characteristic of most early transition metal η^4-diene complexes and are indicative of the excellent acceptor ability of these ligands in **1** and **2**.[24] Little variation is seen in the Ti–C distances for the η^4-$C_{14}H_{10}$ group in **2**, and the average value of 2.31(1) Å is indistinguishable from the corresponding distance of 2.32(2) Å found in **9**, the only previously known (η^4-arene)titanium complex.[21] Analogous Ti–C distances in **1** are more variable and, except for Ti–C(22), are 0.02 to 0.13 Å longer than those in **2**. The longer Ti–C bonds in **1** relative to corresponding ones in **2** may be a result of a more crowded environment about the titanium center, since the titanium in **1** is formally seven coordinate (seven two-electron bonds), whilst that in **2** is six coordinate.

Another indication that the titanium center in **1** is relatively crowded is the fact that the Ti–C bonds to the η^6-anthracene unit are significantly longer in this complex than in **7**, which contains six-coordinate titanium.[19] Compounds **1** and **7** are otherwise closely related in that both contain fused-ring η^6-arenes, which are bent about C(1) and C(4) with dihedral angles of 15.1 and 12.4°, respectively. This folding results in three different sets of Ti–C distances, which for **1** have the following average values: Ti–C(1,4) 2.317(8), Ti–C(2,3) 2.35(1), and Ti–C(11,12) 2.63(3) Å. The Ti–C (quaternary) distances in **1** are about 0.27 Å longer than those in **7** and indicate that the formally η^6-anthracene unit is appreciably "ring-slipped" and has acquired a substantial degree of η^4-character.

The presence of the η^2-anthracene unit in **2** was unexpected. On the basis of the 18-electron formalism, both anthracenes should bind in a tetrahapto fashion, but the η^5-C_5Me_5 ligand may be sufficiently bulky to prevent this possibility. To our knowledge, the only other well-characterized (η^2-anthracene)-metal(0) compounds are the aforementioned nickel species of the formulation $[Ni(\eta^2\text{-}C_{14}H_{10})(PR_3)_2]$ (**6**, R = alkyl).[7b, f] As in the case of the nickel complexes, the η^2-anthracene group in **2** is nearly planar—the dihedral angle between the planes defined by C(21–23) and C(24–34) is only 6.2°. The C–C distances for the uncoordinated carbon atoms in the η^2-anthracene groups of **2** and the nickel complexes **6** are also similar and close to those reported for free anthracene.[25] However, the C–C distance of 1.476(4) Å of the two coordinated carbons in **2** is significantly longer than corresponding distances of 1.422(6) to 1.423(5) Å reported for **6**. This difference indicates that the 16-electron titanium(0) center more strongly participates in backbonding to the η^2-anthracene ligand than do the undoubtedly less strongly reducing 16-electron nickel(0) units. The average Ti–C distance of 2.268(5) Å for the η^2-anthracene group is longer than the Ti–C distances of 2.217–2.247(8) Å found for $[Ti(\eta^6\text{-}C_6H_6)_2]$ (**8a**),[20a] but shorter than those for the η^4-anthracene group in **2**, vide supra. Other structural parameters for **1** and **2** are unexpectional, including those of the $[K(18\text{-crown-6})(THF)_2]$ cation, which is well separated from **2** in the crystalline lattice. Extension of this study to the synthesis of related anthracene complexes of the early transition metals is currently under examination in this laboratory.

Experimental Section

1: A solution of $[TiCl_4(dmpe)]$ (1.75 g, 5.15 mmol) in THF (125 mL, −50°C) was added to a magnetically stirred slurry of $NaC_{14}H_{10}$ (21 mmol) in THF (100 mL, −60°C) and slowly warmed to 0°C over 4 h. The reaction mixture was then cooled to −60°C, filtered at −60°C, and warmed to 0°C. After removal of about 150 mL of THF in vacuo, excess pentane was added to precipitate a black microcrystalline powder. The latter was recrystallized from THF/pentane at 0°C to provide 1.54 g of **1** as sparkling black crystals. Correct C,H analysis, m.p. 194°C (with decomp.); ^{1}H NMR (300 MHz, $[D_8]$THF, 0°C, numbering as in Figure 1): $\delta = 0.92$, 1.06 (m, each 6H, PCH_3), 1.62, 2.29 (m, each 2H, PCH_2), 3.18, 3.94, 4.38, 5.38 (m, each 2H, $H_{1-4, 21-24}$), 6.08, 6.38 (s, each 2H, $H_{9, 10, 29, 30}$), 6.76, 7.02 (m, each 2H, $H_{5-8, 25-28}$); $^{13}C\{^1H\}$NMR (75.4 MHz, $[D_8]$THF, 0°C): $\delta = 13.8$, 15.7 (br, PCH_3), 27.7 (t, PCH_2), 77.3, 93.8, 105.1, 105.8 (s, $C_{1-4,21-24}$), 111.1, 120.8 (s, $C_{9, 10, 29, 30}$), 122.6, 123.9, 125.5, 125.7 (s, $C_{5-8, 25-28}$), 127.5 (s, $C_{11, 12}$), 133.9, 135.3 (s, $C_{13, 14, 33, 34}$), 148.6 (s, $C_{31, 32}$); $^{31}P\{^1H\}$NMR (121.4 MHz, $[D_8]$THF, 0°C): $\delta = 35.5$ (s, dmpe). $^1H,^{13}C$-correlated NMR spectra and trends previously established for monoanthracene or mononaphthalene metal(0) complexes,[7, 23] allowed resonances to be assigned to hydrogens and carbon on bound and unbound anthracene rings, but for quaternary carbon signals at $\delta = 148.6$ and 127.5, the available data were insufficient to permit more detailed assignments. X-ray quality dark purple, nearly black needles of **1** · THF were grown from pentane/THF at −30°C for one week under an argon atmosphere.[18a]

2: A solution of $[TiCl_3(C_5Me_5)]$ (1.43 g, 4.94 mmol) in THF (50 mL, 0°C) was added to a solution of $KC_{14}H_{10}$ (19.9 mmol) in THF (100 mL, 0°C). The reaction mixture was stirred at 0°C for 3 h. Following filtration at 0°C, 18-crown-6 (1.43 g, 5.4 mmol) was added and stirred with the filtrate for 3 h at 0°C. After removal of about 50 mL of solvent and filtration at −70°C, all but 25 mL of solvent was removed in vacuo. Addition of pentane (200 mL) caused precipitation of a black solid, which was recrystallized from THF/pentane and then THF/ether to give 1.36 g of microcrystalline black **2**. Correct C,H analysis, mp 165°C; ^{1}H NMR (300 MHz, $[D_8]$THF, 25°C, numbering as in Figure 2): $\delta = 1.65$ (s, 15H, $C_5(CH_3)_5$), 3.45 (s, 24H, 18-crown-6), 5.43, 5.77 (m, each 4H, $H_{1-4, 21-24}$), 6.62, 6.80 (m, each 4H, $H_{5-8, 25-28}$), 6.91 (s, 4H, $H_{9, 10, 29, 30}$); $^{13}C\{^1H\}$NMR (75.4 MHz, $[D_8]$THF, 25°C): $\delta = 15.9$ (s, $C_5(CH_{3)5}$), 76.0 (s, 18-crown-6), 108.5, 113.4 (s, $C_{1-4, 21-24}$), 118.9 (s, $C_{9, 10, 29, 30}$), 119.1 (s, $C_5(CH_3)_5$), 121.2, 124.8 (s, $C_{5-8, 25-28}$), 133.3 (s, $C_{11-14, 31-34}$). As in the case of **1**, $^1H,^{13}C$-correlated NMR spectra and trends previously established for similar complexes[7, 23] allowed resonances to be assigned to bound and unbound rings for the equivalent anthracene ligands in **2**. Black blocks of X-ray quality crystals of $[K(10\text{-crown-6})(THF)_2] \cdot$ **2** $\cdot$ 1/2 pentane were grown from pentane/THF at −30°C over a period of three weeks under an argon atmosphere.[18b]

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[18] a) Crystal data for **1**·THF: $C_{38}H_{44}OP_2Ti$, $M = 626.57$, monoclinic, $P2_{1/c}$, $a = 20.5789(1)$, $b = 9.6620(1)$, $c = 16.6477(2)$ Å, $\beta = 98.797(1)°$, $V = 3271.18(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.272\ \mathrm{g\,cm^{-3}}$, $F(000) = 1328$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.388\ \mathrm{mm^{-1}}$, $\lambda = 0.71073$ Å, $T = 173(2)$ K. The 16421 reflections measured on a Siemens SMART CCD area detector diffractometer yielded 5719 unique data ($2\theta_{max} = 50°$, $R_{int} = 0.0525$, semi-empirical absorption corrections). The structure was solved by direct methods and refined by full-matrix least-squares method on F^2 with statistical weighting, anisotropic displacement parameters, constrained isotropic H atoms to give $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.1581$ on all data, conventional $R = 0.0666$ on F values of 5720 reflections having $F_o^2 > 2\sigma(F_o^2)$, GOF = 1.095 for all F^2 values and 463 refined parameters. Largest difference peak and hole (e Å^{-3}): 0.690, −0.528. All calculations were performed with SGI INDY R4400-SC or pentium computers with SHEXTL-Plus program suite. b) Crystal data for $[K(18\text{-crown-}6)(thf)_2]\cdot\mathbf{2}\cdot 1/2$pentane: $C_{60.5}H_{81}KO_8Ti$, $M = 1023.25$, triclinic, $P\bar{1}$, $a = 13.0974(2)$, $b = 15.6482(2)$, $c = 15.7479(2)$ Å, $\alpha = 96.170(1)$, $\beta = 107.993(1)$, $\gamma = 111.119(1)°$, $V = 2775.09(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.225\ \mathrm{g\,cm^{-3}}$, $F(000) = 1098$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.282\ \mathrm{mm^{-1}}$, $\lambda = 0.71073$ Å, $T = 173(2)$ K. The 14.304 reflections measured on a Siemens SMART CCD area detector diffractometer yielded 9364 unique data ($2\theta_{max} = 50°$, $R_{int} = 0.0280$, semi-empirical absorption corrections). The structure was solved by direct methods and refined by the same procedure used for **1** to give $wR2 = 0.1711$ on all data, conventional $R = 0.0637$ on F values of 9368 reflections having $F_o^2 > 2\sigma(F_o^2)$, GOF = 1.075 for all F^2 values and 635 refined parameters. Largest difference peak and hole (e Å^{-3}): 1.771, −0.707. One molecule of pentane was located near an inversion center. It was ill-behaved until bond length constraints were employed for all 1,2 and 1,3 interatomic pairs after freeing C(3)S from placement on the inversion center. These atoms were refined isotropically with a common parameter for all carbon atoms. One large unidentified peak remains in the difference map near one of the THF oxygen atoms. Calculations were performed as detailed above for **1**. c) Crystallographic data (excluding structure factors) for the two structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100606. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code + (44)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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Distance Dependence of Photoinduced Electron Transfer in DNA

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The DNA helix is a useful molecular material for examining how the π stack mediates electron transfer. In recent years photoinduced electron transfers in DNA were investigated in many systems in which a donor and an acceptor randomly associate with DNA[1–6] or a donor and an acceptor are covalently linked at the terminus of DNA to avoid a multiplicity of the separation distance.[7, 8] The clearest evidence for mediation of electron transfer by the base pairs is the distance dependence; the efficiency of the reaction is represented by the β value. For a DNA–dye mixture, estimations of the β value have already been carried out.[3a,5b] Although a series of determinations of the β value is desirable, the lack of a method for introducing the dye precisely "into" the DNA helix makes it difficult to evaluate the distance dependence clearly. Here we report the distance dependence of electron transfer in a DNA helix using a novel system in which a chromophore is precisely fixed in DNA of defined sequence.

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