led to the immediate formation of orange solution formed immediately. Stirring for 16 h gave a dark orange-rust solution which was evaporated to dryness to give an orange-red solid. Yield: 0.088 g (88 %). ^{1}H NMR (C_6D_6): $\delta = 7.43$ (m, 6H; C_6H_5), 7.01 (m, 9H; C_6H_5), 5.83 (s, 5H; Cp), 0.50 (br s, 3H; CH_3), −0.03 (br s, 12H; $AlCH_3$), −0.21 (s, 6H; $AlCH_3$), −0.39 (m, 9H; $AlCH_3$); $^{31}P\{^1H\}$ (C_6D_6): $\delta = 25.2$ (s); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 134.2$, 132.1, 129.3, 127.3 (PC_6H_5), 113.2 (s; Cp), Al- and Ti-bound methyl resonances are unobserved. Elemental analysis calcd (%) for $C_{34}H_{50}Al_4NPTi$: C 61.91, H 7.64, N 2.12; found: C 61.65, H 7.37, N 2.01.

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[12] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-141319, and -141320. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Diffraction experiments were performed on a Siemens SMART System CCD diffractometer and solved by employing the SHELX-TL software package. Data for complex **3**: Orthorhombic, space group *Fdd*2; $a = 33.064(5)$ $b = 36.522(7)$, $c = 9.8244(19)$ Å, $V = 11\,863(4)$ Å^3, $Z = 16$, $R = 0.0449$, $Rw = 0.1103$, GOF = 1.104. Data for complex **6**: Orthorhombic, space group *Pbca*; $a = 18.825$ (3), $b = 18.7742(3)$, $c = 23.9904(4)$ Å, $V = 8479.0(2)$ Å^3, $Z = 8$, $R = 0.0517$, $Rw = 0.1291$. GOF = 1.034.

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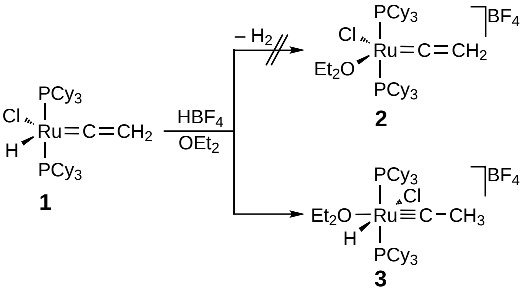
The First Example of an Equilibrium between a Carbene and an Isomeric Carbyne Transition Metal Complex[**]

Pablo González-Herrero, Birgit Weberndörfer, Kerstin Ilg, Justin Wolf, and Helmut Werner[*]

Dedicated to Professor Herbert W. Roesky
on the occasion of his 65th birthday

By attempting to generate a cationic, possibly solvated, vinylideneruthenium(II) complex with a 14-electron configuration at the metal center, we recently found that the reaction of the starting material **1** with HBF_4 in dichloromethane/diethyl ether leads to the formation of the ruthenium carbyne **3** instead of the anticipated ruthenium vinylidene **2** [Eq. (1)].[1] Although compound **3** is a highly efficient catalyst for olefin metathesis, including the cross-olefin metathesis of cyclopentene with methyl acrylate to afford multiply unsaturated esters $CH_2(C_5H_8)_nCHCO_2Me$ ($n = 1-3$), the lifetime of the cationic species containing a $Ru\equiv C$ bond is rather limited.[1, 2] We therefore set out to prepare more stable ruthenium(II) carbynes and discovered in the course of these studies the first example of an equilibrium between a cationic metal carbene and the isomeric cationic metal carbyne.



(1)

The dichloro(vinylidene)ruthenium(II) complex **4**[3] reacts with excess of HCO_2Na or CH_3CO_2Na in THF or acetone to give exclusively the monosubstituted products **5** and **6** in 77 and 82 % yield, respectively [Eq. (2); L = P*i*Pr$_3$]. The corresponding benzoato(chloro) complex **7** can be prepared from **4** and $PhCO_2H$ (ratio 1:1) in the presence of NEt_3. The reaction of **4** with either CF_3CO_2Na or CF_3CO_2K in THF or acetone leads, however, even after prolonged stirring, to a mixture containing **4**, **8** (major components), and the disubstituted compound **9** (minor component). Treatment of **4** with one

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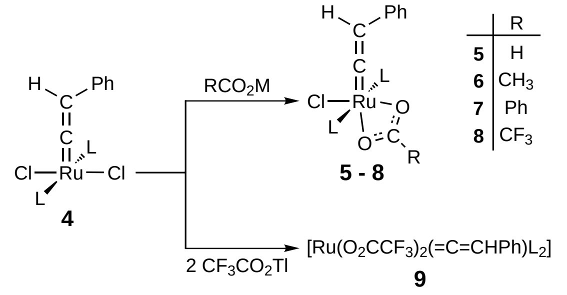
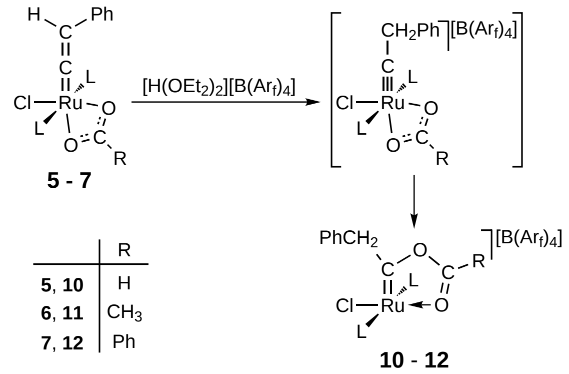


	R
5	H
6	CH_3
7	Ph
8	CF_3

(2)

equivalent of CF_3CO_2Tl in THF affords predominantly **8** (ca. 84%) together with small amounts (ca. 8% each) of **4** and **9**, which could not be separated either by fractional crystallization or column chromatography. An analytically pure sample of the bis(carboxylato) compound **9** was prepared in high yield from **4** and CF_3CO_2Tl (ratio 1:2.5) in acetone. The ^{13}C NMR spectra of **5**–**9** display, due to $^{13}C-^{31}P$ coupling, a triplet for the α-carbon atom of the vinylidene ligand at $\delta \approx 351-353$ (for **5**–**8**) and $\delta = 362.1$ (for **9**), the low-field chemical shift being typical for mononuclear vinylideneruthenium(II) complexes.[3, 4]

Protonation of **5**–**7** with $[H(OEt_2)_2][B(Ar_f)_4]$ ($Ar_f = 3,5-C_6H_3(CF_3)_2$)[5] in dichloromethane gave the cationic complexes **10**–**12** in nearly quantitative yield [Eq. (3); L = P*i*Pr$_3$]. While the ^1H and ^{13}C NMR spectra of **10**–**12** (typical features are given in the Supporting Information) could not provide conclusive proof as to whether a carbene- or a carbyneruthenium derivative was generated, the single-crystal X-ray structure analysis of **10** confirmed the formation of a metal carbene (Figure 1).[6] The coordination geometry around the ruthenium center is distorted square-pyramidal with the carbene carbon at the apical and the chloro, the oxygen, and the two phosphorus atoms at the basal positions. In contrast to the Cl-Ru-O1 axis, which is almost linear, the P1-Ru-P2 axis is significantly bent, both phosphorus atoms pointing away from the Ru–C1 bond. An analogous square-pyramidal configuration has been found for the ruthenium carbenes $[RuCl_2(=CHCH_2Ph)(PiPr_3)_2]$[7] and $[RuCl_2(=CHR)(PCy_3)_2]$ ($R = 4-C_6H_4Cl$, $CH=CPh_2$)[8] as well as for the related vinylidenes $[RuCl_2(=C=CHPh)L_2]$ (L = P*i*Pr$_3$, PCy$_3$).[3] Compared with the Ru–C bonds in $[RuCl_2(=CHCH_2Ph)(PiPr_3)_2]$ and $[RuCl_2(=CHR)(PCy_3)_2]$, the Ru–C1 bond length in **10** is rather short, whereas the C1–O2 distance is about 0.07–0.15 Å longer than in Fischer-type ruthenium carbenes containing a Ru=C(OR)R′ unit.[9] The plane of the chelate ring (Ru, C1, O2, C9, O1) (main deviation from planarity 0.017 Å) lies essentially perpendicular to the plane containing the ruthenium and the phosphorus atoms, which probably minimizes the steric repulsion between the ring atoms and the isopropyl groups. With regard to the mechanism of formation of **10**–**12**, we assume that in the initial step a cationic six-coordinate carbyne complex is generated as an intermediate [see Eq. (3)] which affords the more stable metal carbene by an intramolecular 1,2-shift of the weakly bound carboxylate oxygen atom to the carbyne carbon atom.



	R
5, 10	H
6, 11	CH_3
7, 12	Ph

(3)

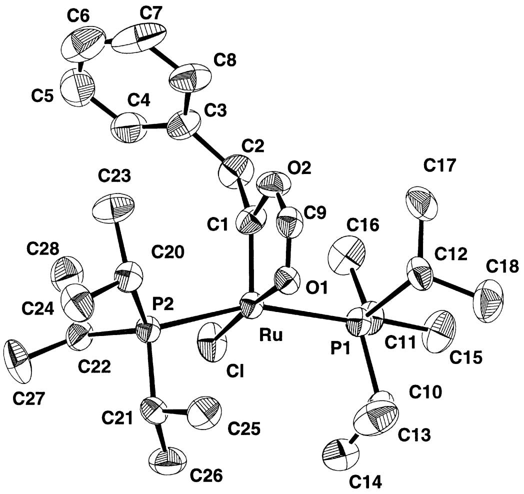
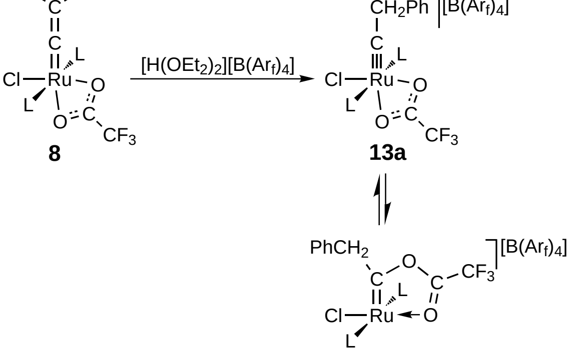


Figure 1. Molecular structure of the cation of **10**. Selected bond lengths [Å] and angles [°] with estimated standard deviations: Ru-C1 1.787(7), Ru-Cl 2.3306(17), Ru-O1 2.108(4), Ru-P1 2.4291(19), Ru-P2 2.4569(19), O1-C9 1.211(8), O2-C9 1.309(8), C1-O2 1.453(7), C1-C2 1.521(10); C1-Ru-O1 79.6(2), C1-Ru-Cl 105.5(2), C1-Ru-P1 97.2(2), C1-Ru-P2 103.4(2), Cl-Ru-O1 174.93(14), P1-Ru-P2 159.11(6), Cl-Ru-P1 88.36(6), Cl-Ru-P2 89.55(6), O1-Ru-P1 91.42(12), O1-Ru-P2 88.85(12), Ru-C1-C2 135.6(5), Ru-C1-O2 117.0(5), C2-C1-O2 107.2(6), C1-O2-C9 111.2(5), O1-C9-O2 122.3(6), Ru-O1-C9 109.9(4), C1-C2-C3 117.1(6).

Following the hypothesis that nucleophilic attack at the carbyne carbon atom would be less favored with an electron-poor carboxylato ligand, we also treated compound **8** with $[H(OEt_2)_2][B(Ar_f)_4]$ [Eq. (4); L = P*i*Pr$_3$]. Despite the presence of small amounts of **4** and **9** in the starting material, an analytically pure product **13** could be isolated by crystallization from dichloromethane at −78 °C. The composition of **13**



13b

(4)

was analogous to that of **10**–**12** and corresponded to that of a 1:1 adduct of **8** and $HB(Ar_f)_4$. However, in contrast to **10**–**12**, the signals in the ^1H and ^{31}P NMR spectra of **13** at room temperature are somewhat broad, indicating that in solution a dynamic process takes place. A variable-temperature NMR study (using CD_2Cl_2 as the solvent) confirmed that indeed in solution two different species are present. Thus, at 190 K the ^{31}P NMR spectrum displays two sharp singlets at $\delta = 61.7$ and 50.8 which coalesce at 230 K and give rise to one singlet at $\delta = 56.5$ at 293 K. Similarly, in the ^1H NMR spectrum two signals are observed for the $\mathrm{C}\mathit{H}_2\mathrm{Ph}$ protons at $\delta = 5.20$ and 4.59 (intensity ratio 1:2) at 190 K which coalesce at about 225 K and afford one singlet at $\delta = 4.88$ at 290 K. Since the chemical shift of the more intense resonance signal at $\delta = 4.59$ is almost identical to that of the ruthenium carbyne $[RuCl_2(\equiv CCH_2Ph)(P\mathit{i}Pr_3)_2][B(Ar_f)_4]$,[10] and the chemical shift of the less intense resonance signal at $\delta = 5.20$ is comparable to that of the ruthenium carbenes **10**–**12**, we conclude that in solution an equilibrium between the two isomers **13a** and **13b** [Eq. (4)] exists. The difference in free energy between **13a** and **13b** has been calculated as 0.25 kcal mol^{-1} at 180 K.[11]

An X-ray diffraction study revealed that the single crystals, which precipitated from a solution of **13** in dichloromethane at −78 °C, consisted of the dominating isomer **13a**.[6] The coordination geometry around the metal center (see Figure 2) can be described as distorted octahedral with a significant bending of the C1-Ru-O1 axis. The Ru–C1 bond length of 1.660(4) Å is one of the shortest M–C bond lengths found for carbyne transition metal complexes.[12] Apart from the nearly linear Ru-C1-C2 axis, the most characteristic structural feature of **13a** is the difference between the distances Ru–O1 (2.336(3) Å) and Ru–O2 (2.133(3) Å). This significant difference not only indicates that the Ru–O1 interaction is rather weak, but also explains why there is only a low energy barrier for the interconversion between the two isomers **13a** and **13b**. A similar bonding situation of the trifluoroacetato ligand exists in the enynylruthenium(II) compound $[Ru\{C(=CHPh)(C\equiv CPh)\}(\kappa^2\text{-}O_2CCF_3)(CO)(PPh_3)_2]$, in which the bond lengths Ru–O1 and Ru–O2 are 2.353 and 2.234 Å, respectively.[13] It should be emphasized that if the single crystals studied crystallographically are dissolved in CD_2Cl_2, the ^1H and ^{31}P NMR spectra of the solution equally display somewhat broadened signals indicating that the equilibrium between **13a** and **13b** is regenerated. Moreover, it is worth mentioning that to the best of our knowledge **13a** is the first carbyneruthenium complex which has been studied crystallographically.

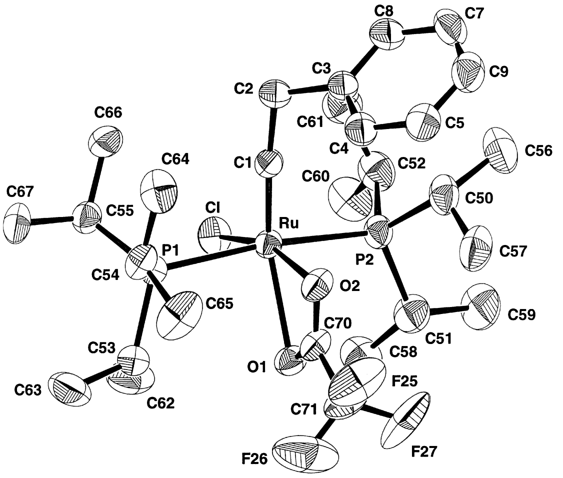


Figure 2. Molecular structure of the cation of **13a**. Selected bond lengths [Å] and angles [°] with estimated standard deviations: Ru-C1 1.660(4), Ru-Cl 2.3143(11), Ru-O1 2.336(3), Ru-O2 2.133(3), Ru-P1 2.4823(11), Ru-P2 2.4922(11), C1-C2 1.489(6), C2-C3 1.524(7), O1-C70 1.244(5), O2-C70 1.253(5); C1-Ru-O1 154.74(16), C1-Ru-O2 96.18(16), C1-Ru-Cl 102.35(15), C1-Ru-P1 95.06(14), C1-Ru-P2 93.40(14), O1-Ru-O2 58.56(11), O1-Ru-Cl 102.90(8), O1-Ru-P1 86.58(8), O1-Ru-P2 88.09(8), O2-Ru-Cl 161.45(9), O2-Ru-P1 92.23(9), O2-Ru-P2 92.26(9), Cl-Ru-P1 85.23(4), Cl-Ru-P2 87.66(4), P1-Ru-P2 169.94(4), Ru-C1-C2 173.0(4), C1-C2-C3 110.9(4), Ru-O1-C70 84.8(2), Ru-O2-C70 93.8(3), O1-C70-O2 122.9(4).

In summary, we have shown that, by using $[H(OEt_2)_2][B(Ar_f)_4]$ as the proton source, vinylideneruthenium(II) complexes of the general composition $[RuCl(\kappa^2\text{-}O_2CR)(=C=CHPh)(P\mathit{i}Pr_3)_2]$ (R = H, CH_3, Ph, CF_3) can be readily protonated at the β-carbon atom of the vinylidene unit to give the corresponding cationic carbyneruthenium derivatives. The main conclusion is that it critically depends on the substituent R of the carboxylate whether a subsequent intramolecular shift of the carboxylate oxygen atom to the carbyne carbon atom to give a carbene is energetically preferred. For R = CF_3, the difference in energy between the metal carbyne and the metal carbene is quite small and therefore it is possible to observe—as far as we are aware for the first time—[12, 14] an equilibrium between two isomers containing a M≡C and a M=C bond.

Experimental Section

All reactions were carried out under argon. The NMR data of the phenyl groups and the $B(Ar_f)_4^-$ ion are omitted for clarity. Abbreviations: v = virtual coupling, $N = {}^3J(P,H) + {}^5J(P,H)$ or ${}^1J(P,H) + {}^3J(P,H)$.

The syntheses and spectroscopic data of compounds **5**–**8** and **10**–**12** are given in the Supporting Information.

13a: A mixture of **8** (and small amounts of **4** and **9**; in total 181 mg, proportion of **8** 84 %, 0.27 mmol of Ru) and $[H(OEt_2)_2][B(Ar_f)_4]$ (268 mg, 0.27 mmol) was treated with CH_2Cl_2 (2 mL) at −78 °C. The resulting suspension was stirred and allowed to warm to room temperature for about 15 min. Addition of pentane (20 mL) to the brown-orange solution led to the precipitation of a yellow solid which was recrystallized from CH_2Cl_2 (2 mL) at −78 °C; yield 347 mg (99 % based on initial content of **8** in the starting material); m.p. 97 °C (decomp); ^1H NMR (400 MHz, CD_2Cl_2, −20 °C): $\delta = 4.86$ (br, 2H; $\mathrm{C}\mathit{H}_2\mathrm{Ph}$), 2.62 (m, 6H; $\mathrm{PC}\mathit{H}\mathrm{CH_3}$), 1.30 (dvt, $N = 14.8$, $^3J(H,H) = 7.2$ Hz, 18H; $\mathrm{PCHC}\mathit{H}_3$), 1.27 (dvt, $N = 15.3$, $^3J(H,H) = 7.2$ Hz, 18H; $\mathrm{PCHC}\mathit{H}_3$); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, −20 °C): $\delta = 64.9$ (s; $\mathit{C}\mathrm{H_2Ph}$), 24.8 (vt, $N = 10.2$ Hz; $\mathrm{P}\mathit{C}\mathrm{HCH_3}$), 19.6, 19.0 (both s; $\mathrm{PCH}\mathit{C}\mathrm{H_3}$), $\mathrm{Ru}\equiv\mathit{C}$, $\mathit{C}\mathrm{F_3CO_2}$ and $\mathrm{CF_3}\mathit{C}\mathrm{O_2}$ not observed; $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, −20 °C): $\delta = 56.5$ (br); ^{19}F NMR (376.4 MHz, CD_2Cl_2, −20 °C): $\delta = -73.96$ (br; $\mathrm{C}\mathit{F}_3\mathrm{CO_2}$).

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[6] Data for the X-ray structure analyses: **10**: Crystals from $CHCl_3$, $C_{59}H_{62}BClF_{24}O_2P_2Ru$ ($M_r = 1468.36$); crystal size $0.25 \times 0.20 \times 0.20$ mm^3; monoclinic, $P2_1/n$ (no. 14), $a = 20.287(4)$, $b = 15.739(2)$, $c = 20.271(5)$ Å, $\beta = 92.52(1)°$, $Z = 4$, $V = 6466(2)$ Å^3, $\rho_{calcd} = 1.508$ g cm^{-3}; $T = 193(2)$ K; $2\theta = 50.06°$; 11694 reflections measured, 11351 were unique ($R_{int} = 0.0325$), and 6414 observed ($I > 2\sigma(I)$); CAD4 (Enraf-Nonius), $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite-monochromated; LP and empirical absorption correction (Ψ scans, min. transm. 91.35%). The structure was solved by the Patterson method (SHELXS-97); G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467) and refined with the full-matrix-least-squares method (SHELXL-97; G. M. Sheldrick, a program for crystal structure refinement, University of Göttingen, **1993**); $R_1 = 0.0678$, $wR_2 = 0.1293$ (for 6414 reflections with $I > 2\sigma(I)$), $R_1 = 0.1377$, $wR_2 = 0.1649$ (for all 11351 data); data-to-parameter ratio 12.94; residual electron density $+0.585/-0.508$ e Å^{-3}. The hydrogen atoms H2A, H2B, and H9 were found in a differential Fourier synthesis and refined isotropically by setting the displacement parameter to 120% of the equivalent isotropic U_{eq} value of C2 and C9. One CF_3 group of the anion was found rotation disordered. Two independent positions were found and refined anisotropically with the occupancy factors 80:20 with restraints to have the same U_{ij} components and the anisotropic displacement parameters in the direction of the bond. **13a**: Crystals from CH_2Cl_2, $C_{60}H_{61}BClF_{27}O_2P_2Ru$ ($M_r = 1536.36$); crystal size $0.21 \times 0.19 \times 0.15$ mm^3; monoclinic, $P2_1/n$ (no. 14), $a = 18.882(3)$, $b = 15.579(1)$, $c = 22.468(3)$ Å, $\beta = 91.40(2)°$, $Z = 4$, $V = 6607(1)$ Å^3, $\rho_{calcd} = 1.544$ g cm^{-3}; $T = 173(2)$ K; $2\theta = 50.06°$; 62685 reflections measured, 11647 were unique ($R_{int} = 0.0701$), and 7096 observed ($I > 2\sigma(I)$); IPDS (Stoe), $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite-monochromated. The structure was solved and refined as described for **10**; $R_1 = 0.0470$, $wR_2 = 0.1121$ (for 7096 reflections with $I > 2\sigma(I)$), $R_1 = 0.0825$, $wR_2 = 0.1270$ (for all 11647 data); data-to-parameter ratio 11.92; residual electron density $+0.633/-1.108$ e Å^{-3}. The CF_3 group of the trifluoroacetato ligand was found disordered and refined anisotropically with restraints on U_{ij} and occupancy factors of 78:22. Also three of the CF_3 substituents on the $B(Ar_f)_4$ counterion were found rotation disordered and refined in the same way (occupancy factors: 66:36 (F4–F6), 78:22 (F7–F9) and 56:44 (F22–F24). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-142920 (**10**) and CCDC-142921 (**13a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Model Studies of Phytochrome Photochromism: Protein-Mediated Photoisomerization of a Linear Tetrapyrrole in the Absence of Covalent Bonding[**]

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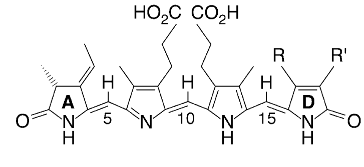
Dedicated to Professor Günther Wilke
on the occasion of his 75th birthday

Open-chain tetrapyrroles, such as phytochromobilin (**1**) and phycocyanobilin (**2**), serve as chromophores in a number of chromoproteins. Their photoreactivity is largely regulated by the protein environment. Whereas **2** functions as an antenna chromophore in the light-harvesting pigments of cyanobacteria,[1] **1** is the chromophore of the plant photoreceptor phytochrome,[2] where it reversibly photoisomerizes around the $C_{15}-C_{16}$ double bond thereby converting the physiologically dormant P_r form into the active P_{fr} state.[2, 3] This photochromic control, triggered by a double-bond isomerization, is not restricted to **1**. For example, **2** in the phytochrome of the alga *Mesotaenium caldariorum* functions as a photochemical trigger analogous to **1**.[4] Furthermore, **2** can also assume this role in recombinant phytochromes of higher plants.[5] In all these photoreceptors, the chromophore is invariably bound by a covalent thioether bond to a cysteine residue of the protein.



1 $R = CH_3$, $R' = CH{=}CH_2$
2 $R = CH_3$, $R' = CH_2CH_3$
3 $R = CH{=}CH_2$, $R' = CH_3$

We have now explored whether covalent chromophore bonding to the apoprotein is a prerequisite to the phototrigger function. We find, for the first time, that such is not the case. Rather, the chromophore binding pocket of the apoprotein can accommodate a chromophore sufficiently well to control the host–guest interactions driving the $P_r \rightleftarrows P_{fr}$ photocycle, without the need for covalent bonding.

The boundary conditions for the influence of the protein matrix on the absorption and photochemical properties of the phytochrome chromophore have not yet been studied thoroughly. The regioselective double-bond photoisomerization at

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