first part of this statement has now been verified, possibly a consequence of the previously observed property of metallabenzenes to form more stable metal – π bonds than classical arenes.[3] An additional intra-ring interaction of the two ring metals, as observed for the first time in **2**, could make a further contribution to the stabilization of multidecker structures.

Experimental Section

2: A solution of bis(dimethylpentadienyl)ruthenium (**1**) (0.29 g, 1.0 mmol) in nonane (35 mL) was refluxed with $Ru_3(CO)_{12}$ (1.28 g, 2.0 mmol) overnight. The solvent was evaporated under reduced pressure and the residue was taken up in hexane and purified by chromatography on silica gel. The yellow fraction was collected and recrystallized from benzene or toluene, yield 0.11 g (17%). ^{13}C NMR (125.7 MHz, CD_2Cl_2): $\delta = 198.9$ (CO), 193.9 (CO), 128.3 (C1), 111.3 (C2), 94.4 (C3), 25.5 (CH_3); ^1H NMR (500 MHz, CD_2Cl_2): $\delta = 6.23$ (t, $^4J = 1.5$ Hz, 2H), 5.62 (d, $^4J = 1.5$ Hz, 4H), 1.72 (s, 12H, CH_3); IR (cm^{-1}, hexane): $\tilde{\nu} = 2074$ m, 2049 m, 2010 s, 1995 w, 1980 m.

Received: March 13, 1998 [Z11585IE]
German version: *Angew. Chem.* **1998**, *110*, 2196 – 2197

Keywords: aromaticity · carbonyl complexes · metallacycles · metal – metal interactions · sandwich complexes

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[8] a) Crystal structure analysis: $C_{20}H_{18}O_6Ru_3$, ENRAF-Nonius CAD4; $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, graphite monochromator; intensity collection with ω-2θ range at 203 K. Fragment of a yellow platelet $0.6 \times 0.4 \times 0.3$ mm, triclinic, space group $P\bar{1}$ (no. 2); $a = 8.563(3)$, $b = 9.103(3)$, $c = 15.607(3)$ Å, $\alpha = 105.55(2)$, $\beta = 98.25(3)$, $\gamma = 109.03(3)°$, $V = 1071.8(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.037$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 20.81$ cm^{-1}, $F(000) = 636$; 4790 reflections registered with $3 < \theta < 26°$, absorption correction by the Gauss-method[14] with transmission coefficients between 0.477 and 0.588, 4082 symmetry-independent reflections with $I > \sigma(I)$ in structure solution[15] and refinement[16] for 263 parameters; all hydrogen atoms were refined isotropically, $R = 0.023$, $R_w = 0.045$, $w^{-1} = \sigma^2(F_o)$. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101246. 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).

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Mechanism of Reduction of Diphenylacetylene by Metallic Lithium

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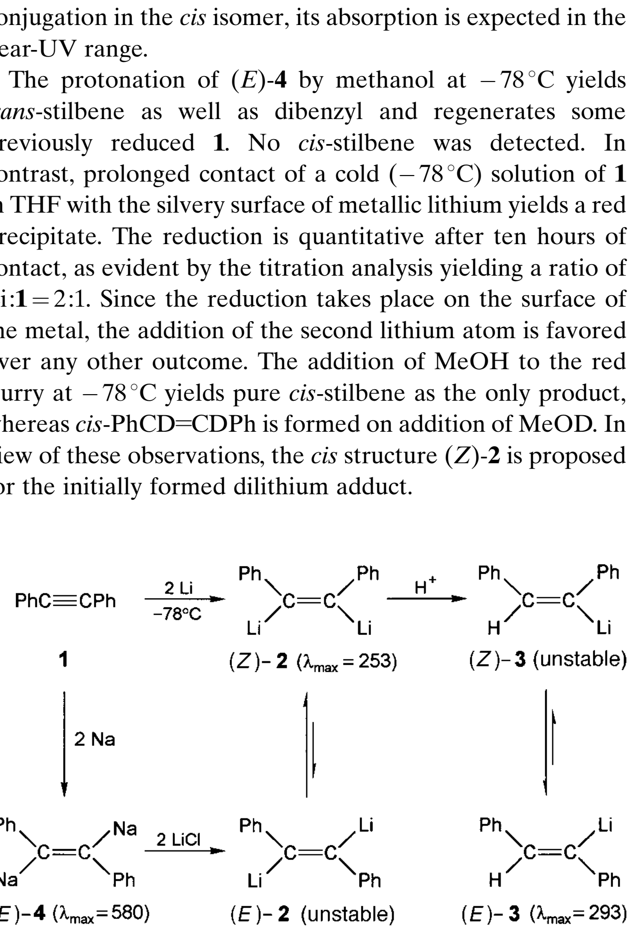
The reduction of a cold (– 78 °C) solution of diphenylacetylene (tolane, **1**) in THF by metallic sodium or lithium was reported previously.[1] When the solution is kept for five hours in contact with a sodium mirror, **1** is reduced quantitatively to the disodium adduct (*E*)-**4**. Its absorption at long wavelength ($\lambda_{max} = 580$ nm, $\varepsilon = 6.4 \times 10^4$) implies a conjugated *trans* structure of the adduct. Since steric hindrance prevents the conjugation in the *cis* isomer, its absorption is expected in the near-UV range.

The protonation of (*E*)-**4** by methanol at – 78 °C yields *trans*-stilbene as well as dibenzyl and regenerates some previously reduced **1**. No *cis*-stilbene was detected. In contrast, prolonged contact of a cold (– 78 °C) solution of **1** in THF with the silvery surface of metallic lithium yields a red precipitate. The reduction is quantitative after ten hours of contact, as evident by the titration analysis yielding a ratio of Li:**1** = 2:1. Since the reduction takes place on the surface of the metal, the addition of the second lithium atom is favored over any other outcome. The addition of MeOH to the red slurry at – 78 °C yields pure *cis*-stilbene as the only product, whereas *cis*-PhCD=CDPh is formed on addition of MeOD. In view of these observations, the *cis* structure (*Z*)-**2** is proposed for the initially formed dilithium adduct.



The addition of a cold solution of LiCl in THF to the cold solution of (*E*)-**4** yields again the red precipitate that forms *cis*-stilbene on protonation by MeOH. Apparently, the *trans*-disodium adduct (*E*)-**4** is converted into the *cis*-dilithium adduct upon substitution of sodium by lithium. Although the mechanism of this conversion is unknown, we might conclude that the *cis*-dilithium adduct (*Z*)-**2** is more stable than its *trans* isomer (*E*)-**2**.

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1433-7851/98/3715-2136 $ 17.50+.50/0

The red precipitate dissolves on warming its slurry to 25 °C. Monoprotonation by THF[1] produces the easily isomerized[2] vinyl carbanion (*Z*)-**3**, which is rapidly converted into (*E*)-**3** (absorbing at $\lambda_{max} = 293$ nm). *trans*-Stilbene is formed on addition of MeOH, and *trans*-PhCD=CHPh when MeOD is added.

Reactions of radical anions and carbanions are profoundly affected by the nature of cations and solvents.[3–6] The reduction of **1** in other solvents could be instructive, especially in diethyl ether. Then the undesired protonation by the solvent might be avoided. Indeed, no deuterated products were produced when the solution of (*Z*)-**2** in perdeuterated diethyl ether was kept at 25 °C for 24 hours.

A cold (−78 °C) solution of **1** in diethyl ether is reduced quantitatively to the *soluble* adduct (*Z*)-**2** when kept in contact with the silvery surface of lithium for ten hours. The shape of the spectrum of (*Z*)-**2** ($\lambda_{max} = 253$ nm, $\varepsilon = 1.6 \times 10^4$) remains unaltered in the course of the reduction despite its rising intensity. This observation complies with the known high degree of disproportionation of lithium salts of radical anions in diethyl ether.[7]

The strikingly different spectra of the dilithium adduct in diethyl ether and that of the disodium adduct in THF indicate their greatly diverse structures, which is unaccountable by the modification of their solvation or ionicity. Compound (*E*)-**4** seems to be a conjugated *trans* adduct, and (*Z*)-**2** a non-conjugated *cis* adduct. The results of their protonation and deuteration support this conjecture. Pure *cis*-stilbene is produced on addition of MeOH to a cold solution of (*Z*)-**2**, and *cis*-PhCD=CDPh is formed on addition of MeOD. In contrast, *trans*-stilbene is the product of protonation of (*E*)-**4**.

Cis-stilbene is still formed on protonation of a solution of (*Z*)-**2** in diethyl ether that is rapidly warmed to 25 °C. However, some slow reaction sets up at this temperature, as indicated by fading of the peak at 253 nm and the rising absorption at 278 nm (Figure 1). Monitoring these changes at 278 nm reveals the zero-order kinetics of this reaction (Figure 2). At ambient temperature this "253–278" conversion is completed within 24 hours. Thereafter, the addition of MeOH produces *trans*-stilbene, but surprisingly *trans*-PhCD=CHC$_6$H$_4$D is formed on addition of MeOD. The aromatic deuterium atom of this deuterated *trans*-stilbene is located in the *ortho* position (as shown by NMR spectroscopy), and the deuterated phenyl group is linked to the vinylic CH group. The latter conclusion is derived from the mass spectrum of the benzaldehyde formed by ozonolysis of the deuterated stilbene. Only peaks for C$_6$H$_5$CDO and C$_6$H$_4$DCHO are observed, but none for C$_6$H$_4$DCDO.

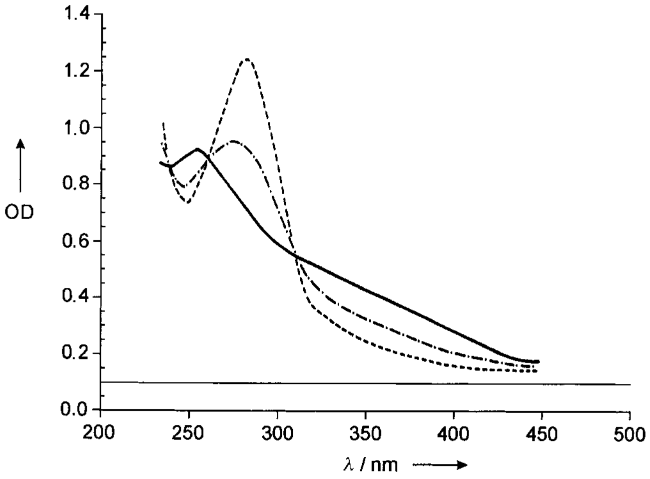


Figure 1. UV/Vis spectra (OD = optical density) of the initial *cis*-dilithium adduct (*Z*)-**2** ($\lambda_{max} = 253$ nm) and the product of its conversion (*E*)-**5** ($\lambda_{max} = 278$ nm): solution kept for 0 (–), 2 (-----), and 10 h (– · – · –) at room temperature. Note the isosbestic points at 257 and 310 nm.

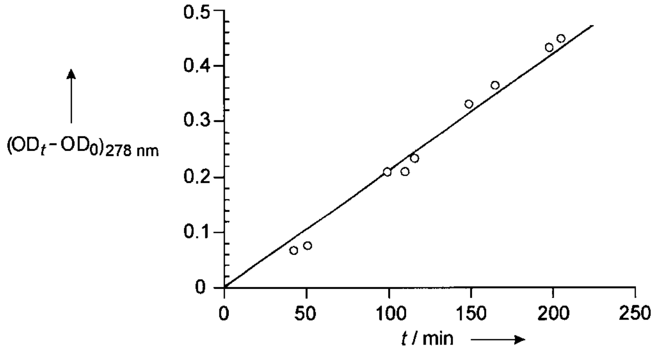


Figure 2. Plot of ($\mathrm{OD}_t - \mathrm{OD}_0$) versus time t for the dilithium adduct of diphenylacetylene in diethyl ether monitored at 278 nm: zero-order kinetics.

Although long-lived intermediates are not formed in the above process, as demonstrated by the isosbestic points at 257 and 310 nm, its zero-order kinetics implies that some intermediate present in minute concentration but regenerated by the reaction participates in the overall process. Two questions arise:

1) Why is *cis*-(*Z*)-**2** the most stable isomer of the dilithium adduct while, in contrast, *trans*-(*E*)-**4** is the stable isomer of the disodium adduct?

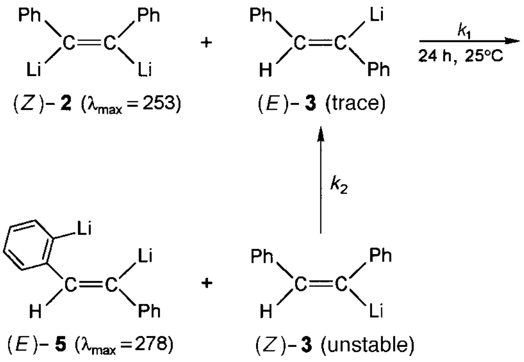
2) What is the mechanism of the 253–278 conversion that leads to the zero-order kinetics? Moreover, why does the addition of MeOD to the finally converted adduct lead to deuteration of a specific phenyl group?

The authors of reference [1] believed at the time of publication that the *trans*-dilithium adduct (*E*)-**2** should be more stable than its *cis* isomer (*Z*)-**2** because the conjugation stabilizing the *trans* adduct is lost for the *cis* isomer due to the steric hindrance. However, recent ab initio computations[8] revealed the double-bridged structure of vicinal dilithium adducts, which is contrast to that of the disodium adduct. The bridging allows each lithium atom to interact with both phenyl groups, thus providing even larger stabilization than the conjugation. The *cis* isomers are therefore still more stable than the *trans* isomers, even for monophenylated dilithioethenes,[9, 10] although the *trans* form seems to be preferred for the aliphatic dilithioethenes.[11, 12] Indeed, dialkylacetylenes yield exclusively the *trans*-dilithioalkenes on reduction by metallic lithium.[13] However, a direct *cis*–*trans* isomerization is precluded in the latter systems.[14]

The mechanism of the (*Z*)-**2** → (*E*)-**5** rearrangement, presented below, was proposed in the thesis of one of us.[10] It accounts for all the reported observations. The presence of a minute amount of moisture or any protonating agent in the solution of (*Z*)-**2** yields a tiny amount of monolithiated *trans*-

stilbene (*E*)-**3**. Its lithiation by (*Z*)-**2** then produces *ortho*-lithiated (*E*)-**5**, which absorbs at 278 nm and is the final product of the 253–278 conversion.

The proposed mechanism accounts for the formation of the *trans*-stilbene carrying two deuterium atoms, one vinylic and one aromatic, upon addition of MeOD. The monolithium adduct (*E*)-**3**, but not (*Z*)-**3**, is lithiated by (*Z*)-**2** since the agostic effect[15] of its vinylic lithium atom activates its *ortho* proton. The lack of activation of the (*Z*)-**3** protons accounts for its inertness. The isomerization of (*Z*)-**3** to (*E*)-**3** regenerates the latter and allows for the repetition of the process.



The 253–278 conversion is expected to accelerate on addition of the independently prepared intermediate (*E*)-**3** to the solution of the primary dilithium adduct (*Z*)-**2** in diethyl ether. This has been experimentally verified.[10] A solution of (*E*)-**3** (5 mmol), prepared by allowing lithium to react with α-chloro-*trans*-stilbene in diethyl ether, was added to one of two aliquots (6 mmol each) of the primary solution of the dilithium adduct (*Z*)-**2** in diethyl ether. After both aliquots had been kept at 20 °C for four hours, the analysis showed 10 % conversion in the aliquot containing the added (*E*)-**3**, but only 2 % in the other.

The intermediate (*E*)-**3** is continually formed through the isomerization of (*Z*)-**3** and destroyed by its reaction with (*Z*)-**2**. It is plausible to assume that its minute concentration is stationary, that is, $d[(E)\text{-}\mathbf{3}]/dt = k_2[(Z)\text{-}\mathbf{3}] - k_1[(Z)\text{-}\mathbf{2}]\cdot[(E)\text{-}\mathbf{3}] = 0$. Hence, $[(E)\text{-}\mathbf{3}] = k_2[(Z)\text{-}\mathbf{3}]/k_1[(Z)\text{-}\mathbf{2}]$, and the rate of the 253–278 conversion, equal to $k_1[(Z)\text{-}\mathbf{2}]\cdot[(E)\text{-}\mathbf{3}]$, is $k_2[(Z)\text{-}\mathbf{3}]$; that is it is constant for a constant concentration of (*Z*)-**3** but increases with increasing concentration of (*Z*)-**3**. The observed zero-order kinetics of the conversion is therefore accounted for at low concentrations of (*E*)-**3**.

Experimental Section

High-vacuum technique was used during this study. The oxides coating the chunks of lithium are stripped away by keeping the metal for a few hours in a solution of anthracene in diethyl ether. Shaking and decanting removed the anthracene and the stripped residues (see reference [16] for details of this operation to leave the chunks with a silvery surface). The stilbenes were isolated by evaporation of the solvents, and the residues were then recrystallized.

Received: January 26, 1997 [Z11409IE]
German version: *Angew. Chem.* **1998**, *110*, 2216–2218

Keywords: agostic interactions · kinetics · lithium · rearrangements · reductions

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Rearrangement of 5-Substituted 5-Aminopentadienals[**]

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Markus Neuenschwander[*]

*Dedicated to Professor Klaus Hafner
on the occasion of his 70th birthday*

As typical "push–pull" (PP) acetylenes,[1] dialkylaminopropinals react easily with carboxylic acids and HCl to give 3-X-substituted 3-aminopropenals, which nearly quantitatively rearrange to 3-acyloxy- and 3-chloroacrylicamides.[2, 3] Similarly, PP-enynes of type **1** are expected to add acids, while the hereby formed 5-substituted 5-aminopenta-2,4-dien-1-als **2** could be prone to a vinylogous rearrangement to give 5-substituted pentadienecarboxamides **6** after extrusion of X^- (**2**→**3**), ring closure (**3**→**4**), addition of X^- (**4**→**5**), and ring opening (**5**→**6**). Whereas simple PP-enynes **1** remained unknown for a long time,[4] they have been made available recently by two synthetic sequences.[5, 6] As a result, reactions of **1** with acids may be investigated in more detail now.

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[**] Aminoacrylic Compounds, Part 31. This work has been supported by the Swiss National Foundation (project no. 20–50331.97). Part 30: reference [7].