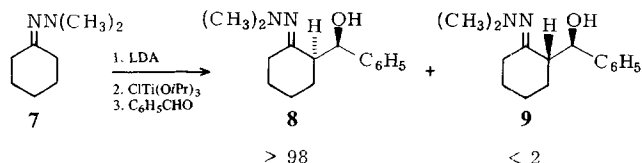


Table 1. *Erythro*-selective addition of titanium reagents **3** to aldehydes **4**.

R ¹	X	R ²	Conversion [%]	5 : 6
CH ₃	O <i>i</i> Pr	C ₆ H ₅	a (80)	91 : 9
CH ₃	NEt ₂	C ₆ H ₅	a (61)	85 : 15
C ₆ H ₅	O <i>i</i> Pr	C ₆ H ₅	b (95)	98 : 2
C ₆ H ₅	O <i>i</i> Pr	<i>p</i> -NO ₂ C ₆ H ₄	c (40)	98 : 2
C ₆ H ₅	O <i>i</i> Pr	CH ₃	d (95)	96 : 4
C ₆ H ₅	NEt ₂	CH ₃	d (50)	≈ 90 : 10
C ₆ H ₅	O <i>i</i> Pr	CH(CH ₃) ₂	e (78)	98 : 2
(CH ₃) ₂ CH	O <i>i</i> Pr	C ₆ H ₅	f (78)	94 : 6
CH ₃	O <i>i</i> Pr	CH ₃	g (61)	95 : 5
CH ₃	O <i>i</i> Pr	C(CH ₃) ₃	h (70)	93 : 7

pressure liquid chromatography^[1]. The product ratio was determined by analysis of the 400-MHz ¹H-NMR spectra.

The *erythro*-selectivity is also observed with titanated ketone-hydrazones (e.g. **7** → **8**), a finding which is to be compared with the *erythro*-selective behavior of titanium enolates from ketones^[5].



In the case of **3** (R¹ = C₆H₅, X = N(C₂H₅)₂) it was possible to record a ¹H-NMR spectrum which is in line with the *E*-configuration. The observed stereoselectivity is therefore surprising, because *E*-configured ketone-enolates usually react *threo*-selectively^[1,2]. In the case of a cyclic transition state, both chair and boat conformations are conceivable.

Aside from chlorotitanium trisopropoxide, titanium trisopropoxide can also be used for the titaniation. However, in this case ate-complexes are formed which show less pronounced *erythro*-selectivity. Finally, titanated Schiff bases likewise behave *erythro*-selectively.

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CAS Registry numbers:

1 (R¹ = CH₃), 7422-93-7; **1** (R¹ = C₆H₅), 65259-56-5; **1** (R¹ = (CH₃)₂CH), 13063-58-6; **3** (R¹ = CH₃, X = OCH(CH₃)₂), 83314-04-9; **3** (R¹ = CH₃, X = N(C₂H₅)₂), 83314-05-0; **3** (R¹ = C₆H₅, X = OCH(CH₃)₂), 83314-06-1; **3** (R¹ = C₆H₅, X = N(C₂H₅)₂), 83314-07-2; **3** (R¹ = (CH₃)₂CH, X = OCH(CH₃)₂), 83314-08-3; **4** (R² = C₆H₅), 100-52-7; **4** (R² = *p*-NO₂C₆H₄), 555-16-8; **4** (R² = CH₃), 75-07-0; **4** (R² = CH(CH₃)₂), 78-84-2; **4** (R² = C(CH₃)₃), 630-19-3; **5** (R¹ = CH₃, R² = C₆H₅), 83314-09-4; **5** (R¹ = C₆H₅, R² = C₆H₅), 83314-10-7; **5** (R¹ = C₆H₅, R² = *p*-NO₂C₆H₄), 83314-11-8; **5** (R¹ = C₆H₅, R² = CH₃), 83314-12-9; **5** (R¹ = C₆H₅, R² = CH(CH₃)₂), 83314-13-0; **5** (R¹ = (CH₃)₂CH, R² = C₆H₅), 83314-14-1; **5** (R¹, R² = CH₃), 83314-15-2; **5** (R¹ = CH₃, R² = C(CH₃)₃), 83314-16-3; **6** (R¹ = CH₃, R² = C₆H₅), 83314-17-4; **6** (R¹ = C₆H₅, R² = CH₃), 83314-18-5; **7**, 10424-93-8; **8**, 83314-19-6; **12**, 83314-20-9; *N*-propylidencyclohexanamine, 1195-49-9; titanium tetraisopropoxide, 546-68-9; Cl[TiOCH(CH₃)₂]₃, 20717-86-6; TiCl₄, 7550-45-0; BrTi(NEt₂)₃, 24690-84-4.

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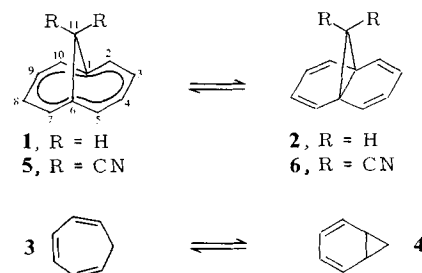
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Theoretical Investigations on the Valence Tautomerism between 1,6-Methano[10]annulene and Tricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene

By Dieter Cremer* and Bernhard Dick

1,6-Methano[10]annulene **1** must, on the basis of its physical and chemical properties, be described as a Hückel aromatic system with a delocalized π -electron decet^[1a-d]. Investigations on C-11-substituted 1,6-methano[10]annulenes, however, suggest that **1** can transform into the valence tautomer tricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene **2** in solution^[1c,d]. There is the possibility of a rapid reversible valence tautomerism of the type **1** \rightleftharpoons **2**, similarly to that assumed for the system cycloheptatriene **3** - norcaradiene **4**^[1e-g].



According to experimental and theoretical estimates^[2], **4** is destabilized by about 4–12 kcal/mol compared to **3**. Accordingly, the equilibrium **3** \rightleftharpoons **4** is shifted far over to the side of the cycloheptatriene. However, detection of the norcaradiene component has so far only been possible in an indirect way. Thus, **3** reacts like **1** with dienophiles to give Diels-Alder products, indicating a previous rearrangement **3** \rightleftharpoons **4** or **1** \rightleftharpoons **2**. However, it cannot be ruled out that the norcaradiene component is first formed at the moment of reactive collision with the dienophile^[2a].

To clarify this problem we have determined the energy profile of the valence tautomeric processes **1** \rightleftharpoons **2** and **3** \rightleftharpoons **4**, respectively, by *ab initio* calculations and therefrom obtained the energy differences $\Delta E = E(\mathbf{2}) - E(\mathbf{1})$ and $\Delta E = E(\mathbf{4}) - E(\mathbf{3})$ ^[3]. After taking into account vibration and entropy effects values of 4.5 and 5.6 kcal/mol, respectively, result for the difference in the free energies ΔG^0 , which corresponds to concentrations of about 0.05% **2** and 0.01% **4** at room temperature.

The valence tautomerization of **1**, like that of **3**, is characterized by an asymmetric double-well potential (Fig. 1). According to our calculations, an asymmetric single-well potential, as has been discussed for the 11-cyano-11-methyl derivative^[4a], can be ruled out for the rearrangement **1** \rightarrow **2**. For the energy barriers ΔE^\ddagger of the forward and reverse reactions, we find values of 7.3 and 2.3 kcal/mol, respectively. These values are about 3 kcal/mol smaller than the barriers calculated for the equilibrium **3** \rightleftharpoons **4**. Appar-

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ently formation of the cyclopropane bond is favored as a result of the shorter 1,6-distance in **1** (2.26 Å as opposed to 2.50 Å in **3**^[3]), whereas in **2** the interaction of the Walsh orbitals of the three-membered ring with the π -orbitals of the butadiene moieties indicates the far better π -conjugation in **1**.

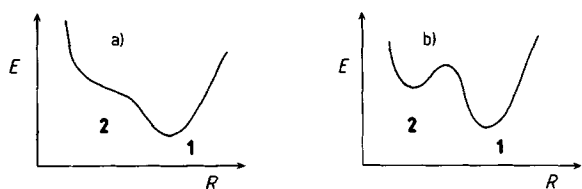


Fig. 1. Schematic representation a) of an asymmetric single-well potential and b) of an asymmetric double-well potential for the valence tautomeric equilibrium $1 \rightleftharpoons 2$. R is distance between C-1 and C-6.

According to experimental and theoretical investigations on cycloheptatrienes, substituents can shift the valence tautomeric equilibrium to the side of the norcaradiene^[4b-e]. Thus, Ciganek synthesized 7,7-norcaradienedicarbonitrile as the first norcaradiene derivative in this way^[4b].

The electronic influence of the two CN groups has been calculated to amount to about 10 kcal/mol^[3] in the case of the cycloheptatriene. If this value is extended to the system $1 \rightleftharpoons 2$, then it can be predicted that tricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene-11,11-dicarbonitrile **6** is more than 5 kcal/mol more stable than the valence tautomeric 1,6-methano[10]annulene-11,11-dicarbonitrile **5**. This prediction is confirmed by the synthesis of **6** and its spectroscopic and structural chemical characterization carried out by Vogel *et al.*^[5].

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1, 2443-46-1; **2**, 174-23-2; **3**, 544-25-2; **4**, 14515-09-4; **5**, 61997-35-1; **6**, 61997-37-3.

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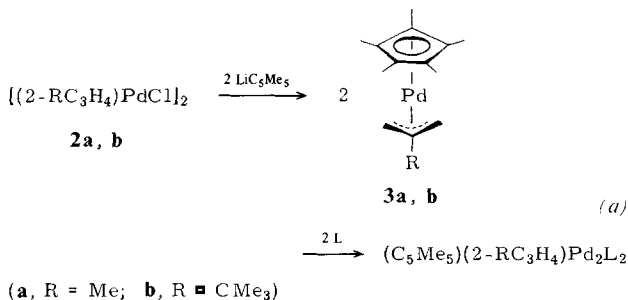
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Synthesis of $\text{Pd}(\eta^2\text{-CH}_2=\text{C}_5\text{Me}_5)\text{L}_2$: Formation of a Fulvene Ligand by Metal-Assisted H-Shift from Pentamethylcyclopentadienyl**

By Hans-Jürgen Kraus and Helmut Werner*

Dedicated to Professor Rudolf Hoppe on the occasion of his 60th birthday

In connection with our studies on the chemistry of dinuclear palladium complexes of the type $(\text{C}_5\text{H}_5)(2\text{-RC}_3\text{H}_4)\text{Pd}_2\text{L}_2$ (**1**)^[10] we attempted the preparation of the corresponding pentamethylcyclopentadienyl compounds *via* reaction sequence (a). We expected these compounds to exhibit greater kinetic stability than the C_5H_5 complexes **1** regarding cleavage of the $\text{C}_5\text{Me}_5\text{-Pd}_2$ bond^[12].



The reaction of **2a** or **2b** with LiC_5Me_5 in pentane (25 °C, 2 h) leads to **3a** and **3b**, respectively (*ca.* 85% yield, red crystals, m.p. 15–17 °C and 58 °C, respectively, correct elemental analysis, ¹H-NMR and mass spectra).

3b does not react with $\text{P}(i\text{Pr})_3$ or PPh_3 , even on prolonged heating at 50–60 °C. Reaction with PMe_2Ph and PMePh_2 leads to cleavage of both the $\text{C}_5\text{Me}_5\text{-Pd}$ as well as the allyl-Pd bond, with formation of the known palladium(0) compounds $\text{Pd}(\text{PR}_3)_4$. In contrast, the reactions with PMe_3 and $\text{P}(\text{OMe})_3$ in toluene (50–60 °C, 5 h) afford the 1,2,3,4-tetramethylfulvene complexes **4** and **5** in 80–90% yield as bright yellow, air-sensitive solids which are readily soluble in all the common solvents and can be stored almost indefinitely at -30 °C under nitrogen.

The room-temperature ¹H-NMR spectra of **4** and **5** (in C_6D_6) indicate that the compounds have a fluxional structure in solution. Considerably broadened singlets are observed both for the protons of the exocyclic CH_2 -groups as well as for the methyl protons of the ring. Signal sharpening occurs (in $(\text{CD}_3)_2\text{CO}$), and on cooling at -10 °C (**4**) and -25 °C (**5**), respectively, the splitting pattern to be expected for the constitution given in Scheme 1 is observed. From the large upfield shift of the signal of the $\text{C}=\text{CH}_2$ protons of $\delta = 5.47$ in the free tetramethylfulvene to $\delta = 2.54$ and 3.04 in **4** and **5**, respectively, the large PH-coupling constants, and the observation of two (and not of four) signals for the $\text{C}-\text{CH}_3$ groups, it can be concluded that the PdL_2 moiety is coordinated to the exocyclic $\text{C}=\text{C}$ double bond. The palladium atom should lie in a plane with the two phosphorus atoms and the carbon atoms of the $\text{C}=\text{CH}_2$ bond. The platinum compounds $\text{Pt}(\eta^2\text{-CH}_2=\text{C}_5\text{Ph}_4)\text{L}_2$ (L = PPh_3 , PMePh_2 , PMe_2Ph , AsPh_3 ,

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[**] Investigations on the Reactivity of Metal- π -Complexes, Part 38. This work constitutes part of the Dissertation by H.-J. Kraus, Universität Würzburg 1981.—Part 37: [12].