ing longer and shorter bonds (mean values 1.39(2) and 1.48(2) Å), corresponding to a cyclohexatriene, are present in the μ_3 -bridging ligand of 3.^[2]

 $\begin{array}{l} [Os_3(CO)_9(\mu_3 \mbox{-}\eta^2 \mbox{:} \eta^2 \mbox{:} \eta^2 \mbox{-} C_6H_6)] \mbox{ 2} \\ [Ru_6C(CO)_{11}(\mu_3 \mbox{-} \eta^2 \mbox{:} \eta^2 \mbox{:} \eta^2 \mbox{-} C_6H_6)(\eta^6 \mbox{-} C_6H_6)] \mbox{ 3} \end{array}$

On metal single crystals benzene and other aromatic hydrocarbons are adsorbed molecularly parallel to the closepacked surfaces (e.g. Ni(111) or Rh(111)).^[9] However, there is some uncertainty about the orientation relative to the surface metal atoms (C₆ centroid above a metal atom, a 2-fold (M₄) or 3-fold (M₃) metal site).^[9,10] According to LEED investigations (LEED = low energy electron diffraction) of coadsorbates C₆H₆/CO and C₆H₆/2CO on Rh(111) (planar benzene fixed in 3-fold coordination sites) benzene has, at least in these cases, the Kekulé structure with strongly alternating bond lengths.^[11] In contrast, a planar arene with virtually equal bonding fixed in a 3-fold metal coordination site is present in 1— a remarkable finding in view of the postulated analogy between metal surfaces and clusters.^[12]

The unsaturated side chain on the benzene ring appears to be the prerequisite for the formation of **1**. We assume initial attack of a CpCo fragment at this site. Assembly of the metal cluster could then proceed (if necessary after shifting of the double bond into the α -position to the arene) via an intermediate with methylstyrene as a doubly η^4 -coordinating diene (3–6- η , 1–2:7–8- η). Related structures, albeit with metal atoms coordinating the bridging ligands from opposite sides, were derived from NMR spectroscopic data for [{Fe(CO)₃}₂]-complexes of substituted styrenes^[13] and [{(C₅Me₅)Co}₃(η^4 : η^4 : η^4 -biphenyl)].^[14] Reaction of the intermediate with a further CpCo fragment and rearomatization of the arene could then lead to **1**.

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- [4] Procedure: trans-β-methylstyrene (6.31 g, 53.4 mmol) was added dropwise at room temperature to a solution of [CpCo(C₂H₄)₂] (4.81 g, 26.7 mmol) in petroleum ether (100 mL, b.p. 40-60°C). After 1 h the mixture was heated for a further 3 h at 60°C, then cooled to room temperature again and all volatile components removed in a vacuum. The residue was dissolved in toluene/petroleum ether (1:1) and chromatographed on Al₂O₃/5% H₂O. Dark brown needles of 1 (3.49 g, 7.12 mmol, 80% based on Co) were obtained from the eluate at 5°C; m.p. 182°C; correct C,H analyses).
- [5] ¹H-NMR (200.1 MHz, [D₈]toluene, 25°C): $\delta = 5.76$ (dq, $J_{HH} = 15.6$, 1.5 Hz, 1 H; H-6), 5.44 (dq, $J_{HH} = 15.6$, 6.5 Hz, 1 H; H-7), 4.58 (s, 15 H; Cp), 4.4 (m, 2 H; arene-H), 4.2 (m, 3 H; arene-H), 1.57 (dd, $J_{HH} = 6.5$, 1.5 Hz, 3 H; CH₃). ¹³C-NMR (50.3 MHz, [D₆]benzene, 25°C): $\delta = 140.1$ (d; olefin-C), 116.4 (d; olefin-C), 82.7 (d; Cp), 56.1 (s; C-1), 41.8 (d; arene-C), 40.9 (d; arene-C), 39.2 (d; arene-C), 18.4 (q; CH₃). MS (direct chemical ionization) m/2 490 (43% rel. int., M^{\oplus}), 370 (100, [(CpCo)₃ 2 H]^{\oplus}), 247 (20, [(CpCo)₂ H]^{\oplus}), 207 (22), 189 (87, [Cp₂Co]^{\oplus}), 124 (28, [CpCo]^{\oplus}), 118 (15, [PhC₃H₃]^{\oplus}), 117 (19, [PhC₃H₄]^{\oplus}), 91 (8, [C₇H₇]^{\oplus}), 59 (15, Co^{\oplus}), 44 (19).
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flections measured (Weissenberg diffractometer, $M_{0,K\alpha}$, ω scan), 2893 observed ($I \ge \sigma(I)$), numerical absorption correction; 337 parameters refined (Co, C anisotropically, H isotropically, CH₃ as rigid group), R = 0.026, $R_w = 0.027$. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshyfen 2 (FRG), on quoting the depository number CSD-52636, the names of the authors, and the journal citation.

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Reactions of

2,2,4,4-Tetramethyl-3-methylenecyclobutylidene; Thermal Rearrangements of a 2-Methylenebicyclo[2.1.0]pentane**

By Udo H. Brinker* and Wolfgang Erdle

Dedicated to Professor Emanuel Vogel on the occasion of his 60th birthday

Small ring carbenes are important reactive building blocks for the synthesis of highly strained, polycyclic compounds.^[1] Cyclobutylidenes preferentially undergo ring contractions to give methylene cyclopropanes.^[2] We have examined the extent to which possible interactions between carbene center and an exo-methylene group in the 2-^[3] or 3-position influence the rearrangement behavior of 2,2,4,4-tetramethyl-3-methylenecyclobutylidene 4. Besides ring contraction to give 7 there are further intramolecular reactions open to 4, e.g. insertion into a C-H bond of the neighboring CH₃ groups with formation of the strained 2methylenebicyclo[2.1.0]pentane 6. A spectacular addition of the carbene 4 or of the diazo group in 3 to the exo double bond could result in formation of the tetramethyl-substituted [1.1.1]propellane 8 or the corresponding 4,5-dihydro-3H-pyrazole. That is, the highly-strained propellane skeleton^[4] would either have to be formed directly via the structurally integrated allylcarbene^[5] in 4 with concomitant formation of three cyclopropane rings or only after cleavage of N_2 from the dihydropyrazole.

The 3-methylenecyclobutanone $1^{[6]}$ required for the formation of the tosylhydrazone-sodium salt 2 was synthesized from commercially available 2,2,4,4-tetramethyl-1,3cyclobutanedione.^[6] The reaction of 1 with *p*-toluenesulfonylhydrazide afforded the corresponding tosylhydrazone in 92% yield, which on reaction with sodium hydride furnished the sodium salt 2 in almost quantitative yield (97%).

Upon flash pyrolysis^[4] of **2** at 240–290°C (10^{-4} – 10^{-5} torr) a pink-colored pyrolyzate was obtained whose IR spectrum (CCl₄) showed a strong band at 2020 cm⁻¹ (R₂C=N=N valence vibration). The diazo compound **3**

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could be enriched if the decomposition of 2 took place between 120 and 130°C ($<10^{-4}$ torr). The half-life of ca. 6700 s at 31.5°C shows that 3 is kinetically highly stabilized in comparison to the diazocyclobutane, which is unstable at room temperature.⁽⁷⁾ The "longevity" of 3 at 240-290°C is also reflected in the relatively high yield of azine 5 (20-30%). At these temperatures in addition to some toluene (ca. 3%) seven hydrocarbons are formed in a total yield of 72% (isolated by preparative gas chromatography). 1-Isopropylidene-2,2-dimethyl-3-methylenecyclopropane

7,^[8] which could be formed by a cyclobutylidene-methylenecyclopropane rearrangement of **4**, is isolated in 35% (42% relative) yield. A 1,3-insertion of the carbene carbon into one of the C-H bonds of the four methyl groups results in formation of the strained 1,3,3-trimethyl-2-methylenebicyclo[2.1.0]pentane **6**^[8] (27% relative, 15% isolated). As will be shown below, the methylenecyclopentenes **9** (10%, 8%)^[8] and **10** (6%, 3%)^[8] as well as the allene **11** (11%, 7%)^[8] are secondary products of **6**. In addition, diisopropylidenecyclopropane **12**,^[9] which could not be formed directly from the carbene **4**, was isolated in 2-3% (4% relative) yield.

Two possible routes come into consideration for the formation of **12** from **4**: 1. The intermediary tetramethyl[1.1.1]propellane **8** resulting from the intramolecular carbene addition (or a 1,3-dipolar cycloaddition of **3** via 4,5dihydro-3*H*-pyrazole and subsequent N₂ cleavage) rearranges directly to **12**. The parent compound [1.1.1]propellane^[5] yields exclusively dimethylenecyclopropane at 430 °C under flow pyrolysis conditions!^[10] 2. An isomerization of **7** takes place, and the geminal cyclopropane methyl groups are moved to the terminal carbon of the double bond via methylenecyclopropane rearrangement.^[11] In the flow pyrolysis^[12, 13] of 7 at 550 °C (0.1 torr, quartz tube filled with quartz chips)^[12] 12 is formed in 61% yield. This result suggests that 2-3% of 7 is also converted into $12^{[14]}$ under the conditions of the flash pyrolysis.^[3, 12]

In addition, 1,1-dimethyl-2-(2-methyl-1-propenylidene)cyclopropane $13^{[13b, 14]}$ could be identified as a further product (<1%) of the pyrolysis. In the carbene 4 the 1,3-C-H insertion to give 6 (+9+10+11) dominates over the ring contraction to 7 (+12) in the ratio of ca. 1.2:1.

The photolysis (Pyrex, Philips HPK, 125W) of an ethereal suspension of 2 between 0 and 20 °C afforded the hydrocarbons 7 and 6 in 40 and 35% yield, respectively. In addition, ca. 5–10% azine 5, 0.8% 12 and ca. 1% ketone 1 were isolated. 2 was decomposed thermally and photochemically also in the presence of styrene and α -methylstyrene. In the photolysis the spiro[2.3]hexanes 14 are formed in yields of 28–35%. The long lifetime of the diazo compound 3 suggests that spirohexane formation takes place by 1,3-dipolar cycloaddition of 3 via intermediary dihydropyrazoles.^[15]



The thermolysis of 6 in the gas phase at 140-190 °C leads to formation of 9, 10, and 11; their formation follows a first order rate law with the given activation parameters (see formula). This suggests formulating the forma-



tion of 9, 10, and 11—as in the case of the unsubstituted bicyclo[2.1.0]pentane^[16]—via a diradical 15. Consistent with this interpretation the flow pyrolysis^[13a] of the allene 11 affords, besides *p*-xylene, the isomers 9 and 10 (9:10:11=7:4:89). The assumption of an intermediary diradical also makes the markedly lower activation energies compared to the parent system understandable. For the formation of 9 and 10 these are ca. 11 kcal mol⁻¹ lower compared to the cyclopentene formation (E_a =45.6 kcal mol⁻¹),^[16] whereby the resonance stabilization of the allyl radical should make the greatest contribution.

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Annelated Isoindoles with an 18*n*-Electron System**

By Richard P. Kreher* and Thomas Hildebrand Dedicated to Professor Klaus Hafner on the occasion of his 60th birthday

The radialenes 1 and 2 of naphthalene^[2] have been postulated as reactive intermediates and have been suggested as precursors for tetrahydrodicyclobuta[a,f]- and tetrahydrodicyclobuta[a,c]naphthalenes, respectively. By bridging with two alkylimino groups, it is possible to establish the labile radialene structure. The corresponding tetracyclic heteroarenes 3 and 4 are stabilized by cyclic conjugated 18π -electron systems. Noteworthy in the heteroarene 3 are the annelated 2*H*-isoindole moieties and the central triene system; the isoelectronic heteroarene 4, on the other hand, is characterized by a "nonperturbed" peripheral benzenoid ring system.⁽³⁾



The convergent synthesis of the tetracyclic heteroarenes **3** and **4** makes use of the *N*-oxide route^[4] for formation of the pyrrole rings. The preparative effort involved is mainly determined by the requirement of obtaining the corresponding tetrafunctional naphthalenes.



Scheme 1. Synthesis of 3 and 4, $R = CMe_3$. a) HBr/formaldehyde in acetic acid/phosphoric acid, 6.5 h reflux. b) *N*-Bromosuccinimide in CCl₄, 45 min reflux, c) *tert*-Butylamine in benzene added over 3 d under reflux, 16 h room temperature. d) Acetic anhydride/triethylamine in CHCl₃; 15 min 0°C, 2 h room temperature. e) *N*-Bromosuccinimide in CCl₄, 1 h reflux. f) *tert*-Butylamine in CHCl₃ added over 3 d under reflux, 2 h reflux. 5b : 98% yield, m.p. 163-164°C; 6b: 71% yield, m.p. = 151°C.

The synthesis of the heteroarene 3, $R = CMe_3$, starts from commercially available 2,6-dimethylnaphthalene (Scheme 1). An acceptable yield is obtained by halomethylation^[5] of the reactive 1,5 positions. Radical bromination of the methyl groups in the 2,6 positions is followed by facile cyclization with *tert*-butylamine leading to 5a. Acetolysis of the *N*,*N*-dioxide 5b, which is likewise easily carried out, results in aromatization to form 3.

In order to synthesize the heteroarene 4, $R = CMe_3$, synthetically accessible 1,2,3,4-tetramethylnaphthalene^[6] is substituted via radical bromination (Scheme 1). The subsequent ring closure occurs in spite of competing reactions with a satisfactory yield of 6a. Compound 6a is converted into the *N*,*N*-dioxide 6b, which, in turn, is caused to undergo aromatization.

The structural differences in the isoelectronic heteroarenes 3 and 4 are manifested in their chemical behavior. Cycloaddition reactions, which are expected for 3, are indeed observed. Treatment with N-methylmaleimide results, via addition to a pyrrole ring, in the formation of a 1:1 cycloadduct having the topology of 2H-benz[e]isoindole; the reactivity of this 14π -electron system is decreased by

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