The potential applications of indium-mediated deoxygenative reactions are of considerable scope. Further investigations[9] are underway and will be fully reported in due course.

Experimental Section

7a: Under N_2, allyl bromide (0.530 mL, 6.09 mmol) was added to indium powder (particle size: 100 mesh; Aldrich, 459 mg, 4.00 mmol) in THF (2 mL), which resulted in an exothermic reaction. After 70 min **5a** (235 mg, 1.00 mmol) was added as a solid. After 4 h LiBr (347 mg, 4 mmol) was added (exothermic reaction), and after a further 12 h air was admitted to the reaction vessel. Et_2O (10 mL) and 1M HCl (30 mL) were then introduced, and the biphasic mixture was shaken vigorously at intervals of 10 min over a period of 1 h. The organic phase was separated, dried (Na_2SO_4), and concentrated. Chromatographic purification (silica gel, hexane/EtOAc 19/1) afforded **7a**[6] (249 mg, 83 %) as a colorless oil. Elemental analysis calcd for $C_{23}H_{24}$: C 91.95 %, H 8.05 %; found: C 91.59 %, H 8.30 %. **7b**, **7c**, **14**, and **15** were prepared similarly. Tenfold scale-up with **5a** afforded **7a** in similar yield.

Received: September 23, 1997
Revised version: December 22, 1997 [Z 10961 IE]
German version: *Angew. Chem.* **1998**, *110*, 1653–1655

Keywords: allyl complexes · cyclopropanes · indium · ketones · rearrangements

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[7] Compound **5a** reacts with $(C_3H_5)_2In_2I_4$ to give **9a** (and with **1** to give **6a**), as shown by ^1H NMR spectroscopy in $[D_8]$THF. Removal of THF from **9a** under reduced pressure (0.1 Torr), addition and subsequent removal of $PhCH_3$, and dissolution of the residue in $[D_8]$THF resulted in a fluxional ^1H NMR spectrum that revealed no trace of **9a**.

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1,4-Addition of a Terminal Phosphinidene Complex to [5]Metacyclophane**

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In general, carbenes[1] and related electron-deficient species such as the metal complexes of phosphinidenes (phosphanediylenes) $[RPW(CO)_5]$[2] react with 1,3-dienes by [2+1] cycloaddition (1,2-addition) to furnish only vinylcyclopropanes or vinylphosphiranes, respectively. However, as vinylphosphiranes tend to rearrange to the corresponding phospholenes, products are frequently isolated that seemingly result from a formal [4+1] cycloaddition (1,4-addition).[3, 4] To our knowledge, there is so far only one exception: A direct 1,4-addition does occur, in competition to 1,2-addition, in the reaction of dihalocarbenes with 1,3-dienes which are frozen in a cisoid conformation.[5]

We here report on the 1,4-addition of a phosphinidene complex and highlight three exceptional aspects. 1) It is the first genuine 1,4-addition of a phosphinidene complex, 2) it is the first addition of a phosphinidene complex to a benzene ring, and 3) it is, as far as we know, the first [4+1] cycloaddition to an aromatic ring.

Because of its high strain energy and its bent benzene ring, [5]metacyclophane **1** reacts under unusually mild conditions with dienophiles at C8 und C11 by a [4+2] cycloaddition (Diels–Alder reaction).[6] We therefore considered **1** to be a promising candidate for 1,4-additions with phosphinidene complexes. Indeed, reaction of **1** with the precursor **2** of the phosphinidene complex **3** (with 10 % CuCl as catalyst in toluene at 55 °C)[7] gives the 1,4-adduct **4** as the only product in the form of light yellow crystals in 52 % yield after column chromatography and crystallization from pentane (Scheme 1).

The NMR data of **4** are in good agreement with those of other 7-phosphanorbornadienes (e.g. **2**). The phosphorus center is slightly more shielded ($\delta(^{31}P) = 191.1$) than in reference compounds ($\delta(^{31}P) = 208–240$[7a, 8]); the two olefinic carbon atoms *anti* to the $W(CO)_5$ substituents display a strong coupling to the phosphorus atom ($^2J(P,C) = 21.2$ and

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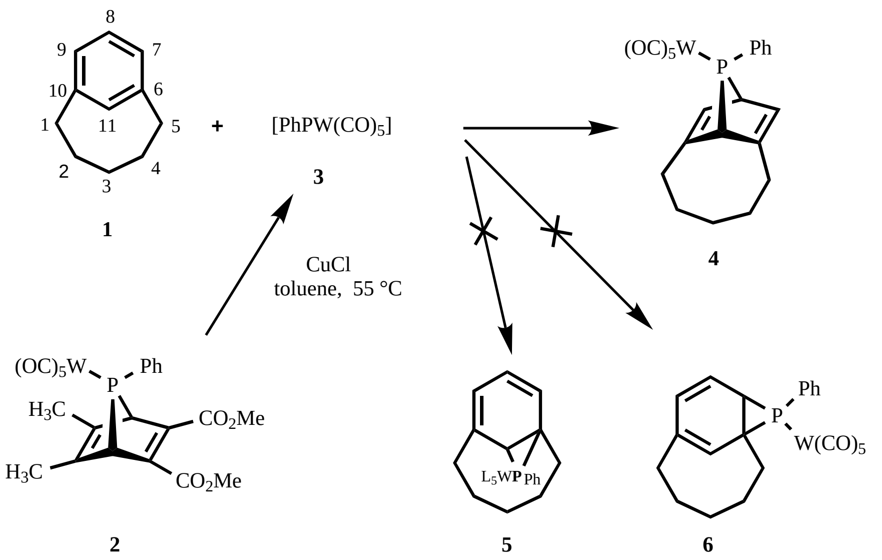
[**] We thank the CAOS/CAMM Centrum (Katholieke Universiteit Nijmegen) and the Section of Theoretical Chemistry (Vrije Universiteit) for computing time. These investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).



Scheme 1.

17.3 Hz), whereas the corresponding coupling of the *syn*-carbon atoms is small (^2J(P,C) = 6.2 and 4.2 Hz).[7c, 8, 9]

The structure derived from the spectra was corroborated by a single-crystal X-ray structure determination (Figure 1).[10] Again, the structural parameters of 4 show good agreement with those of other 7-phosphanorbornadienes;[7a, 8] the only exceptions are the double bonds of the norbornadiene skeleton, which in **4** are clearly twisted (C1-C2-C3-C4 – 165.1(4)°, C8-C9-C12-C1 169.0(4)°). A certain degree of strain is also apparent from the C-C-C angles of the pentamethylene bridge; these angles are enlarged for the three central methylene groups (117.1 – 118.5°), but less so than in the 8,11-dichloro derivative of **1** (122°).[11] The somewhat reduced strain in **4** is also indicated by the bond angles at the benzylic methylene groups (111.9 – 112.6°), which are larger than those of the reference cyclophane mentioned (104.7°).[11]

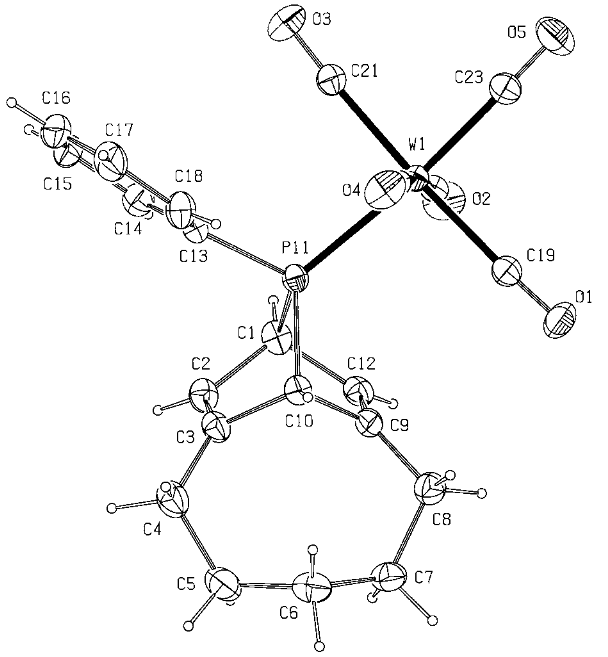


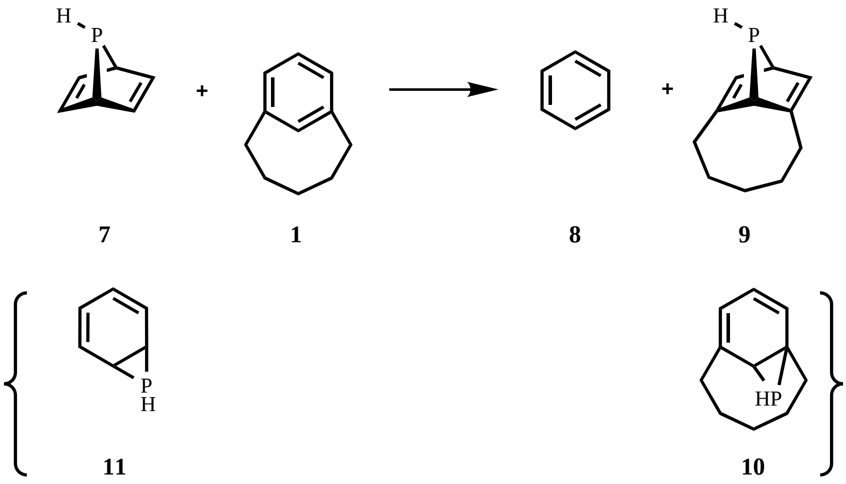
Figure 1. Structure of **4** in the crystal. Selected bond lengths [Å] and angles [°]: W1 – P11 2.487(1), P11 – C13 1.817(4), P11 – C1 1.864(4), P11 – C10 1.874(4), C1 – C2 1.526(6), C1 – C12 1.540(5), C2 – C3 1.331(6), C3 – C10 1.529(5), C9 – C12 1.334(6), C9 – C10 1.527(5); C13-P11-C1 107.92(18), C13-P11-C10 109.15(17), C1-P11-C10 79.74(17), C13-P11-W1 111.27(12), C1-P11-W1 121.42(14), C10-P11-W1 123.30(12), C2-C1-C12 106.5(3), C2-C1-P11 100.8(3), C12-C1-P11 95.6(2), C3-C2-C1 111.2(3), C2-C3-C10 109.6(3), C12-C9-C10 109.7(3), C9-C10-C3 105.1(3),C9-C10-P11 97.1(3), C3-C10-P11 102.0(2), C9-C12-C1 110.8(3), C3-C4-C5 112.6(4), C4-C5-C6 117.3(5), C5-C6-C7 117.1(4), C6-C7-C8 118.5(5), C7-C8-C9 111.9(4); C1-C2-C3-C4 – 165.1(4), C8-C9-C12-C1 169.0(0).

One must consider the possibility that this reaction, like the addition of other phosphinidene complexes, might proceed via a 1,2-adduct such as **5** or **6**, which in a second step rearranges to **4**. To investigate this alternative, the reaction progress was monitored by ^{31}P NMR spectroscopy. However, no indications for an intermediate product were obtained. ^{31}P NMR experiments also showed that **4**, being a 7-phosphanorbornadiene complex, is remarkably stable: In sharp contrast to **2**, **4** remained unchanged even on prolonged heating at 70 °C in toluene in the presence of CuCl.

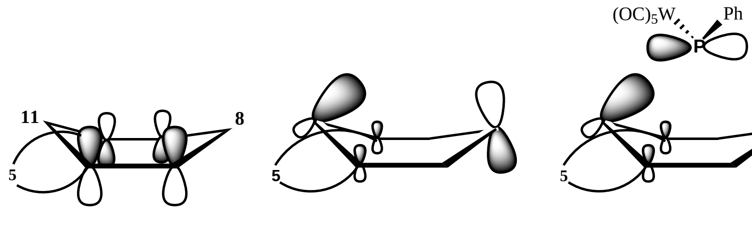
Theoretical calculations were performed (ADF[12]) in order to better understand the reasons for this increased stability of **4**. The homodesmotic reaction **7**+**1** → **8**+**9** (Scheme 2) has a reaction enthalpy of – 140 kJ mol^{-1}. This value is similar to the strain energy of **1** (174 kJ mol^{-1}), and shows that the strain in **9** (and likewise that in **4**) is considerably diminished, probably due to the removal of the "anti-Bredt" situation (cf. the formal double bond between C6 and C11 in **1**). Furthermore, the reverse reaction is strongly endothermic, which explains the stability of **4**. In contrast, the analogous cheletropic cleavage of **2** yields (besides the intermediate **3**) a planar, strain-free benzene derivative with ease.[2a]

The calculations also support the mechanism of the reaction of **3** with **1** as being a direct 1,4-addition. According to frontier orbital theory, this reaction is largely governed by the interaction between the HOMO or HOMO – 1 of **1** and the LUMO of **3** (Figure 2).

Both the HOMO (– 8.10 eV) and the HOMO – 1 (– 8.42 eV) of **1** are clearly higher in energy than the corresponding orbitals of *m*-xylene (RHF/6-31G*:[13] – 8.59 and – 8.89 eV, respectively), which will reduce the activation barrier of the cycloaddition. As the HOMO of **1** has a node in the mirror plane of the molecule, its interaction with the LUMO of **3** can only proceed by 1,2-addition at C6/C7 under formation of **6** (Scheme 1). However, this reaction pathway is unlikely because it hardly reduces the "Bredt strain", let alone that quite complicated rearrangements are required to get from **6** to **4**. The 1,2-addition at C6/C11, which would furnish the less strained **5** (removal of the "anti-Bredt double bond" between C6 and C11!), can only occur through the HOMO – 1, but is unfavorable because of the small coefficient at C6.



Scheme 2.



HOMO: –8.10 eV **HOMO-1: –8.42 eV**

Figure 2. Frontier orbitals of **1** and **3**.

Therefore, it is more likely that the addition of **3** to **1** is governed by the interaction between the LUMO of **3** and the HOMO − 1 of **1**, resulting in a symmetry-allowed 1,4-addition at C8 and C11 (Figure 2). Favorable factors in this reaction pathway are the high coefficients of the HOMO − 1 at C8 and C11; the boat shape of the aromatic ring of **1** and the pyramidalization at C8 and especially at C11, which minimize the geometric changes required for the cycloaddition; the increased electron density at the concave side of the aromatic boat of **1**, which increases the overlap with **3**; and the gain in reaction enthalpy, which in the model (Scheme 2) is 9.2 kJ mol^{-1} higher for the formation of **9** than for **10**. In contrast, on addition of the phosphinidene HP: to (planar) benzene, the 1,2-adduct **11** is more stable than the 1,4-adduct **7** (Scheme 2; ADF: 65.8 kJ mol^{-1}; MP2(fc)/6-31G*: 53.1 kJ mol^{-1}[9]).

In conclusion, both the experimental data and the theoretical analysis support a direct, one-step 1,4-addition of phosphinidene complex **3** to the aromatic ring of **1**.

Experimental Section

4: A solution of **1** (41 mg, 0.28 mmol), **2** (177 mg, 0.27 mmol), and CuCl (≈10 mol %) in dry toluene (1.5 mL) was heated under nitrogen to 55 °C for 2 h. After evaporation of the volatile components in vacuo, the residue was dissolved in pentane/benzene (9/1), subjected to chromatography on silica, and crystallized from pentane to afford **4** as light yellow crystals (81 mg, 0.14 mmol, 52 %); m.p. 83 °C. ^{31}P NMR (250 MHz, CDCl$_3$): $\delta = 191.1$ (^{1}J(P,W) = 224.4 Hz); {^{1}H}^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 24.81$ (s; C6), 33.08 (s; C4), 33.4 (s; C5), 33.4 (s; C8), 33.55 (s; C7), 52.17 (d, ^{1}J(C,P) = 20.2 Hz; C10), 60.64 (d, ^{1}J(C,P) = 26.2 Hz; C1), 128.17 (d, ^{3}J(C,P) = 7.3 Hz; *m*-Ar, C15, C17), 128.39 (d, ^{2}J(C,P) = 8.8 Hz; *o*-Ar, C14, C18), 128.77 (d, ^{4}J(C,P) = 0.9 Hz; *p*-Ar, C16), 129.33 (d, ^{2}J(C,P) = 4.2 Hz; C2), 129.96 (d, ^{2}J(C,P) = 17.3 Hz; C12), 142.75 (d, ^{1}J(C,P) = 17.2 Hz; *i*-Ar, C13), 154.20 (d, ^{2}J(C,P) = 6.2 Hz; C3), 154.89 (d, ^{2}J(C,P) = 21.2 Hz; C9), 196.81 (d, ^{2}J(C,P) = 6.7 Hz; *cis*-CO, C19–C22), 199.74 (d, ^{2}J(C,P) = 23.7 Hz; *trans*-CO, C23); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.963$ (m, ^{2}J(H,H) = −14.0, ^{3}J(H,H) = 10.8, ^{3}J(H,H) = 9.2, ^{3}J(H,H) = 4.2, ^{3}J(H,H) = 1.2 Hz; H6), 1.068 (m, ^{2}J(H,H) = −14.5, ^{3}J(H,H) = 11.8, ^{3}J(H,H) = 9.2, ^{3}J(H,H) = 4.2, ^{3}J(H,H) = 1.2 Hz; H10), 1.438 (m, ^{2}J(H,H) = −15.7, ^{3}J(H,H) = 9.2, ^{3}J(H,H) = 9.2, ^{3}J(H,H) = 1.1, ^{3}J(H,H) = 1.1 Hz; H7), 1.912 (m, ^{2}J(H,H) = −15.7, ^{3}J(H,H) = 9.8, ^{3}J(H,H) = 9.8, ^{3}J(H,H) = 1.2, ^{3}J(H,H) = 1.2 Hz; H8), 2.041 (m, ^{2}J(H,H) = −14.0, ^{3}J(H,H) = 9.8, ^{3}J(H,H) = 4.2, ^{3}J(H,H) = 4.2, ^{3}J(H,H) = 1.1 Hz, ^{4}J(H,H) ≈ 1.0 Hz; H5), 2.110 (m, ^{2}J(H,H) = −13.1, ^{3}J(H,H) = 10.8, ^{3}J(H,H) = 4.2, ^{4}J(H,H) ≈ 1.2 Hz; H3), 2.160 (m, ^{2}J(H,H) = −14.5, ^{3}J(H,H) = 9.8, ^{3}J(H,H) = 4.6, ^{3}J(H,H) = 4.2, ^{3}J(H,H) = 1.1, ^{4}J(H,H) ≈ 1.0 Hz; H9), 2.372 (m, ^{2}J(H,H) = −13.1, ^{3}J(H,H) = 4.2, ^{3}J(H,H) = 4.2, ^{4}J(H,H) < 1 Hz; H4), 2.453 (m, ^{2}J(H,H) = −13.2, ^{3}J(H,H) = 11.8, ^{3}J(H,H) = 4.6, ^{4}J(H,H) ≈ 1.6 Hz; H12), 2.762 (m, ^{2}J(H,H) = −13.2, ^{3}J(H,H) = 4.2, ^{3}J(H,H) = 4.2, ^{4}J(H,H) < 1 Hz; H11) 3.482 (m, ^{4}J(H,H) = 2.6, ^{4}J(H,H) = 1.4, ^{4}J(H,H) = 1.4, ^{2}J(H,P) = 2.8 Hz; H13), 3.878 (m, ^{3}J(H,H) = 4.2, ^{3}J(H,H) = 3.8, ^{4}J(H,H) = 2.6, ^{2}J(H,P) ≈ 0.3 Hz; H1), 5.951 (m, ^{3}J(H,H) = 3.8, ^{4}J(H,H) = 1.4, ^{4}J(H,H) < 1, ^{4}J(H,H) ≈ 1.2, ^{3}J(H,P) = 7.6 Hz; H2), 6.466 (m, ^{3}J(H,H) = 4.2, ^{4}J(H,H) = 1.4, ^{4}J(H,H) < 1, ^{4}J(H,H) ≈ 1.6, ^{3}J(H,P) = 8.0 Hz; H14), 7.159 (m, ^{3}J(H,H) = 7.6, ^{4}J(H,H) = 1.6, ^{4}J(H,H) = 1.2, ^{5}J(H,H) = 0.6, ^{3}J(H,P) = 8.9 Hz; *o*-Ar), 7.286 (m, ^{3}J(H,H) = 7.5, ^{4}J(H,H) = 1.2, ^{5}J(H,P) = 1.3 Hz; *p*-Ar), 7.358 (m, ^{3}J(H,H) = 7.6, ^{3}J(H,H) = 7.5, ^{4}J(H,H) = 1.4, ^{5}J(H,H) = 0.6, ^{4}J(H,P) = 1.9 Hz; *m*-Ar); HR-MS: calcd for $C_{22}H_{19}O_5P^{182}W$ [M^+]: *m*/*z* 578.0480; found: 578.0479 ± 0.0004; elemental analysis calcd for $C_{22}H_{19}O_5PW$: C 45.70, H 3.31, P 5.36; found C 45.28, H 3.27, P 5.32.

Received: December 30, 1997 [Z 11304 IE]
German version: *Angew. Chem.* **1998**, *110*, 1656–1658

Keywords: cycloadditions · cyclophanes · density functional calculations · phosphinidene complexes · phosphorus

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[10] Crystal structure data of **4**: $C_{22}H_{19}O_5PW$, $M_r = 578.19$, triclinic, $P\bar{1}$, $a = 9.8924(7)$, $b = 9.9756(6)$, $c = 12.7670(9)$ Å, $\alpha = 110.216(5)$, $\beta = 89.861(6)$, $\gamma = 118.064(5)°$, $V = 1023.6(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.876$ g cm^{-3}, $T = 150(2)$ K, $(\sin\theta/\lambda)_{max} = 0.649$ Å^{-1}, transparent, colorless crystal, $0.22 \times 0.22 \times 0.62$ mm; of 8335 measured relections, 4694 were unique ($R_{int} = 0.0373$), R values ($I > 2\sigma I$): $R1 = 0.0268$, $wR2 = 0.0624$, all data: $R1 = 0.0315$, $wR2 = 0.0643$. Diffractometer: Enraf–Nonius CAD4T with rotating anode. The structure was solved by automated Patterson methods (DIRDIF-96),[14] and refined by SHELXL-97[15] on F^2; 338 parameters, no restraints. Non-hydrogen atoms were refined with anisotropic temperature factors, and hydrogen atoms with isotropic temperature factors. The absorption correction (Routine DELABS), graphical presentation of the structure, and check for higher symmetry were performed with the program PLATON.[16] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100938. 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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Stabilization of *p*-Phenylenebis(*N-tert*-butylaminoxyl) Relative to *p*-Benzoquinonediimine *N*,*N*′-Dioxide**

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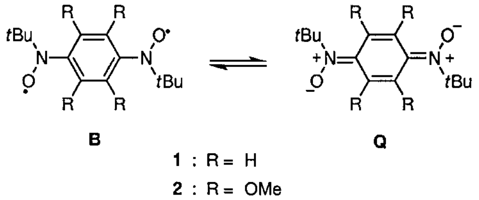
For typically triplet *m*-quinodimethane derivatives,[1, 2] recent theoretical and experimental work revealed that they can have singlet ground states when sterically and/or electronically perturbed.[3–7] We designed the diradical *p*-phenylenebis(*N-tert*-butylaminoxyl) **B**, which is expected to be stabilized as the closed-shell *p*-benzoquinonediimine *N*,*N*′-dioxide **Q** (Scheme 1). The synthesis, X-ray crystal structure analysis, and EPR characterization of unsubstituted **1** and its tetramethoxy derivative **2** are reported here.



Scheme 1. Equilibrium between the benzenoid (**B**) and quinonoid forms (**Q**) of **1** and **2**.

The *p* isomers were prepared, analogous to the procedure used to synthesize the triplet *m* isomers,[3] by the oxidation of the corresponding hydroxyamines with Ag_2O. The resulting orange and red powders were crystallized from diethyl ether to give orange prismatic and red bricklike crystals of **1** and **2**, respectively. The X-ray crystal structure analysis (see Experimental Section) of **1** revealed the presence of two pairs of independent molecules A and B in the unit cell. The molecular structures are very similar and have a C_2 symmetry axis at the center of the ring which is nearly coplanar with the planes of the aminoxyl groups (Figure 1, top; Table 1). In the unique molecule of **2** a C_2 axis passes through the midpoints of the C2–C3 and C2*–C3* bonds. The planes of the aminoxyl groups are almost perpenducular to the centeral ring (Figure 1, bottom). Although the two aminoxyl groups in most of the reported *m* isomers have *syn* configuration in the crystal,[2c, 3] the observed *anti* form in **2** can be rationalized

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[**] This work was supported by a Grant-in-Aid for COE Research "Design and Control of Advanced Molecular Assembly Systems" (no. 08CE2005) from the Ministry of Education, Science, Sports, and Culture, Japan.