than using "standard" carbon–carbon bond forming techniques.[16]

Supplementary Material Available: Structural report for compound **6** giving methods for data collection, data reduction, structure solution and refinement, tables of crystal data, intensity measurements, structure solution and refinement, positional and thermal parameters, general temperature factor expressions, bond distances, bond angles, and intensity data, and a drawing of a single molecule showing 30% probability ellipsoids (22 pages); listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(16) This is the shortest total synthesis of (±)-trichodermol so far recorded, requiring 16 steps from 4-methylanisole, which augurs well for the future use of **4** and related complexes. For comparison, Raphael's synthesis of trichodermin uses 19 steps from 4-methylanisole and was plagued by a difficult internal aldol reaction to generate the C ring. Still's synthesis of trichodermol elegantly overcomes this problem, but it involves 24 steps from 4-methylanisole (ref 2).

Spiropentane as a Tensile Spring

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Highly strained compounds are especially suitable for revealing relationships between structure and reactivity.[2] The synthesis and exact structure determination of molecules comprising unusual topologies, i.e., compounds that contain bond distances and bond angles which deviate substantially from normal values is of prime importance. Structure determinations of spiropentane (**1**)—the parent system—and the ethano- and benzene-bridged spiropentanes **2**[3] and **3**,[4] respectively, provide the opportunity to test the limits of current theoretical work dealing with calculations of structure and physical data of "unusual" molecules. To study the influence of spiropentane (**1**) on the ethano bridge C4–C4' in **2** and the corresponding benzene bond C4–C5 in **3** we performed single-crystal X-ray structure determinations of **1**, **2**, and **3** including X–X electron density determinations.

According to ab initio calculations, in **1** twisting by ψ is energetically more favorable than bending by Φ.[5] Connecting C2 and C5 or C3 and C4 of **1** with an ethano bridge in a trans fashion yielding **2** should, therefore, lead to additional stress through twisting and bending (Figure 1).

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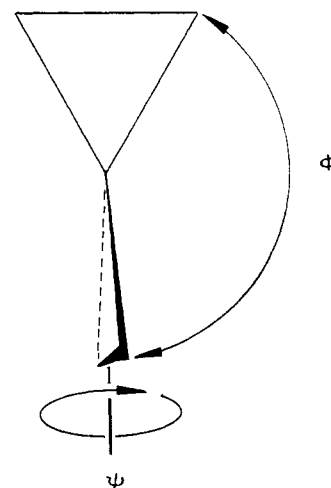

Figure 1. *Twisting* by ψ is performed by rotating the lower three-membered ring against the upper; *bending* by Φ is performed by buckling the 2-fold axis at the spiro atom. By both operations the nonspiro atoms are brought closer together.

The strain energy of **2** has been calculated to be 80 kcal/mol,[5] thus, exceeding that of **1** by ca. 17 kcal/mol.[6] The considerable strain is also reflected in an unusual rearrangement of **2** when exposed to a platinum complex.[7] One furthermore expects that the C4–C4' bridge in **2** is expanded by the spiropentane unit working like a tensile stress inducing spring.

Electron diffraction studies of spiropentane (**1**)[8] and tricyclo-[4.1.0.0^{1,3}]heptane (**2**) are known.[9] To interpret the PE spectrum of **2**, MO calculations were performed.[10] The length of the C4–C4' bond was calculated to be only 1.500 Å in contrast to the electron structure determination.[9]

It has been shown that annulation of small rings to benzene does *not* lead to alternating bond distances in the aromatic ring[11] in the sense of a Mills–Nixon effect.[12] However, if like in **3**, instead of a three- or four-membered ring a spiropentane is connected to benzene, alternating bond distances might be expected.

The crystallization of **1** (mp –115 °C), **2** (mp –105 °C), and **3** (mp +15 °C) were performed according to a previously described procedure.[13] The results of the X-ray structure and the X–X electron density determinations are shown in Figures 2 and 3.[14]

The slight distortion from the ideal C_{2v} symmetry of **1** (Φ = 179.6° and ψ = 90.2°) in the crystal is probably due to packing effects (lowest intermolecular H⋯H 2.321 Å with H atoms im-

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(14) Crystal structure determination at –163 °C, Mo Kα radiation, Nicolet R3 diffractometer. **1**: crystallization at –121 °C, rhombohedral, *R3̄*, *a* = *b* = 19.346 (2) Å, *c* = 6.285 (1) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, *V* = 2037.2 (5) Å³, *Z* = 18, D_x = 1.000 g/cm³, 1847 observed independent intensities, $2\theta_{max}$ = 80°, $F_o \geq 4\sigma(F)$, *R* = 0.040, R_w = 0.045 for 953 observed reflexions ($2\theta_{max}$ = 55°). **2**: crystallization at –112 °C, orthorhombic, *Pbcn*, *a* = 7.940 (3) Å, *b* = 11.254 (4) Å, *c* = 6.417 (2) Å, $\alpha = \beta = \gamma = 90°$, *V* = 573.4 (3) Å³, *Z* = 4, D_x = 1.094 g/cm³, 800 observed independent intensities, $2\theta_{max}$ = 70°, $F_o \geq 4\sigma(F)$, *R* = 0.041, R_w = 0.048 for 595 observed reflexions ($2\theta_{max}$ = 55°). **3**: crystallization at 11 °C, monoclinic, *P2$_1$/c*, *a* = 6.169 (1) Å, *b* = 17.812 (3) Å, *c* = 7.587 (1) Å, $\alpha = \gamma = 90°$, $\beta = 112.51$ (1)°, *V* = 770.0 (2) Å³, *Z* = 4, D_x = 1.203 g/cm³, 3898 independent observed intensities, $2\theta_{max}$ = 85°, $F_o \geq 4\sigma(F)$, *R* = 0.043, R_w = 0.049 for 1562 observed reflexions ($2\theta_{max}$ = 55°).
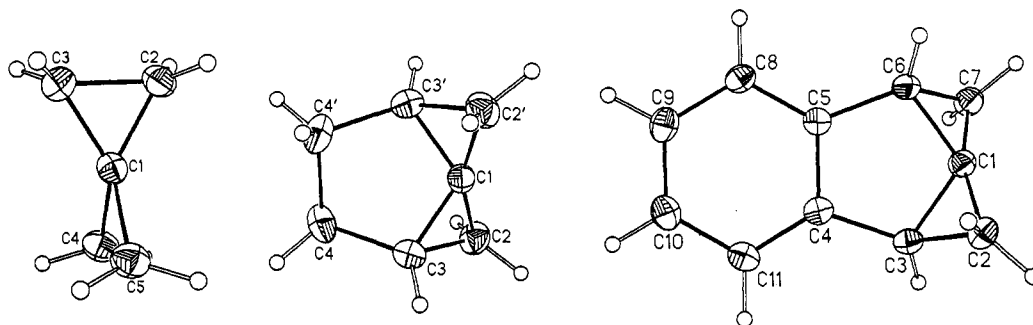
Figure 2. Presentation of **1**, **2**, and **3** with thermal probability plots of 50%. Bond lengths (Å) and angles (deg) with thermal libration correction bond distances given in parantheses. **1**: C1–C2 1.482 (1.488), C1–C3 1.476 (1.484), C1–C4 1.476 (1.483), C1–C5, 1.475 (1.482), C2–C3 1.527 (1.536), C4–C5 1.527 (1.537), C2–C1–C3 62.2, C4–C1–C5 62.3, C2–C1–C4 137.6, C3–C1–C5 136.7, all esd's 0.001 Å and 0.1°. **2**: C1–C2 1.481 (1.487), C1–C3 1.477 (1.487), C2–C3 1.537 (1.546), C3–C4 1.526 (1.536), C4–C4' 1.550 (1.555), C2–C1–C2' 158.2, C3–C1–C3' 110.1, C2–C1–C3 62.6, C1–C3–C4 105.7, C3–C4–C4' 103.4, all esd's 0.001 Å and 0.1°. **3**: C1–C2 1.481 (2) (1.483), C1–C3 1.491 (1) (1.494), C2–C3 1.544 (1) (1.547), C3–C4 1.496 (1) (1.498), C4–C5 1.414 (2) (1.416), C1–C6 1.495 (2) (1.498), C5–C6 1.499 (1) (1.501), C1–C7 1.480 (2) (1.483), C6–C7 1.522 (2) (1.554), C5–C8 1.390 (2) (1.391), C8–C9 1.398 (1) (1.400), C9–C10 1.390 (2) (1.392), C4–C11 1.387 (1) (1.389), C10–C11 1.401 (2) (1.403), C7–C1–C2 164.0, C6–C1–C3 109.0, C7–C1–C6 62.9, C2–C1–C3 62.6, C1–C6–C5 105.2, C1–C3–C4 105.5, C6–C5–C4 109.9, C3–C4–C5 109.7, C6–C5–C8 129.4, C3–C4–C11 129.8, C4–C5–C8 120.3, C5–C4–C11 120.4, C5–C8–C9 119.1, C4–C11–C10 118.8, C8–C9–C10 120.5, C11–C10–C9 120.9, esd's for angles are 0.1°, for bond lengths given in parentheses.
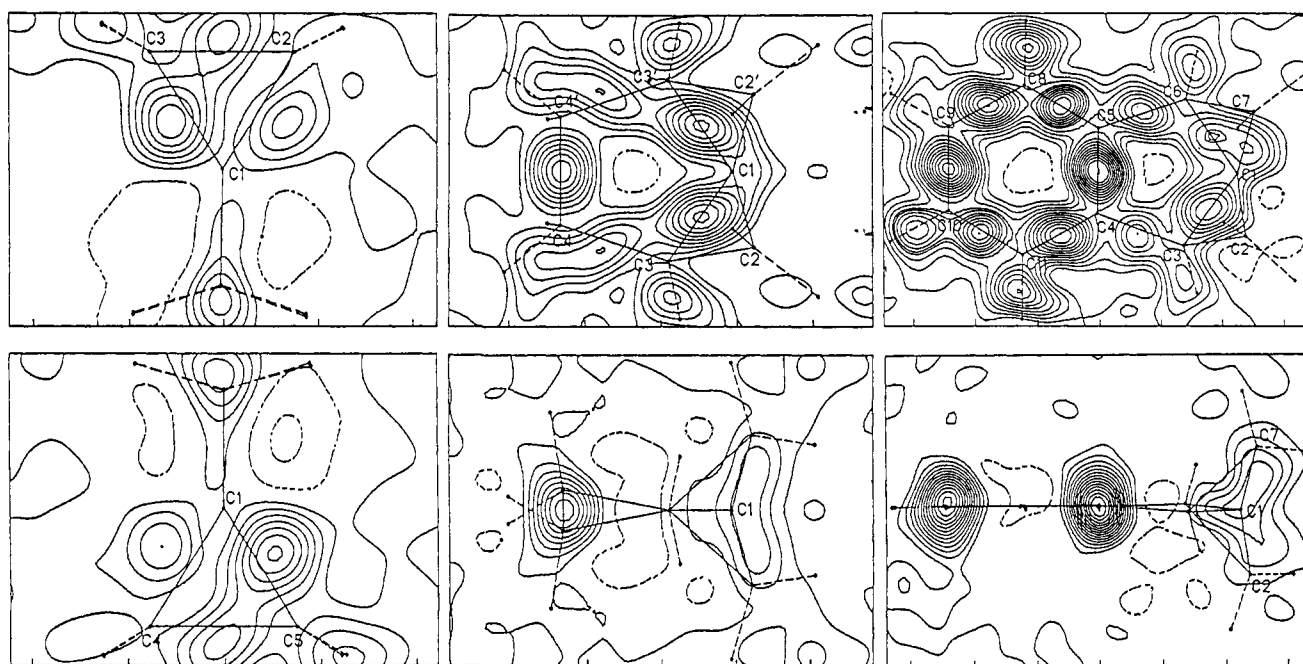
Figure 3. Presentation of X–X electron densities with a distance of 0.05 e/Å (positive) and 0.1 e/Å (negative, dotted lines). **1**: left, top and bottom, sections through the planes of the three-membered rings; **2**: middle, top section through the plane C1–C3–C3'; middle, bottom perpendicular to the upper within the C_2 axis; **3**: right, top section through the benzene ring; bottom, perpendicular to the upper, within the C_2 axis.

posed to 1.08 Å). This is also reflected in the X–X electron densities showing the exocyclic shifted maxima (Figure 3). From the spiroatom lateral bond distances are 1.477 Å and the distal bond distances are 1.527 Å, which are longer than calculated[10] (1.469 and 1.519, respectively). Nonbonding intramolecular distances with 2.750 Å (av) are essentially longer than those obtained from MO calculations (2.265 Å).[10] The exocyclic angles at the spiroatom are almost the same (137.1°, av). Our parameters are equivalent to the electron diffraction studies with respect to the standard deviations given there.[9]

For **2**, possessing crystallographic C_2 axis, the five-membered ring is twisted (C3–C4–C4'–C3' = 34.2°), and distances differ essentially from those calculated.[5,10] The prime example being the C4–C4' bond length, (1.550 Å; 1.555 Å with librational correction) which disagrees with MO calculations (1.500 Å,[10] 1.576 Å[5]). Considering the librational corrected bond length, it is slightly longer than the average bond length in cyclopentane (1.546 Å)[15] and significantly longer than in butane (1.539 Å).[16]

both determined by electron defraction. The expansion is also indicated by the exocyclic shifts of the electron density maxima at the C3–C4 and C3'–C4' bond, respectively. The distortion at the spiroatom is documented by the C2···C2' and C3···C3' distances (2.909 and 2.424 Å) as well as by the angles C2–C1–C2' and C3–C1–C3' (158.2° and 110.1°). The bending by Φ (154.0°) is much higher than the twisting by ψ (80.0°) as predicted by Wiberg's calculations.[5]

3 has C_2 symmetry within the standard deviations, the benzene ring is planar, and the five-membered ring only slightly twisted (C3–C4–C5–C6 = –6.9°). In comparison to **2** the bending of the spiropentane unit in **3** is greater (Φ = 151.4°), whereas the torsion is released (ψ = 85.2°), keeping the C2···C7 and the C3···C6 distance (2.911 and 2.421 Å) almost the same as in **2** but increasing the C7–C1–C2 angle (164.0°) and decreasing the C6–C1–C3 angle (109.0°).

The benzene ring in **3**, not allowing the twisting which is possible for the ethano bond C4–C4' in **2**, is distorted to expand the

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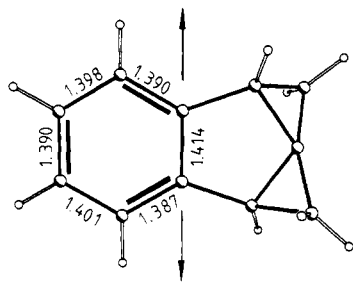
Figure 4.

annulated bond (1.414 Å) and to alternate the distances of the other C–C bonds (1.390, 1.398, 1.390, 1.401, 1.387) leaning toward *one* Kekulé structure (Figure 4).

The X–X electron density distribution (Figure 3) reveal no distortion by a shift of the maxima from the direct atom linkages in the benzene ring, as could be shown by annulation of small-membered rings.[11] Within the five-membered ring the maxima are shifted exocyclic of the bonds C3–C4 and C5–C6, respectively, indicative of the tension of the spring spiropentane.[17]

In tricyclo[2.1.0.0^{1,3}]pentane[18] containing a *zero* bridge between C3–C4 or C2–C5, respectively, bonding and twisting of spiropentane (**1**) comes to an extreme. Here the calculated exocyclic angle at the spiroatom exceeds linearity to 193.91°, thus leading to an inverted carbon.

Supplementary Material Available: Tables of atomic positional parameters and complete listings of bond angles and bond distances of **1**, **2**, and **3** (13 pages); tables of observed and calculated structure factors (61 pages). Ordering information is given on any current masthead page.

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(Binaphtholate)W₂(O-*t*-Bu)₄: The First Metal–Metal Multiple Bond Supported by a Chiral Alkoxide Ligand

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Functionalized binaphthyl subunits are useful templates for controlling the stereochemistry of macrocycles, transition-metal complexes, and main-group hydride reagents.[2-5] Nyori has

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demonstrated that binaphtholate ligands are particularly useful chiral auxiliaries for alane-reducing agents in stereospecific reactions with ketones.[5] Despite the demonstrated utility of main-group binaphtholate complexes in enantiospecific synthesis and probable suitability of binaphtholate substituents as ligands for high valent transition metals, extremely few studies of the coordination chemistry of binaphtholates with transition metals have been forthcoming.[3] We now report the syntheses of (3,3′-R₂-1,1′-bi-2,2′-naphtholate)W₂(O-*t*-Bu)₄ molecules, the first examples of the "W₂(OR)₆" class of metal–metal multiple bonds containing a chiral-supporting alkoxide ligand. To our knowledge, this is the first report of a structurally characterized binaphtholate derivative of a dinuclear transition-metal complex and is representative of a potentially wide-ranging class of easily accessible early transition-metal complexes rendered chiral by this type of supporting ligand.

A toluene solution of 3,3′-dimethylbinaphthol (DMBINOH),[2b] dried over 5 Å molecular sieves, was slowly added to a solution of W₂(O-*t*-Bu)₆[6] in toluene at 0 °C. After 2 h, the solvent was removed in vacuo, and the solid residue was extracted repeatedly with neat toluene. Two recrystallizations from toluene resulted in the isolation of (3,3′-Me₂-1,1′-{2-OC₁₀H₅}₂)W₂(O-*t*-Bu)₄ as nearly equidimensional orange-brown cubes in 55% yield.[7] The analogous (1,1′-{2-OC₁₀H₅}₂)W₂(O-*t*-Bu)₄ product was purified by recrystallization from hexanes. Both products are extremely air and moisture sensitive, decomposing over a few hours in the solid state after exposure to moist air. The ¹H NMR spectra of the complexes (Figure 1) are invariant over a wide temperature range (50 °C through –50 °C) and suggest that the molecule possesses rigorous C_2 symmetry in solution.

The molecular structure of (DMBINO)W₂(O-*t*-Bu)₄, shown in the ball and stick representations in Figure 2,[8] demonstrates that the molecule has a monomeric W₂(OR)₆-type framework consistent with the spectroscopic data. The W–W distance of 2.324 (1) Å is within the normal range observed for homoleptic

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(7) 3,3′-Dimethyl-1,1′-bi-2,2′-naphthol (0.50 g) and W₂(O-*t*-Bu)₆ (1.28 g) yielded crystalline (3,3′-dimethyl-1,1′-bi-2,2′-naphtholate)W₂(O-*t*-Bu)₄ (0.85 g) for an overall 55% yield. Analytical data: ¹H NMR spectrum (benzene-*d*₆, 20 °C) δ = 7.83 (2 H, s, *NAP*(H₄,₄′)), 7.79, 7.38 (2 H, d, *J* = 8.3 Hz, *NAP*(H₅,₅′ and H₈,₈′)), 7.17, 6.95 (2 H, t, *J* = 8.3 Hz, *NAP*(H₆,₆′ and H₇,₇′)), 2.88 (6 H, s, 3,3′-*Me₂*), 1.75, 0.67 (18 H, s O-*t*-*Bu*); ¹³C NMR spectrum (benzene-*d*₆, 18 °C) δ = 167.1 (*NAP* (C₂,₂′)), 134.0, 130.8, 130.4, 128.9, 127.1, 176.4, 125.6, 124.2, 121.6 (*NAP*), 83.6, 75.2 (O*C*Me₃), 35.6, 32.3 (OC*Me₃*), 18.8 (*Me*). Anal. data calcd, C = 46.91, H = 5.43; found, C = 47.16, H = 5.37.

(8) Crystal data for (3,3′-dimethyl-1,1′-bi-2,2′-naphtholate)W₂(O-*t*-Bu)₄ [(DMBINO)W₂(O-*t*-Bu)₄]: An orange crystal (~0.1 × 0.1 × 0.1 mm) obtained by recrystallization from toluene was glued onto a glass fiber and mounted on a Syntex P2₁ diffractometer equipped with a LT-1 low-temperature device. The X-ray experiments were carried out with Cu Kα radiation (λ = 1.5418 Å) at –120 °C in order to avoid decomposition of the crystal by moisture and oxygen. The crystal data were as follows: space group *Pna2₁*; cell dimensions, *a* = 22.745 (3) Å, *b* = 12.398 (3) Å, *c* = 13.150 (3) Å; *Z* = 4; *D*calcd = 1.750 g/cm³. Another possible space group, *Pnam*, was excluded by inspection of a Patterson map, and the space group *Pna2₁* was confirmed by a successful structure refinement. Reflections (4215) were measured up to sin θ/λ = 0.50, and the intensities were corrected for absorption, decay, Lorentz and polarization effects. Independent reflections (2011) were obtained by merging equivalent reflections. *R*int for merging was 0.043. All of the reflections were used in the structure determination and refinements. The positions of two crystallographically independent tungsten atoms were determined by the interpretation of a Patterson map. Successive difference Fourier syntheses revealed the positions of all of the carbon and oxygen atoms. The structure was refined by a full-matrix least-squares method by using anisotropic thermal parameters for tungsten atoms and isotropic thermal parameters for carbon and oxygen atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma(F_o)^2$. Refinement was converged to *R* = 0.044, *R*$_w$ = 0.051, *S* = 0.948 for all data. Although the *R* factor was reduced from 0.0441 to 0.0439 when all of the atoms were anisotropically refined, several thermal parameters became nonpositively defined. Thus, all oxygen and carbon atoms were isotropically refined. The final difference map did not show any significant electron density for the hydrogen atoms and displayed no significant residuals in unexplained positions. Atomic scattering factors including an anomalous dispersion correction factor for the tungsten atoms were taken from *International Tables for X-ray Crystallography*, 1974.