Table I. Spectral Characteristics of Dibenzo[*d,f*]phosphonin Derivatives

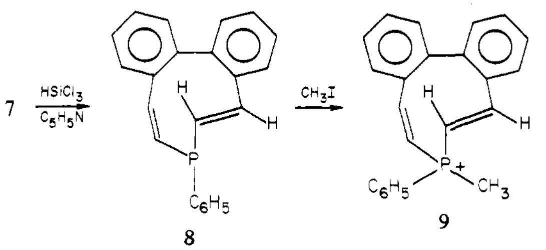
	^{1}H NMR^a			UV		
compd	chemical shift, δ	appearance	assignment	λ_{max} (EtOH)	ε	^{31}P NMR, δ^b
7	6.04	dd; $^2J_{PH}$ = 24 Hz, $^3J_{HH}$ = 14 Hz	trans PC*H*=CH	202	46 000	+17.2
	6.08	dd; $^2J_{PH}$ = 14 Hz, $^3J_{HH}$ = 4 Hz	cis PC*H*=CH	259 (sh)	7 600	
	6.64–7.88	multiplet	aromatic and PCH=C*H*			
8	5.67	dd; $^2J_{PH}$ = 35 Hz, $^3J_{HH}$ = 15 Hz	trans PC*H*=CH	202	43 500	−24.7
	5.97	dd; $^2J_{PH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz	cis PC*H*=CH	255 (sh)	6 600	
	6.77–7.82	multiplet	aromatic and PCH=C*H*			
9	2.37	dd; $^2J_{PH}$ = 14 Hz	P-C*H*$_3$			+1.8
	8.15	dd; $^3J_{PH}$ = 25 Hz, $^3J_{H}$ = 13 Hz	trans PCH=C*H*	202	48 000	
	6.23–7.92	multiplet	aromatic and PC*H*=CH	259 (sh)	10 400	

[a] JEOL MH-100 spectrometer; in $CDCl_3$ solutions. [b] Chemical shifts are referenced to external 85% H_3PO_4, with downfield positive, upfield negative; proton-decoupled FT spectra obtained with a Bruker HFX-90 spectrometer on $CDCl_3$ solutions.

corresponding to **5** resulted only in transannular interaction to regenerate the phenanthrene. Perhaps because of the geometric differences associated with the presence of phosphorus, ring closure did not accompany the formation of **7**. Diol conformation **6** readily accounts for the formation of a trans double bond, since it has the proper anti arrangement of OH and H. Installation of the cis double bond would then follow. Initial cis formation is less likely since the conformation required for it, as revealed by models, has additional features of steric crowding, e.g., from severe 5-OH/4-H peripheral interaction.

The phosphonin synthesis was completed by deoxygenation (95%) of oxide **7** with $HSiCl_3$/pyridine in refluxing benzene. The product (**8**) was a stable solid, mp 68–73 °C. Spectral data are provided in Table I. The cis,trans structure was again clearly evident from ^{1}H NMR data. The ^{1}H chemical shifts are typical of those for 2-phospholenes and do not show the extra deshielding characteristic of phospholes and expected also of a delocalized heteronin. The ring, however, is severely puckered because of the cis,trans geometry and the benzo groups, and the orientation of the p orbitals is highly unfavorable for p_π–p_π overlap. The presence of severe puckering is especially revealed by the magnitude of the two $^2J_{PH}$ values; this constant, well-known[20] to be sensitive to the orientation of the lone pair on P to the coupled proton, has the large value characteristic of 2-phospholenes for one α-H (35 Hz), while the other ^2J value is only 11 Hz. Models show that the dihedral angle (ϕ) relating the lone pair to the α-H of the trans double bond is about 30°, in the range of that in the 2-phospholenes (ϕ ~ 45°), thus allowing assignment of the signal with the larger coupling to this proton. The lone pair orientation to the cis α-H is markedly different (ϕ ~ 120°), accounting[20] for the small size of *J*. The UV absorption is also affected in dramatic fashion by the puckering of the ring; the spectrum consists simply of an intense peak at 202 nm (ε 43 500), with weaker absorption at 255 nm (ε 6600). The characteristic styrenoid and biphenyl absorptions are absent, indicating that puckering has forced the orbitals out of alignment for conjugative interaction. The corresponding dibenzothionin is also known to show no spectral characteristics suggestive of aromaticity.

The phosphonin readily forms a methiodide (**9**, mp 208–209 °C), whose spectral data (Table I) once again reveal the cis,trans structure. The UV spectrum is virtually identical with that of the phosphine, as indeed is that also of the phosphonin oxide **7**. The general similarity of all of these spectra also rules out the presence of any special conjugative effects associated with the various phosphorus functions.



The present work has shown, therefore, that the phosphonin ring can be constructed by standard synthetic methods and that the system may prove to have reasonable stability. Highly puckered dibenzophosphonin **8** is atropic and nonaromatic, and a substance with more favorable geometry must be prepared to assess the presence of heteronin-like aromaticity in this system.

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Cobalt-Mediated Cyclizations of Linear Achiral Diynenes. A One-Step Construction of Complexed Chiral Polycycles

Sir:

The application of intramolecular Diels–Alder reactions ([4 + 2] cycloadditions) has provided the synthetic organic chemist with a powerful tool for the assembly of six-membered rings containing polycyclic natural products.[1] We report a novel construction of such systems based on intramolecular, cobalt-mediated [2 + 2 + 2] cycloadditions in which *three* new carbon–carbon bonds are made with regio- and (in some of the cases examined so far) stereospecificity. This method promises to be a versatile approach to the carbocyclic framework of numerous molecules of synthetic interest[2] (e.g., steroids, terpenes, alkaloids, and other medicinally important molecules). It relies on the ability

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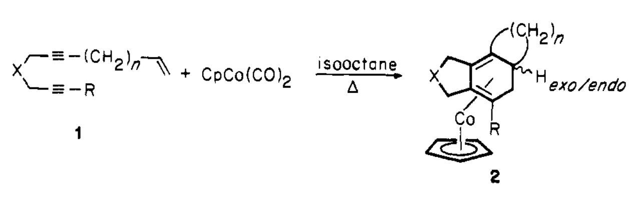
Scheme I



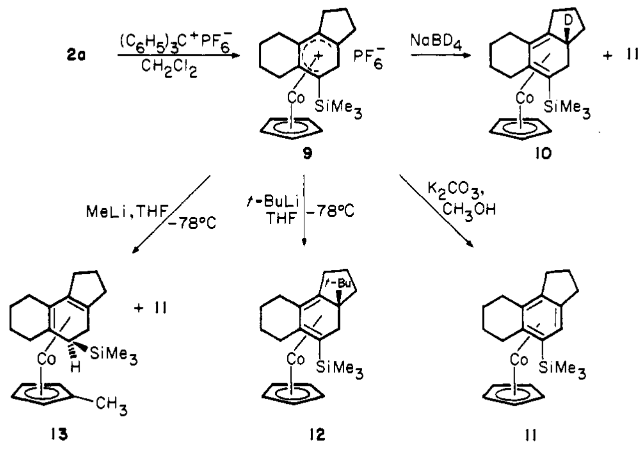
		2 (yield)
a	X = $(CH_2)_2$, *n* = 3, R = $SiMe_3$;	H_{exo} only, 85%
b	X = O, *n* = 3, R = $SiMe_3$;	H_{exo} only, 35%
c	X = $(CH_2)_2$, *n* = 4, R = $SiMe_3$;	H_{exo}:H_{endo} = 1:1, 93%
d	X = $(CH_2)_2$, *n* = 3, R = H;	H_{exo}:H_{endo} = 1:1, 65%
e	X = $(CH_2)_2$, *n* = 4, R = H;	H_{exo}:(H_{endo} + 3rd isomer) = 1:1, 75%

of cobalt to convert acyclic and achiral diynenes to highly functionalizable diene–cobalt complexes containing a new chiral center.

Heating diynene **1** (1 equiv) with $CpCo(CO)_2$ (1.1 equiv) in isooctane under N_2 for 4–5 days followed by chromatography on alumina yielded the complexes **2** (Scheme I). The structure of the products was assigned on the basis of the analytical, chemical, and spectral characteristics.[3,4] In particular, due to the anisotropy of cobalt, proton NMR spectra of (η^4-cyclohexadiene)(η^5-cyclopentadienyl)cobalt complexes in conjunction with decoupling experiments are diagnostic of the relative stereochemistry of the methylene hydrogens, exo positions (with respect to the metal) being relatively shielded, endo positions deshielded.[5] In this way, the stereochemistry around the tertiary center may be readily determined. Furthermore, terminal diene protons and carbons are strongly shielded, the latter particularly so when silylated (δ 42–47), their internal counterparts only weakly so. Further confirmation of spectral assignments was provided by an X-ray structural determination of the isomer of **2c**, spectroscopically characterized as the H_{exo} isomer.[6]

Starting materials (**1**) were prepared[3] by alkylation of the respective diyne with either 5-bromo-1-pentene or 6-bromo-1-hexene (20% Me_2SO–NH_3(l), ca. 50%), followed by trimethylsilylation (Me_3SiCl, ether, room temperature, 95%) and distillation.

Scheme II



Several features of the cyclization are noteworthy. First, **2a** and **2b** *are formed completely stereospecifically*, with the anti-arrangement of metal and tertiary hydrogen. Second, stereospecificity is lost[7] in the formation of **2c–e**, **2e** being contaminated by a third and as yet uncharacterized isomer, presumably derived by hydrogen shifts. Third, separation of the various isomers is possible by fractional crystallization or high-pressure liquid chromatography[8] but is not necessary if only the ligand is desired (vide infra).

Chemical structural proof and amplification of synthetic utility are provided by oxidative degradations. For example, both **2a** and **2c** furnish the free ligand with an aromatized central ring (2,3,6,7,8,9-hexahydro-1*H*-benz[*e*]indene and 1,2,3,4,5,6,7,8-octahydrophenanthrene, respectively) on treatment with bromine (CH_2Cl_2, room temperature, 80%). On the other hand, *the ligand may be removed intact* under different conditions (3 equiv of $CuCl_2 \cdot 2H_2O$, 1.5 equiv of Et_3N, CH_3CN, 10 min) from **2a**, **2b**, and **2c** (1:1 mixture of exo/endo isomers) to yield[3,4] the crystalline silyldienes **3** (85%), **4** (93%), and **5** (80%). Silylated dienes of this type are useful synthetic intermediates.[9] For example, **3** was converted[3,4] (*m*-chloroperbenzoic acid, CH_2Cl_2, 0 °C) to a mixture of the unusual products **6** (55%) and **7** (20%), which were separated by silica gel chromatography. Acid treatment of **6** (5% HCl–H_2O, CH_3OH, room temperature, 0.3 h) furnished **8**.[3,4] Structures were assigned on the basis of spectral measurements.[3]

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(3) All isolated new compounds gave satisfactory spectral (including ^{13}C and high-field (180- or 270-MHz) ^1H NMR) and/or analytical data.

(4) **2a**: red needles; mp 72–74 °C; *m/e* (relative intensity) 370 (M^+, 23%), 368 (3), 297 (77), 73 (100); ^1H NMR (180 MHz) (C_6D_6) δ 0.25 (s, 9 H) 0.53 (m, 1 H), 1.01 (dd, *J* = 16, 8 Hz, 1 H, *exo*-CH_2), 1.31 (dd, *J* = 16, 4 Hz, 1 H, *endo*-CH_2), 1.42–2.97 (m, 14 H), 4.45 (s, 5 H); irradiation at δ 0.53 caused the double doublets at δ 1.01 and 1.31 to simplify to two doublets ($J_{geminal}$ = 16 Hz). Conversely, irradiation at δ 1.16 caused a sharpening of the multiplet at δ 0.53. In addition, deuteration at the tertiary position (cf. **10**) revealed the expected simplification of the central methylene absorptions. ^{13}C NMR (C_6D_6) δ –2.05, 20.3, 20.6, 21.5, 25.4, 27.1, 30.1, 31.8, 33.3, 37.0, 46.3, 72.0, 78.7, 86.7, 91.5. **2b**: red prisms; mp 78–79 °C. **2c** (H_{exo} isomer): red needles; mp 101–102.5 °C. **2d** (H_{exo} isomer): red crystals; mp 48–52 °C. **2d** (H_{endo} isomer): red oil. **2e** (H_{exo} isomer): red crystals; mp 48–51 °C. **3**: colorless needles; mp 44–46 °C. **4**: colorless crystals; mp 24.5–26 °C. **5**: colorless crystals; mp 34–35.5 °C. 6: colorless oil; ^{13}C NMR ($CDCl_3$) δ –0.3, 23.2, 24.3, 26.6, 27.2, 29.7, 29.9, 34.7, 43.4, 45.1, 50.8, 130.5, 133.3, 212.4; $\nu_{C=O}$ 1695 cm^{-1}. 7: colorless crystals; mp 99–102 °C; ^1H NMR (60 MHz) (CCl_4) δ 0.17 (s, 9 H), 1–2.6 (m, 15 H), 6.03 (t, *J* = 4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.0, 20.2, 22.9, 25.9, 29.5, 31.3, 33.7, 37.7, 45.0, 80.8, 123.8, 129.5, 139.6, 140.6; λ_{max} (CH_3OH) 256 (ϵ 21 000) nm; ν_{OH} 3400 cm^{-1}. **8**: Colorless oil; λ_{max} (CH_3OH) 247 nm; $\nu_{C=O}$ 1660 cm^{-1}. **11**: dark red oil; *m/e* (rel intensity) 368.1364 (calcd 368.1370, M^+, 100%); ^1H NMR (270 MHz) (C_6D_6) δ 0.23 (s, 9 H), 1.4–2.8 (m, 14 H), 4.47 (s, 5 H), 5.15 (br s, 1 H); ^{13}C NMR (C_6D_6) δ –1.9, 21.5, 22.2, 24.1, 25.8, 28.0, 28.3, 29.6, 42.1, 76.4, 78.9, 86.0, 91.1, 111.2, 145.0. **12**: red crystals; mp 95–97 °C. **13**: red oil; *m/e* (relative intensity) 384.1679 (calcd 384.1683, M^+, 100%); 79 (CH_3Cp, 42%); ^1H NMR (180 MHz)(C_6D_6) δ –0.06 (s, 9 H), 0.23 (dd, *J* = 17, 3.5 Hz, 1 H, *exo*-CH_2), 0.92 (dd, *J* = 17, 11.5 Hz, 1 H, *endo*-CH_2), 1.06–3.0 (m, 15 H), 2.13 (s, 3 H), 3.94 (bs, 1 H), 4.03 (br s, 1 H), 4.26 (br s, 1 H), 4.30 (br s, 1 H).

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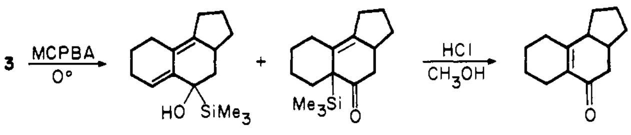

7 6 8

Since **3** may be thought of as the B,C,D portion of the steroid nucleus, oxidation to **8** is significant in light of the medicinal importance of the corticosteroids incorporating an 11-oxo function.

The synthetic *advantages of metal complexation* are demonstrated in Scheme II. Hydride abstraction from **2a** [$(C_6H_5)_3C^+PF_6^-$, CH_2Cl_2, −78 °C, room temperature, 70%) gave red, air-stable salt **9** (mp 219–224 °C dec).[3] Treatment with $NaBD_4$ (CH_3OH–petroleum ether, −78 °C, room temperature) yielded a 1:1 mixture of **10** (*m/e* 371) and **11**. The latter was obtained pure on reaction of **9** with base (K_2CO_3, CH_3OH–petroleum ether, 0 °C, 85%).[3,4] To our knowledge, this is the first reported neutral benzene complex of CpCo. ^{13}C NMR[4] data indicate that the metal is bound in the tetrahapto mode, as shown. The complex **11** is unstable and decomposes with liberation of the ligand. Reaction of **9** with KCN (CH_3OH–petroleum ether, room temperature, 87%) gave this ligand directly (mp 44–46 °C). Nucleophilic carbon–carbon bond formation is achieved with alkyllithium reagents. This is significant in light of the presence of angular alkyl substituents in many natural products. *tert*-Butyllithium (4 equiv, THF, −78 °C, 80%) resulted in the angular derivative **12**.[3,4] Surprisingly, methyllithium (5 equiv, THF, −78 °C, 60%) attacked the cyclopentadienyl ring, followed by what appears to be a cobalt-mediated hydrogen shift to the tricyclic ligand, resulting in **13**,[3,4] in addition to some **11** (15%). The presence of a methylated cyclopentadienyl ring in **13** is evident from mass spectroscopy and NMR measurements, although the assignment of the stereochemistry in the other ligand is tentative. It relies on the unusually high-field proton chemical shifts of the trimethylsilyl group (relative to **2a–c**, **11**, and **12**) and a single hydrogen, which we believe to be its neighbor. Moreover, the carbon spectrum reveals the absence of a terminal silyl diene carbon. Attack of methyllithium on **9** in this manner, if occurring by a simple nucleophilic mechanism, violates the Davis–Green–Mingos rules.[11]

It is evident that the described methodology should provide a powerful simplification of synthetic approaches to molecules containing the hydrophenanthrene, hydrobenzindan, and hydrodicyclopentabenzene frameworks.[2] Advantages are the simultaneous formation of three new carbon–carbon bonds to furnish three annelated rings in one step,[12] facile ligand liberation, use of silicon to mask extensive functionality, and the exploitation of the metal as an electronically activating and sterically directing group. The generation of a chiral center from achiral material in the cobalt-mediated step suggests the possibility of effecting asymmetric inductions by chiral and optically active cobalt. The latter possibility and the application of this reaction to the synthesis of natural products are under intensive investigation.

Acknowledgments. We thank Rudi Nunlist for valuable help in the measurement of high-field NMR spectra, Dr. K. M. Straub for field desorption mass spectra, Dr. M. P. Klein for allowing us generous access to instrumentation, and C. Chang, T. R. Gadek, and J. A. King for useful discussions and additional experimental results. This work was supported by NIH Grant GM 22479 and (in part) by NSF Grant CHE 79-03954.

Supplementary Material Available: Physical data of isolated compounds, including selected proton decoupling experiments and chemical shift assignments; copy of 180-MHz ^1H NMR spectrum of **2b**; ORTEP plot of the structure of **2c** (H_{exo} isomer); experimental procedures leading to **2a**, **9**, and **12** (8 pages). Ordering information is given on any current masthead page.

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(11) S. G. Davies, M. L. H. Green, and D. M. P. Mingos, *Tetrahedron*, **34**, 3047 (1978).

(12) The intermolecular variant of this reaction will be reported in due course.

(13) Fellow of the Alfred P. Sloan Foundation (1976–1980) and Camille and Henry Dreyfus Teacher Scholar (1978–1983).

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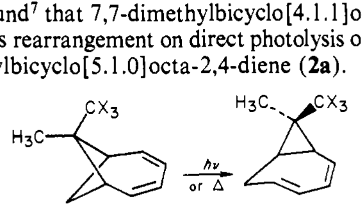
Stereochemistry of the Thermal and Photochemical Rearrangement of 7,7-Dimethylbicyclo[4.1.1]octa-2,4-diene to 8,8-Dimethylbicyclo[5.1.0]octa-2,4-diene

Sir:

In 1974, Klarner[1] reported that the norcaradiene ring-walk, first discovered by Berson and Willcott,[2] proceeds with inversion of configuration at the migrating carbon atom. This finding, which is the opposite of that anticipated on the basis of the Woodward–Hoffmann rules for [1,5] sigmatropic shifts,[3] has been questioned by Baldwin and Broline.[4] Nevertheless, subsequent studies by Klarner and co-workers[5] have confirmed that, at least in the systems investigated by them, the norcaradiene ring-walk does proceed with a large preference for inversion over retention at the migrating carbon.[6]

We have found[7] that 7,7-dimethylbicyclo[4.1.1]octa-2,4-diene (**1a**)[8] undergoes rearrangement on direct photolysis or on pyrolysis to 8,8-dimethylbicyclo[5.1.0]octa-2,4-diene (**2a**). Both **1a** and **2a** are homologues of 7,7-dimethylnorcaradiene, but the stereochemistry of the [1,5] sigmatropic shift that transforms **1a** to **2a** is much easier to study than the corresponding norcaradiene ring-walk. Unlike the ring-walk, the rearrangement of **1a** to **2a** is not degenerate, and in contrast to norcaradiene, neither hydrocarbon is in reversible equilibrium with a valence isomer. Thus, the determination of whether the transformation of **1** to **2** proceeds with retention or inversion requires only a suitably labeled migrating carbon in **1** and a method for establishing the stereochemistry at this center in **2**.



1a, X = H
b, X = D

2a, X = H
b, X = D

In order to minimize possible perturbations of the stereochemical outcome by differences in bulk between the two substituents at the migrating carbon, we utilized **1b**, in which CD_3 replaces the endo CH_3 group in **1a**. Since **1a** is synthesized from α-pinene,[8] the fact that α-pinene-*9,9,9-d_3* had been prepared[9] made **1b** especially attractive for study. However, instead of using the route of Gibson and Erman,[10] which leads to a mixture of α- and β-pinenes, we instead elected to cleave[11] the cyclic ether **3**[10,12] before oxidizing. The remaining steps required to transform **3**

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