

sume that step a of our mechanism is reversible, the carbon-carbon bond breaking of the entering alkyne is allowed to be a possible reaction.¹⁷

Registry No. 1, 94570-76-0; 2, 94596-67-5; 3, 94570-77-1; 4, 94570-78-2; 5, 94570-79-3; 6, 94570-80-6; Fe₃(CO)₉(CCH₃)(COC₂H₅),

88055-72-5; Fe₂(CO)₆(CH₃CCCH₃)₂, 12212-46-3; C₆H₅C≡CC₆H₅, 501-65-5; (CH₃)₃SiC≡CSi(CH₃)₃, 14630-40-1; CH₃C≡CCH₃, 503-17-3; HC≡CH, 74-86-2; *tert*-butylacetylene, 917-92-0; phenylacetylene, 536-74-3.

Supplementary Material Available: Tables of anisotropic thermal parameters, structure factors, hydrogen parameters, and least-squares planes (43 pages). Ordering information is given on any current masthead page.

(17) We thank one of the referees for this suggestion.

Cobalt-Mediated Synthesis of Tricyclic Dienes Incorporating Fused Four-Membered Rings. Unprecedented Rearrangements and Structural Characterization of a Cobalt-Diene Complex by Two-Dimensional NMR Spectroscopy

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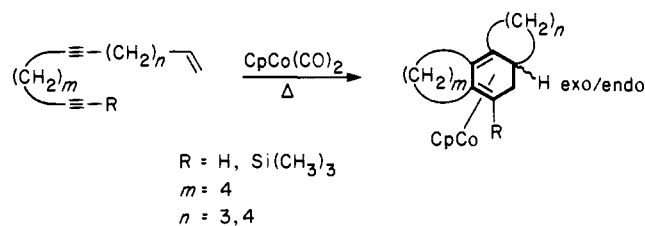
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Abstract: The CpCo(CO)₂-mediated intramolecular (2 + 2 + 2) cycloaddition of enediynes **6** and **9** leads to two tricyclic diene systems **13** and **21** incorporating four-membered rings, a novel transformation. Both cyclizations give unprecedented and unexpected products, the former catalytically and by intra-ring diene rearrangement, the latter stoichiometrically but involving an inter-ring diene shift. A sequence of 2D NMR experiments in conjunction with labeling experiments has pinpointed both structural and mechanistic details.

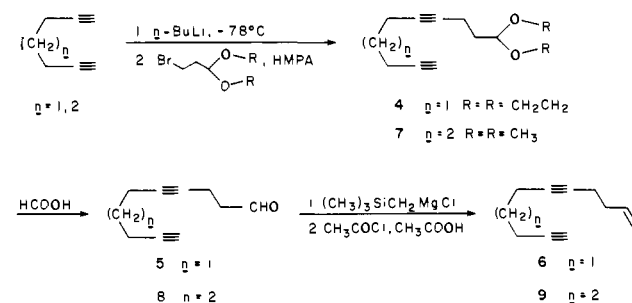
Constructing complex organic compounds in a chemo-, regio-, stereospecific, and expeditious manner is the synthetic organic chemist's most important goal. Elucidating the structure of such products in a rapid and inexpensive manner is the goal of structural chemists. We have shown that metal-mediated (2 + 2 + 2) cycloadditions provide a powerful, selective, and rapid entry into complex structures.¹ In this connection, we have recently employed (cyclopentadienyl)cobalt-promoted intramolecular (2 + 2 + 2) cycloadditions of α,δ,ω -enediynes to give novel steroids.² In these, as well as model transformations,^{1,3} the ring size was restricted to five and six members (Scheme I).

In order to explore further the potential of this transformation, it was of interest to investigate whether systems incorporating four-membered rings could also be constructed in this manner. Such products might be valuable synthetic intermediates by virtue of their built-in strain and also because of their rare topology. For example, the hydrocyclobuta[*a*]naphthalene nucleus **1** has been generated in studies aimed at developing new fragrant terpenes of the norlabdane type.⁴ In addition, the hydrocyclobutandane

Scheme I



Scheme II



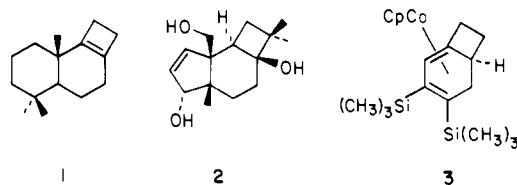
framework occurs in various fungal antibacterial metabolites, as exemplified by the sesquiterpene alcohol punctatin A, **2**.⁵ We

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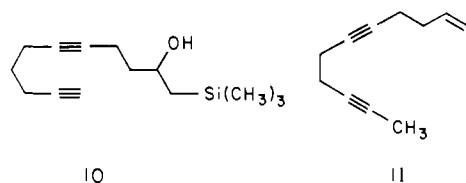


were encouraged by a successful intermolecular variant of our approach in which 1,5-hexenyne was cocyclized with bis(trimethylsilyl)ethyne to furnish **3** with complete stereospecificity, albeit in only moderate yield.⁶ The double bonds in this and related products were positioned as expected, an observation which is significant, as we shall see. This paper reports on the unprecedented cyclization of the two enediyne **6** and **9** in the presence of $\text{CpCo}(\text{CO})_2$ to give **13** and **21**. Both provide the desired tricyclic frameworks but with *rearranged double bonds*. Moreover, **6** accomplishes this task *under catalytic conditions*, the first enediyne to cyclize in this manner, a finding of obvious synthetic utility.

The structure of complex **21** could not be established by the usual spectroscopic methods. As the compound was not crystalline, we could not easily (and expensively) solve this problem by X-ray analysis. However, employment of the powerful combination of three two-dimensional NMR experiments⁷ in conjunction with labeling studies has enabled the structural assignment shown. Especially of note is the use of the two-dimensional nuclear Overhauser experiment to provide the stereochemical information normally available only by X-ray analysis. To date, this is the most comprehensive 2D NMR structure determination of an organometallic complex. The thus defined stereochemistry in **21** has allowed us to elucidate the mechanism of the unusual hydrogen shifts, giving rise to both products **13** and **21**.

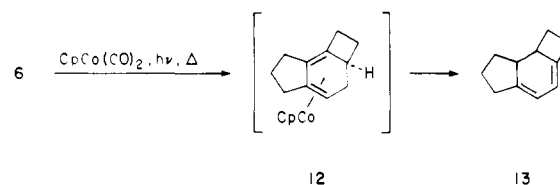
Results and Discussion

Synthesis of Enediyne. The preparation of the required enediyne was straightforward and is outlined in Scheme II. Alkylation of commercially available 1,6-heptadiyne with 3-bromopropanal ethylene acetal⁸ gave **4** (80%) which was hydrolyzed⁹ to result in aldehyde **5** (90%). A "Peterson" olefination¹⁰ with (trimethylsilyl)methylmagnesium chloride, followed by direct treatment with hydrochloric acid,¹¹ did not result in the expected **6** but rather in the silyl alcohol intermediate **10** prior to elimination (80%). Treatment of this species with KH in THF¹¹ furnished

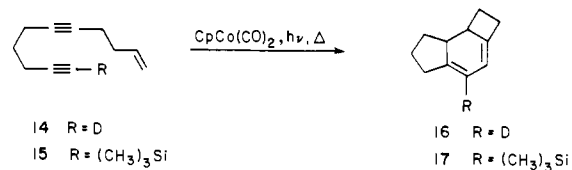


a mixture of the enediyne **11** and **6** (4:1, 85%), the former being the product of a base-catalyzed isomerization. A more successful approach involved exposure of the freshly generated **10** to acetyl chloride and acetic acid,¹² a procedure which resulted in the desired **6** in 60% yield, 43% overall from the starting diyne. The Peterson procedure was chosen because Wittig methylenation gave poorer

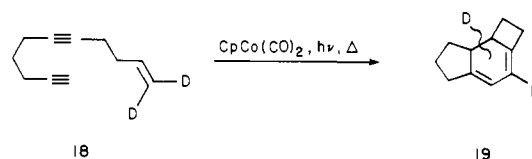
Scheme III



Scheme IV



Scheme V



yields. The latter method was employed in order to generate the 1,1-dideuterated analogue **18** by reaction of **5** with dideuterio-methylenephosphorane (35%). 11-Deuteration and trimethylsilylation to **14** and **15** were achieved in quantitative yield by deprotonation of **6** with ethylmagnesium bromide, followed by D_2O or chlorotrimethylsilane quench. Finally, as a more direct alternative to Scheme II, the alkylation of 1-lithio-1,6-heptadiyne with 4-bromo-1-butene was explored (THF, HMPA) to give only 25% of **6**, in addition to recovered diyne (60%), indicating extensive elimination occurring from the alkenyl halide.

The homologous enediyne **9** was prepared in a manner analogous to that of **6** (Scheme II). Commercial 1,7-octadiyne was alkylated with 3-bromopropanal dimethyl acetal (75%) and the product **7** hydrolyzed with formic acid⁸ to **8** (94%). Olefination then resulted in **9** (60%), synthesized in 42% overall yield from the starting diyne. 1,1-Di and 12-monodeuteration to **24** and **22** was accomplished as in the preparation of the analogous isotopomers of **6**. In addition, 3,3,4,4,7,7,10,10-octadeuteration to **26** was achieved by a novel extension of the reversible sulfur dioxide-ene reaction with alkenes¹⁴ as applied to alkynes¹⁵ (SO_2 , D_2O , 90 °C).

Catalytic Conversion of 6 in the Presence of $\text{CpCo}(\text{CO})_2$. When enediyne **6** was exposed to 1 equiv of $\text{CpCo}(\text{CO})_2$ in boiling and irradiated¹⁶ toluene, instead of the anticipated complex **12**, an air-sensitive colorless isomer of **6** was obtained (Scheme III). This compound could be prepared in best yield (80%) by employing only catalytic quantities of the metal. The structure of the product was assigned based on its spectroscopic behavior.

The mass spectrum showed the correct molecular ion at m/e 146, and the analytical data were consistent with a hydrocarbon of the composition $\text{C}_{11}\text{H}_{14}$. That this compound was not simply the free ligand in **12** was readily apparent from the NMR spectra of its protons and carbons. Both revealed the presence of two vinylic C-H units, the hydrogens at δ 5.44 and 5.68 being only weakly coupled. A relatively deshielded absorption was seen at 3.12 ppm in the proton spectrum, assigned to the tertiary allylic cyclobutyl hydrogen. There were, in addition, three sets of multiplets centered at δ 2.7 (3 H), 2.35 (4 H), and 2.0 (4 H), a pattern consistent with that expected^{1,2,16} for the diene **13** and

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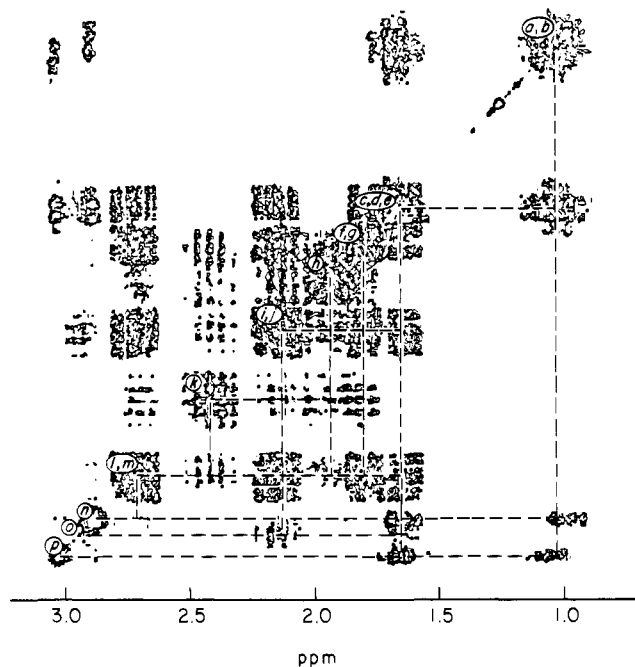


Figure 3. Four-contour plot of the two-dimensional ^1H - ^1H J -correlated spectrum of **21**.

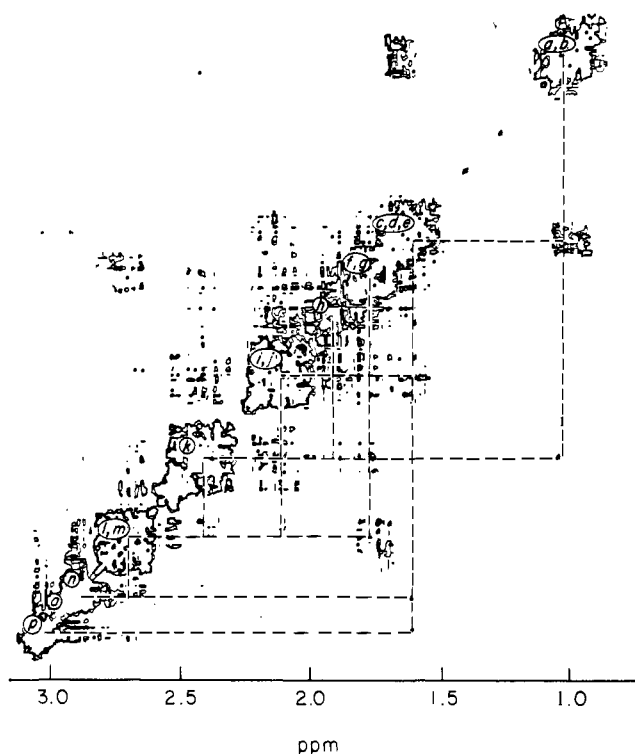


Figure 4. Two-contour plot of the two-dimensional ^1H - ^1H nuclear Overhauser effect spectrum of **21**.

reveals the presence of a hydrogen of given chemical shift (recorded on the horizontal axis) directly bound to a carbon with the chemical shift indicated on the vertical axis. Whenever two diastereotopic hydrogens are present bound to one carbon, two signals are seen in the proton chemical shift dimension correlating with the single signal in the carbon chemical shift dimension. A projection onto the proton axis results in the proton NMR spectrum (not shown in Figure 2) and projection onto the carbon axis furnishes the carbon spectrum. In the contour plot resulting from COSY,²⁰ the proton signals are plotted along the diagonal

(Figure 3). The presence of two mutually coupled hydrogens is indicated by a contour pattern at the intersection of the horizontal and vertical axes, emanating from the two respective proton signals on the diagonal. A similar contour plot is used in the 2D NOE²¹ spectrum. Again, pairs of cross peaks symmetrical with respect to the diagonal indicate nuclear Overhauser enhancement and hence relative proximity between hydrogens with the corresponding chemical shifts.

In the CSCM spectrum (Figure 2) the two tertiary vinyl carbon signals at 49.8 and 52.1 ppm are correlated with proton signals n and p (see Figures 1 and 5) at 3.01 and 2.86 ppm, consistent with the original assignment of the latter as vinyl hydrogens (H-9, H-12). In the COSY spectrum (Figure 3), it is seen that the two pairs of hydrogens giving rise to signals a, b and c, d are coupled mutually and in addition to H-9 and H-12. These relationships point uniquely to the presence of the A-ring diene as in **21**, in which the signals a, b and c, d originate from the hydrogens bound to carbons 10 and 11, the higher field absorptions assignable to the pair located exo with respect to the metal (H- β).¹⁻³ Next one can notice (Figure 2) that the two tertiary aliphatic carbon signals at 37.7 and 33.4 ppm correlate with proton signals l and o at 2.70 and 2.95 ppm, respectively. The latter must therefore arise from hydrogens 2 and 5. Since one of the tertiary protons, represented by signal l, is coupled to the vinyl hydrogen associated with pattern n in the COSY spectrum (Figure 3), the signal l can be specifically assigned to H-2 and n to H-12. The remaining tertiary signal o is thus due to H-5 and the remaining vinyl signal p due to H-9. In this way, all nuclei associated with ring A are assignable.

Let us now proceed with the nuclei in the remainder of the molecule. In the CSCM spectrum (Figure 2), the methylene carbon at 25.2 ppm correlates with proton signals e and j at 1.60 and 2.15 ppm, respectively. Likewise, the methylene carbon at 25.5 ppm is related to proton signals f and m at 1.80 and 2.70 ppm, respectively. In the COSY spectrum (Figure 3), H-5 (signal o) is seen to be coupled to the hydrogens giving rise to signals e and j. Hence the latter could be attributed to either of the pairs H-4 or H-6. Absorptions e and j also show coupling to f and m which could be due either to H-3 or H-7. Since f and m couple only to signals e and j and not to l as expected for H-3, the former are assigned to hydrogens H-7 and e and j to H-6. Further inspection of the CSCM spectrum (Figure 2) reveals that signals k and g at 2.40 and 1.80 ppm correlate with the carbon peak at 29.1 ppm. Finally, h and i at 1.95 and 2.15 ppm are associated with the carbon absorption at 21.6 ppm. These two carbon signals are due to the last two unidentified centers, carbons 3 and 4. An unambiguous assignment could not be made without the use of the 2D NOE spectrum. This measurement also allowed the stereochemistry of the cyclobutane ring and of the hydrogens to be established with good certainty.

By examination of molecular models, it is seen that if the cyclobutane ring were cis-fused and arranged exo with respect to the metal, the possibility of NOE between H-11 β and H-3 β exists. No other structure would be expected to give NOE with H-11 β . In the 2D NOE spectrum (Figure 4), signal a (H-11 β) shows an interaction with signal k. We therefore believe k to be due to H-3 β . This assignment establishes the cyclobutane ring as being as shown in **21**. Signal g must then be associated with H-3 α , since g and k are located on the same carbon. Therefore, h and i are due to H-4. The relatively weak NOE between k and h is contrasted by the relatively strong NOE between k and i. This finding suggests that h is due to H-4 α , trans to H-3 β , and that i is due to H-4 β , cis with respect to H-3 β . At this point, only the stereochemical assignments of the pairs of hydrogens H-6 and H-7 need to be made.

The lack of any strong NOE between the overlapping signals l, m (H-2, H-7) and i, j (H-4 β , H-6) suggests that among the hydrogens H-6 and H-7, the pair giving rise to absorptions m and j has a trans relationship. The weak NOE between h, H-4 α , and

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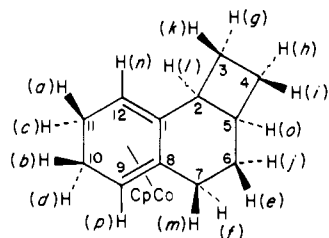
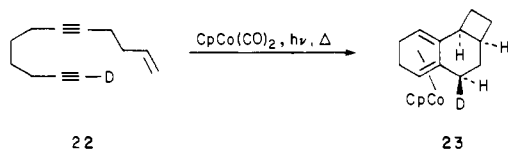


Figure 5. Correlation of the hydrogens in **21** with the peak patterns labeled in Figure 1.

Table I. ^{13}C and ^1H NMR Data and Assignments of **21**

carbon no.	carbon chem shift (δ ppm)	stereochem of attached proton	proton chem shift (δ ppm)	proton signal assignment
1	95.6			
2	37.7	2 α	2.70	l
3	29.1	3 α	1.80	g
		3 β	2.40	k
4	21.6	4 α	1.95	h
		4 β	2.15	i
5	33.4	5 α	2.95	o
6	25.2	6 α	2.15	j
		6 β	1.60	e
7	25.5	7 α	1.80	f
		7 β	2.70	m
8	94.5			
9	52.1		3.01	p
10	26.8	10 α	1.60	c
		10 β	1.00	a
11	26.8	11 α	1.60	d
		11 β	1.01	b
12	49.8		2.86	n
Cp	80.1		4.59	

Scheme VII



signal e, a proton on carbon 6, may be explained by assigning the latter to H-6 β , which in the equatorial position is close to H-4 α . Thus, signal j is due to H-6 α and signal m due to H-7 β . In the postulated preferred conformation of ring B which places H-6 β equatorial, H-6 α and H-7 β can be expected to be trans diaxial, consistent with the lack of NOE between them. The weak enhancement between H-2 and/or H-7 β and H-4 β and/or H-6 α is most likely caused by the proximity of H-4 β and H-7 β . The remaining signal f must arise from H-7 α .

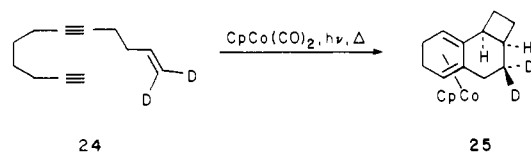
The complete proton assignments are shown in Figure 5. Table I lists the ^{13}C and ^1H NMR spectral data and assignments.

Deuterium-Labeling Experiments. In order to provide data concerning the mechanism of the reaction yielding the unprecedented rearranged product and to corroborate the above assignments, several labeling experiments were performed. In the first, monodeuterated enediyne **22** was exposed to the cyclization conditions to give **23** (Scheme VII) in 88% yield. The spectral data on this compound were very similar to that obtained on **21**, except for the molecular ion in the mass spectrum at m/e 285, the sharply diminished intensity of the peak assigned to C-7, and the reduced intensity and simplification of the peak area m, assigned to H-7 β . Similarly, peak patterns e, f, and j lost some of their complexity.

A second labeling study involved **24** which furnished **25** (Scheme VIII). The signals e and j (H-6) disappeared from the ^1H NMR spectrum and the absorptions assigned to the hydrogens surrounding C-6 simplified extensively. Moreover, now the ^{13}C peak correlated with C-6 suffered a drastic diminution in height.

Finally, the octadeuterated derivative **26** was cyclized to **27** (Scheme IX), providing a most informative set of NMR data.

Scheme VIII



Scheme IX

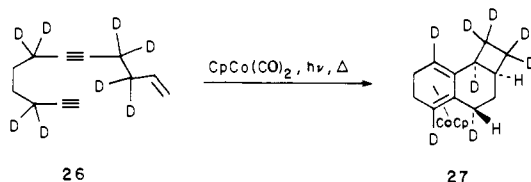


Table II. Coupling in the B Ring of **21** as Established in **27**

proton	conform arrangement	coupling constants, Hz	coupled proton	coupling type ^a
7 β	axial	12.4	6 α	a, a
		<5	6 β	a, e
6 α	axial	12.4	7 β	a, a
		12.4	6 β	gem
		5.0	5	a, e
6 β	equatorial	12.4	6 α	gem
		5	7 β	e, a
		5	5	e, e
5	equatorial	5	6 β	e, e
		<5	6 α	e, a

^aa = axial, e = equatorial, gem = geminal.

In the ^{13}C spectrum, all deuterated carbons were seen to diminish in intensity relative to C-1, C-5, C-6, C-8, C-10, C-11, and the Cp nuclei. The proton spectrum, because of its simplicity, and the removal of signal i from the peak pattern at δ 2.15, which gave a first-order pattern for j (H-6 α), allowed the stereochemical assignments for ring B to be corroborated. Thus, m (H-7 β) simplified to a broad doublet with a large coupling (12.4 Hz), and j turned into a ddd ($J = 12.4, 12.4, 5.0$ Hz) clearly indicative of the trans-diaxial relationship between H-7 β and H-6 α . Models indicate that H-5 α is staggered between H-6 α and H-6 β , leading to relatively smaller coupling. The assignments are depicted in Table II.

Mechanistic Considerations. Although the stereochemical course of the cyclization of **6** could not be ascertained, the data on the formation of **21** from **9** appear to implicate α -hydride migrations within the B ring from proposed intermediate **12** in the first case and from the A ring in **20** in the second. The specificity seems remarkable, no scrambling of label being observable in the experiments involving deuterium.

Related isomerization reactions of complexed alkenes are well-known and thought to proceed through η^3 -allyl hydrides.²² The intra-ring rearrangement of **12** to **13** has similarity to those observed for cyclic diene iron²³ and rhodium²⁴ complexes. Accordingly, we have also observed the stereospecific thermal isomerization of (η^4 -cyclohexadiene-5-*exo-d*₁)(η^5 -cyclopentadienyl)cobalt by exclusive endo-hydrogen shifts at 165 °C.²⁵ However, this process is not detectable at the temperatures typically employed to effect cyclizations of enediyne (boiling toluene). Thus, **12** must be activated with respect to such a rearrangement, and indeed the actual mechanism for the remarkable formation of catalytically derived **13** remains unknown. We do not know

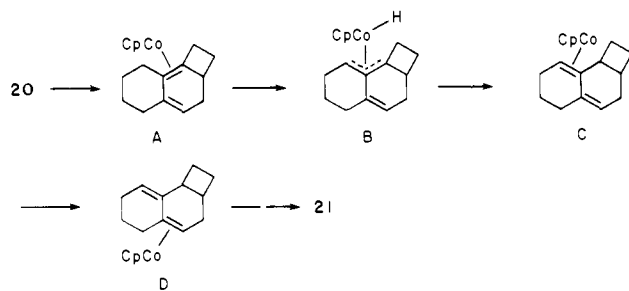
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Scheme X



at this stage whether **13** is a kinetic or thermodynamic product and why it appears unsuitable as a ligand to CpCo.

In contrast to **12**, complex **20** finds a kinetically or thermodynamically controlled pathway which allows the formation of a stable A-ring complex. A plausible (albeit not fully substantiated) mechanism is shown in Scheme X. It involves the η^2 -intermediate A which would be capable of isomerizing one double bond through the allyl hydride B to give C. To our knowledge, the next step, a "walk" along a transoid diene (e.g., C \rightarrow D), is not clearly precedented²² but might have been involved in other related rearrangements.²⁶ *s-trans*-Diene complexes of zirconium and hafnium have recently been reported;²⁷ hence this type of diene complexation is known at least for early transition metals.

Summary and Conclusion

In this study we have shown the usefulness of the combined application of three two-dimensional NMR experiments in elucidating the structure of an organometallic complex. The formation of two rearranged CpCo-cyclohexadiene complexes **13** and **21** was unprecedented in CpCo-mediated (2 + 2 + 2) cycloadditions. Some insight into the mechanism of the formation of these complexes was provided by labeling experiments. The stereospecific and high yielding preparation of **21** could be useful in the construction of tricyclic intermediates en route to more complex molecules. Equally useful may be the observation of a catalytic route to the diene **13**, which possesses the rare and difficult-to-construct ring skeleton of natural products of the type **2**. Synthetic exploitation of this chemistry is under way.

Experimental Section

General Data. ¹H NMR and ¹³C NMR spectra were recorded on home-built UCB-180-MHz, UCB-200-MHz and UCB-250-MHz instruments. (See the 2D NMR experiments for specific details.) NMR data are reported as follows: chemical shift in parts per million downfield of an internal standard (C₆D₆H peak at 7.20 ppm downfield from tetramethylsilane for proton spectra; central peak of the C₆D₆ triplet at 128.0 ppm downfield from tetramethylsilane for carbon spectra). Infrared spectra were obtained on a Perkin-Elmer Model 681 with data station. Mass spectra [reported as *m/e* (rel intensity) at 70 eV] and elemental analyses were provided by the Mass Spectral Service and Microanalytical Laboratory, respectively, in the College of Chemistry at the University of California, Berkeley. Only the most prominent or diagnostic peaks are reported for IR and MS.

All column chromatography was executed with E.M. Reagents silica gel (70–230 mesh ASTM) or Woelm neutral alumina deactivated with water. Thin-layer chromatography was carried out on Analabs analytical silica gel or neutral alumina plates.

Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. When necessary, non-ether solvents were dried over molecular sieves (4 Å). Ether solvents were dried over boiling sodium benzophenone. All reactions involving air- or moisture-sensitive organometallic reagents were carried out under dry nitrogen. Solvents were degassed by freeze/thaw

cycles under high vacuum. Toluene washed with sulfuric acid and distilled from CaCO₃ (anhydrous) onto molecular sieves (4 Å) was used for the cobalt-promoted cyclizations.

General Cyclization Conditions. In a silylated single-necked round-bottom flask equipped with a condenser connected to a vacuum/N₂ line, the enediyne in toluene was degassed by three cycles of freeze/pump/thaw. CpCo(CO)₂ (1.1 equiv) was introduced via syringe to the boiling solution irradiated by a projector lamp (visible light, GE-ENH, 250 W). The reaction was followed by TLC. When no starting material remained, the solution was cooled to room temperature and the solvent removed in vacuo. The residue was purified by column chromatography (alumina, activity 3) under N₂ eluting with *n*-hexane. The solvent was removed in vacuo. The NMR and analytical samples were prepared under N₂ in a Vacuum Atmosphere drybox. Degassed C₆D₆ was used for the NMR samples.

4,9-Decadiynyl Ethylene Acetal (4). To a solution of 1,6-heptadiyne (10.0 g, 0.11 mol) in dry THF (150 mL) at -78 °C was added *n*-butyllithium (36 mmol, 1.62 M in hexane) slowly under nitrogen. Subsequently the solution was stirred for 4 h at -78 °C, the temperature raised to 0 °C, and HMPA (15 mL) added. After the solution was cooled to -78 °C, 3-bromopropanal ethylene acetal⁸ (6.6 g, 36 mmol) was added. The solution was warmed to room temperature and stirred for 12 h. After aqueous workup, distillation yielded starting 1,6-heptadiyne (5.0 g, 54 mmol) and **4** (5.53 g, 80%): clear liquid, bp 66–68 °C (0.2 mm); IR (thin film) 3300, 2120 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 4.90 (t, *J* = 4.8 Hz, 1 H), 3.75 (AA'BB', 4 H), 2.30–2.15 (m, 6 H), 1.90 (t, *J* = 2.6 Hz, 1 H), 1.76 (dt, *J* = 7.8, 4.8 Hz, 2 H), 1.62 (quin, *J* = 7.0 Hz, 2 H); MS, *m/e* 192 (M⁺, 1.7%), 191 (5.4), 177 (2.9), 163 (17), 119 (33), 91 (67), 73 (100). Anal. Calcd for C₁₂H₁₆O₂: C, 74.97; H, 8.39. Found: C, 75.03; H, 8.16.

4,10-Decadiynyl (5). Acetal **4** (2.0 g, 10.4 mmol) was hydrolyzed in formic acid (2.0 mL) overnight at room temperature for 10 h. After neutralization with NaHCO₃, the solution was extracted with pentane and dried, the crude product was filtered through alumina (activity 3) with ether and distilled to yield **5** (1.38 g, 90%): colorless liquid, bp 48–51 °C (0.25 mm); IR (thin film) 3300, 2730, 2120, 1720 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 9.77 (s, 1 H), 2.60 (t, *J* = 7.0 Hz, 2 H), 2.46 (m, 2 H), 2.25 (m, 4 H), 1.93 (t, *J* = 2.6 Hz, 1 H), 1.66 (quin, *J* = 7.0 Hz, 2 H); MS, *m/e* 148 (M⁺, 3.7%), 147 (21), 119 (24), 105 (46), 91 (100), 79 (63).

1-Undecene-5,10-diyne (6). The procedure used for **11** was repeated but scaled up to accommodate **5** (3.2 g, 22 mmol). The mixture was kept at 0 °C after the addition of **5**, and subsequently acetyl chloride (3 mL) followed by glacial acetic (3 mL) added. This solution was heated to reflux for 3 h. Bicarbonate workup and distillation yielded **6** (1.9 g, 60%): colorless liquid, bp 95–97 °C (20 mm); IR (thin film) 3300, 3085, 2120, 1640 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 5.84 (ddt, *J* = 15.3, 7.6, 6.0 Hz, 1 H), 5.08 (dd, *J* = 15.3, 1.7 Hz, 1 H), 4.98 (dd, *J* = 7.6, 1.7 Hz, 1 H), 2.40–2.25 (m, 8 H), 1.94 (t, *J* = 2.6 Hz, 1 H), 1.55 (quin, *J* = 7 Hz, 2 H); MS, *m/e* 146 (M⁺, 3.2%), 145 (18), 131 (43), 117 (69), 91 (93), 77 (100). Anal. Calcd for C₁₁H₁₄: C, 91.08; H, 8.91. Found C, 91.23; H, 9.20.

Enediyne 6 by Direct Alkylation of 1,6-Heptadiyne. *n*-Butyllithium in hexane (0.10 mol) was slowly added to 1,6-heptadiyne (9.2 g, 0.10 mol) in dry THF (150 mL) at -78 °C. The mixture was allowed to warm to 0 °C, and HMPA (15 mL, 0.12 mol) was added, followed by 4-bromo-1-butene (13.5 g, 0.10 mol) in THF (50 mL). The solution was kept at 0 °C for 6 h and then stirred for 12 h at room temperature. Aqueous workup and GC analysis revealed the presence of starting diyne (60%), enediyne **6** (27%), and what was thought to be the product of dialkylation. Fractional distillation gave pure **6** (3.64 g, 25%).

4,10-Undecadiynyl (8). To a solution of 1,7-octadiyne (10.0 g, 0.10 mol) in dry THF (150 mL) at -78 °C was added *n*-butyllithium (36 mmol, 1.62 M in hexane) slowly under nitrogen. After stirring for 4 h at -78 °C, the temperature was raised to 0 °C and HMPA (15 mL) added. After renewed cooling to -78 °C, 3-bromopropanal ethylene acetal (6.6 g, 36 mmol) was introduced. The solution was warmed to room temperature, stirred for 12 h, and subjected to aqueous workup. The excess 1,7-octadiyne was removed in vacuo. The crude product was hydrolyzed in formic acid at room temperature for 12 h. The resulting mixture was neutralized with NaHCO₃, and the solution was extracted with pentane, dried (MgSO₄), and filtered through alumina (activity 3), eluting with ether. Distillation gave **8** (4.0 g, 25%): colorless liquid, bp 97–99 °C (0.15 mm). IR (thin film) 3300, 2730, 2120, 1728 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 9.77 (s, 1 H), 2.65–2.40 (m, 4 H), 2.10 (m, 4 H), 1.93 (t, *J* = 2.5 Hz, 1 H), 1.60 (br s, 4 H); MS, *m/e* 162 (M⁺, 1.2), 161 (7), 133 (25), 119 (27), 105 (37), 91 (100).

1-Dodecene-5,11-diyne (9). (Chloromethyl)trimethylsilane (4.9 g, 40 mmol) was slowly added at 0 °C to magnesium (1.2 g, 50 mmol) in ether (10 mL) and stirred for 2 h at room temperature. The aldehyde **8** (3.80

(26) See, for example: (a) Whitlock, H. W. Jr.; Markezich, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 5290. (b) Markezich, R. L.; Whitlock, H. W., Jr. *Ibid.* **1971**, *93*, 5291. (c) Whitlock, H. W., Jr.; Markezich, R. L. *Ibid.* **1965**, *87*, 3605. (d) Whitlock, H. W., Jr.; Reich, C.; Woessner, W. D. *Ibid.* **1971**, *93*, 2483.

(27) See: (a) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3735 and the references therein. (b) Erker, G.; Wicher, J.; Engel, K.; Krüger, C. *Chem. Ber.* **1982**, *115*, 3300.

g, 25.6 mmol) was then slowly introduced and the solution was first stirred for 2 h at room temperature and then heated to reflux for 2 h. After the solution was cooled to room temperature, acetyl chloride (3 mL) was added, followed by glacial acetic acid (3 mL). The solution was heated at reflux for 3 h. Basic aqueous workup (NaHCO₃) and distillation from CaCO₃ gave enediyne **9** (2.2 g, 60%): colorless liquid, bp 92–94 °C (120 mm); IR (thin film) 3300, 3085, 2120, 1640 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 5.85 (ddt, *J* = 16.5, 9.7, 6.8 Hz, 1 H), 5.06 (d, *J* = 16.5 Hz, 1 H), 4.98 (d, *J* = 9.7 Hz, 1 H), 2.05 (m, 8 H), 1.93 (t, *J* = 2.6 Hz, 1 H), 1.60 (br s, 4 H); MS, *m/e* 160 (M⁺, 0.8%), 159 (4), 145 (10), 131 (28), 117 (64), 91 (100), 79 (58), 77 (55). Anal. Calcd for C₁₂H₁₆: C, 89.94; H, 10.06. Found: C, 89.74; H, 9.99.

1-Undecene-5,9-diyne (11). (Trimethylsilyl)methylmagnesium chloride was prepared from the chloride (1.18 g, 9.63 mmol) according to ref 10, and the aldehyde **5** (0.95 g, 6.4 mmol) in ether (5 mL) was added. After it was stirred at room temperature for 1 h, the mixture was heated to reflux for 1 h, treated with aqueous HCl (2 N, 5 mL) for 12 h, and subsequently worked up with bicarbonate water. Filtration through alumina (activity 3) in ether gave a single compound (GC) presumed to be alcohol **10** (1.2 g, 80%): colorless oil; IR (thin film) 3400, 3300, 2120, 1250 cm⁻¹. The alcohol (1.46 g, 6.2 mmol) in dry THF (5 mL) was slowly added to a suspension of KH (600 mg, 15 mmol) in THF (15 mL) under nitrogen at room temperature. After 24 h of stirring, the mixture was quenched with ethanol and subjected to aqueous workup. A mixture (GC) of the two diynes **6** and **11** (ratio 1:4, 0.87 g, 96%) was obtained. Preparative GLC (20% SE30, 170 °C) gave first **6** and then **15** (600 mg, 66%): colorless oil; IR (thin film) 3300, 3085, 1640 cm⁻¹; ¹H NMR (CDCl₃, 250 MHz) δ 5.85 (ddt, *J* = 14.4, 7.8, 6.0 Hz, 1 H), 5.06 (dd, *J* = 14.4, 1.5 Hz, 1 H), 4.97 (dd, *J* = 7.8, 1.5 Hz, 1 H), 2.30 (m, 4 H), 2.22 (m, 4 H), 1.77 (br s, 3 H); MS, *m/e* 146 (M⁺, 4.1%), 145 (27), 131 (90), 91 (86), 77 (100).

Tricyclo[6.3.0.0^{2,5}]-5,7-undecadiene (13). Enediyne **6** (0.292 g, 2.0 mmol) and CpCo(CO)₂ (0.2 mmol) in toluene (30 mL) were heated at reflux according to the general cyclization procedure for 3 h to yield **2** (0.233 g, 80%): air-sensitive colorless oil; IR (thin film) 3075, 3010, 1655 cm⁻¹; ¹H NMR (250 MHz, C₆D₆) δ 5.68 (br s, 1 H), 5.44 (br s, 1 H), 3.12 (br s, 1 H), 2.8–2.6 (m, 3 H), 2.5–2.2 (m, 4 H), 2.2–1.8 (m, 4 H); ¹³C NMR (63.1 MHz, C₆D₆) δ 145.9, 145.6, 130.7, 133.0, 34.3, 33.5, 31.4, 30.3, 29.6, 29.0, 27.7; MS, *m/e* 146 (M⁺, 13%), 119 (7), 117 (100), 115 (30), 91 (19), 39 (25). Anal. Calcd for C₁₁H₁₄: C, 91.08; H, 8.91. Found: C, 91.18; H, 8.50.

11-Deuterio-1-undecene-5,10-diyne (14). A solution of ethylmagnesium bromide (1.5 mmol, 2.0 M in ether) was added at 0 °C to **6** (0.146 g, 1.0 mmol). After the solution was stirred at room temperature for 3 h, excess D₂O was introduced. The solution was filtered through alumina (activity 3) with pentane. Solvent evaporation yielded **14** (0.140 g, 95%): colorless liquid; IR (thin film) 3070, 2570, 1640 cm⁻¹; deuterium incorporation 98% by ¹H NMR; MS, *m/e* 147 (M⁺, 3.6%), 146 (23), 118 (70), 91 (84), 79 (95), 39 (100).

11-(Trimethylsilyl)-1-undecene-5,10-diyne (15). Enediyne **6** (2 g, 13 mmol) was metallated as in the preparation of **14** and then treated with excess chlorotrimethylsilane to give **15** (2.75 g, 92%): colorless oil; IR (thin film) 3090, 2180, 1645, 1250 cm⁻¹; ¹H NMR (CDCl₃, 250 MHz) δ 5.80 (ddt, *J* = 15.3, 7.6, 6.0 Hz, 1 H), 5.08 (dd, *J* = 15.3, 1.7 Hz, 1 H), 4.98 (dd, *J* = 7.6, 1.7 Hz, 1 H), 2.35–2.20 (8 H, m), 1.75 (quin, *J* = 6.7 Hz, 2 H), 0.13 (s, 9 H); MS, *m/e* 218 (M⁺, 0.6%), 203 (11), 175 (8), 144 (22), 91 (23), 73 (100).

Tricyclo[6.3.0.0^{2,5}]-7-deuterio-5,7-undecadiene (16). Enediyne **14** (0.20 g, 1.3 mmol) in toluene (30 mL) and CpCo(CO)₂ (0.16 mL, 1.3 mmol) were heated at reflux for 4 h according to the general cyclization procedure to yield **16** (0.155 g, 78%): colorless oil; ¹H NMR (250 MHz, C₆H₆) δ 5.69 (s, 1 H), 3.12 (br s, 1 H), 2.8–2.6 (m, 3 H), 2.5–2.2 (m, 4 H), 2.2–1.8 (m, 4 H).

Tricyclo[6.3.0.0^{2,5}]-7-(trimethylsilyl)-5,7-undecadiene (17). Enediyne **15** (0.33 g, 1.51 mmol) was cyclized as usual and the product filtered through alumina (activity 3) to give **17** (0.29 g, 88%): colorless oil; ¹H NMR (250 MHz, C₆D₆) δ 5.78 (s, 1 H), 3.10 (br s, 1 H), 2.57 (m, 3 H), 2.45–2.15 (m, 4 H), 2.10 (br s, 1 H), 2.0–1.9 (m, 2 H), 1.9–1.7 (m, 1 H), 0.27 (s, 9 H); ¹³C NMR (63.1 MHz, CDCl₃) δ 152.9, 144.8, 131.3, 32.5, 31.7, 30.5, 30.2, 29.7, 26.0, -0.75 (one vinyl carbon could not be located).

1,1-Dideuterio-1-undecene-5,10-diyne (18). *n*-Butyllithium in hexane (3.6 mmol) was added to methyl-*d*₃-triphenylphosphonium iodide (1.5 g, 3.6 mmol) suspended in ether (20 mL). After the solution was stirred for 1 h at room temperature, the aldehyde **5** (0.32 g, 2.16 mmol) was added in ether (10 mL), and the resulting mixture was stirred at room temperature for 4 h and subjected to aqueous workup to give **18** (0.13 g, 42%): colorless oil; IR (thin film) 3300, 3070, 3055, 2055, 2120, 1575 cm⁻¹; MS, *m/e* 148 (M⁺, 4.6), 147 (11), 132 (19), 118 (32), 84 (100); 75% deuterium incorporation by ¹H NMR.

Tricyclo[6.3.0.0^{2,5}]-1/2,6-dideuterio-5,7-undecadiene (19). Enediyne **18** (0.148 g, 1 mmol) was cyclized as usual to give **19** (0.07 g, 42%): colorless oil; MS, *m/e* 148 (M⁺, 100%), 133 (58), 120 (78), 83 (90).

(Tricyclo[6.4.0.0^{2,5}]-1(12),8-dodecadiene)(cyclopentadienyl)cobalt (21). Enediyne **9** (0.320 g, 2.0 mmol) in toluene (30 mL) and CpCo(CO)₂ (0.26 mL, 2.2 mmol) were heated at reflux according to the general cyclization procedure for 6 h to yield **21** (0.50 g, 88%): red oil; IR (thin film) 3090, 2970, 2920, 2860, 2825, 1435, 1340, 1160, 1100, 1000, 800 cm⁻¹; ¹H NMR see text; ¹³C NMR (off resonance decoupled) (63.1 MHz, C₆D₆) δ 95.6 (s), 94.5 (s), 80.1 (d, Cp), 52.1 (d), 49.8 (d), 37.7 (d), 33.4 (d), 29.1 (t), 26.8 (t, 2C), 25.5 (t), 25.2 (t), 21.6 (t); MS, *m/e* 284 (M⁺, 34.3%), 282 (7), 280 (10), 252 (13), 214 (11), 187 (27), 164 (61), 160 (43), 132 (91), 104 (100), 91 (76). Anal. Calcd for C₁₇H₂₁Co: C, 71.82; H, 7.45. Found: C, 71.37, H, 7.14.

12-Dueterio-1-dodecene-5,11-diyne (22). A solution of ethylmagnesium bromide (1.5 mmol, 2.0 M in ether) was added at 0 °C to enediyne **9** (0.160 g, 1.0 mmol) in ether (5 mL). After the solution was stirred at room temperature for 3 h, excess D₂O was introduced. The solution was filtered through alumina (activity 3) with pentane. Solvent evaporation gave **22** (0.150 g, 94%): colorless liquid; the deuterium incorporation was 90% by ¹H NMR integration; IR (thin film) 3070, 2580, 1640 cm⁻¹; MS, *m/e* 161 (M⁺, 0.6%), 160 (3), 146 (10), 132 (31), 118 (63), 105 (44), 91 (100).

(Tricyclo[6.4.0.0^{2,5}]-7-deuterio-1(12),8-dodecadiene)(cyclopentadienyl)cobalt (23). Enediyne **22** (0.120 g, 0.74 mmol) in toluene (15 mL) and CpCo(CO)₂ (0.10 mL, 0.84 mmol) were heated at reflux according to the general cyclization procedure for 6 h to yield **23** (0.185 g, 88%): red oil; MS, *m/e* 285 (M⁺, 100%), 281 (15), 280 (10), 253 (27), 252 (22), 215 (17), 214 (13), 188 (26), 187 (29), 124 (9), 59 (7).

1,1-Dideuterio-1-dodecene-5,11-diyne (24). A solution of *n*-butyllithium (4.63 mmol, 1.62 M in hexane) was slowly added under N₂ to a suspension of methyl-*d*₃-triphenylphosphonium iodide (1.89 g, 4.63 mmol) in ether (20 mL) at room temperature. After the solution was stirred for 1 h, aldehyde **8** (0.50 g, 3.08 mmol) in ether (10 mL) was slowly added. The solution was stirred for 4 h, worked up with water, and chromatographed on alumina (activity 3), eluting with hexane to give **24** (0.165 g, 33%): colorless oil; deuterium incorporation was 75% by ¹H NMR integration; IR (thin film) 3300, 3080, 1580 cm⁻¹; MS, *m/e* 162 (M⁺, 30%), 161 (10), 160 (22), 147 (9), 146 (10), 133 (22), 119 (63), 91 (100).

(Tricyclo[6.4.0.0^{2,5}]-7,7-dideuterio-1(12),8-dodecadiene)(cyclopentadienyl)cobalt (25). Enediyne **24** (0.080 g, 0.5 mmol) in toluene (15 mL) and CpCo(CO)₂ (0.08 mL, 0.7 mmol) were heated at reflux for 6 h according to the general cyclization procedure to yield **25** (0.115 g, 80%): MS, *m/e* 286 (M⁺, 100%), 284 (25), 282 (14), 281 (13), 254 (15), 253 (17), 215 (15), 188 (26), 162 (85), 134 (40), 132 (38).

3,3,4,4,7,7,10,10-Octadeuterio-1-dodecene-5,11-diyne (26). Enediyne **9** (0.50 g, 3.1 mmol) in D₂O (5 mL) was placed in a pressure bottle which was cooled to -78 °C and filled with SO₂ (5 mL). The solution was heated to 90 °C at 9 atm for 6 h. More D₂O (10 mL) was added at -78 °C and the solution heated again at 90 °C for 6 h. The gas was allowed to escape at room temperature, and the solution subjected to basic aqueous workup (NaHCO₃) and filtered through alumina (activity 3) to give **26** (0.40 g, 80%): colorless oil; deuterium incorporation 80% by ¹H NMR integration; IR (thin film) 3300, 3090, 2200, 2150, 2120, 1640 cm⁻¹; MS, *m/e* 168 (M⁺, 5.9%), 167 (30), 166 (70), 165 (100), 164 (72), 163 (31), 162 (8), 161 (3.5), 160 (3.1).

(Tricyclo[6.4.0.0^{2,5}]-2,3,3,4,4,7,9,12-octadeuterio-1(12),8-dodecadiene)(cyclopentadienyl)cobalt (27). Enediyne **26** (0.250 g, 1.5 mmol) in toluene (30 mL) and CpCo(CO)₂ (0.24 mL, 2 mmol) were heated at reflux for 4 h according to the general cyclization procedure to yield **27** (0.350 g, 80%): red oil; MS, *m/e* 292 (M⁺, 24.2%), 291 (77), 290 (100), 256 (389), 255 (43), 219 (21), 218 (20), 191 (63), 190 (62), 124 (39), 59 (91).

Two-Dimensional ¹H Nuclear-Overhauser-Effect Spectrum of 21. The data were acquired by using the UCB-180 NMR spectrometer (Bruker superconducting magnet operating on 180.1-MHz proton frequency, Nicolet 1180 computer, Nicolet 239B pulse programmer) and processed with a Nicolet 1180E computer. Nicolet's two-dimensional nuclear Overhauser effect (2D NOE) experiment was used to provide the pulse program. The 90° ¹H pulse was 8.5 μs. The fixed delay was set equal to the T₁ of the methylene protons, 2.0 s. This procedure excluded all couplings with *J* values greater than 0.13 Hz. The incremental delay was equal to the dwell time of 555 μs. The sweep width was 900 Hz. The spectrometer frequency was set at the left edge of the spectrum, 5.3 ppm. Single-phase detection was used. The pulse delay was 2 s. When a 0.1 M solution of **21** in C₆D₆ was scanned, 32 1K transients were collected for each of the 256 incremental spectra. The total time for data acquisition was 10 h. The FID data were apodized by a sine-bell function and Fourier-transformed. After transposing the matrix, the data were

apodized by a sine-bell function, zero-filled, and Fourier-transformed, and the absolute value was taken and symmetrized. The resolution was 1.75 Hz in each dimension. The data were plotted with a Zeta plotter. The total time for data processing and plotting was about 1 h.

Two-Dimensional ^1H - ^1H J-Correlated Spectrum of 21. The data were acquired by using the UCB-200 NMR spectrometer (Cryomagnetics Systems Inc. superconducting magnet operating on 201.9-MHz proton frequency, Nicolet 1180 computer, Nicolet 293A' pulse programmer) and processed with a Nicolet 1180E computer. Nicolet's correlated spectrum (COSY) experiment was used to provide the pulse program. The 90° ^1H pulse was 7.7 μs . The fixed delay was 7.0 μs to emphasize couplings less than 35 Hz. The incremental delay was equal to the dwell time of 500 μs . The sweep width was 1000 Hz. The spectrometer frequency was set at the left edge of the spectrum, 5.3 ppm. Single-phase detection was used. The pulse delay was 2 s. When a 0.1 M solution of 21 in C_6D_6 was scanned, 16 1K transients were collected for each of the 256 incremental spectra. The total time for data acquisition was less than 3 h. The data were apodized by a sine-bell function and Fourier-transformed. After transposing the matrix, the data were apodized by a sine-bell function, zero-filled, and Fourier-transformed, and the absolute value was taken and symmetrized. The resolution was 1.95 Hz in both dimensions. The data were plotted with a Zeta plotter. The total time for data processing and plotting was about 1 h.

Two-Dimensional ^{13}C - ^1H Chemical Shift Correlation Map of 21. The data were acquired by using the UCB-250 NMR spectrometer (Cryomagnetics Systems Inc. superconducting magnet operating on 250.8-MHz proton frequency, Nicolet 1180 computer, Nicolet 293A' pulse programmer) and processed with a Nicolet 1180E computer. Nicolet's chemical shift correlation map (CSCM) experiment was used to provide the pulse program. The 90° ^1H pulse from the decoupler was 36 μs . The 180° ^{13}C pulse was 37 μs . The two fixed delays were 3.0 and 2.5 ms. The incremental mixing delay was 227 μs to give a proton spectral width of 4.4 ppm. Single-phase detection was used. The decoupler frequency

was set at the left edge of the proton spectrum at 4.9 ppm. The spectrometer frequency was set at the left edge of the carbon region, 103 ppm. The sweep width was 88 ppm. The pulse delay was 1.3 s. When a 0.5 M solution of 21 in C_6D_6 was scanned, 72 4K transients were collected for each of the 256 incremental spectra. The total time for data acquisition was 7.5 h. The data were apodized by a sine-bell function and Fourier-transformed in the carbon dimension. After the matrix was transposed to the proton dimension, the data were apodized by a sine-bell function, zero-filled, and Fourier-transformed, and the absolute value was taken. The resolution was 1.4 Hz in the carbon dimension and 2.2 Hz in the proton dimension. The data were plotted with a Zeta plotter. The total time for data processing and plotting was about 2 h.

Acknowledgment. We are grateful to R. Nunlist and Dr. I. Holden for discussions concerning 2D NMR experiments. This work was supported by the NIH GM-22479. E. D. was the recipient of a Fulbright/Ministerio de Universidades e Investigacion (MUI), Spain, Scholarship (1981-1983), R.L.H. of a University of California Regents' Fellowship (1982-1984), and K.P.C.V. of a Camille and Henry Dreyfus Teacher-Scholarship (1978-1983).

Registry No. 4, 94732-58-8; 5, 94732-59-9; 6, 94732-60-2; 7, 87226-59-3; 8, 87226-60-6; 9, 94732-61-3; 10, 94732-62-4; 11, 94732-63-5; 12, 94751-08-3; 13, 94732-64-6; 14, 94732-65-7; 15, 94732-66-8; 16, 94751-09-4; 17, 94732-67-9; 18, 94732-68-0; 19, 94732-69-1; 20, 94751-10-7; 21, 94751-11-8; 22, 94732-70-4; 23, 94751-12-9; 24, 94732-71-5; 25, 94751-13-0; 26, 94732-72-6; 27, 94751-14-1; CpCo(CO)₂, 12078-25-0; $(\text{CH}_3)_3\text{SiCH}_2\text{MgCl}$, 13170-43-9; 1,6-heptadiyne, 2396-63-6; 3-bromopropanal ethylene acetal, 18742-02-4; 4-bromo-1-butene, 5162-44-7; 1,7-octadiyne, 871-84-1; (chloromethyl)trimethylsilane, 2344-80-1; methyl-*d*₃-triphenylphosphonium iodide, 1560-56-1.

Reaction of the Samarium-Hydrogen Bond in $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$ with Carbon Monoxide: Formation, Isomerization, and X-ray Crystallographic Characterization of *cis*- and *trans*- $\{(\text{C}_5\text{Me}_5)_2[(\text{C}_6\text{H}_5)_3\text{PO}]\text{Sm}\}_2(\mu\text{-OCH=CHO})$ ^{1,2}

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Abstract: $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$ (I) reacts with CO in arene solvents to form a product, II, which generates crystals of *cis*- $\{(\text{C}_5\text{Me}_5)_2[(\text{C}_6\text{H}_5)_3\text{PO}]\text{Sm}\}_2(\mu\text{-OCH=CHO})$ (IIIa) when $(\text{C}_6\text{H}_5)_3\text{PO}$ is added. IIIa crystallizes from toluene under hexane diffusion in space group $P\bar{1}$ with unit cell dimensions $a = 18.673$ (7) Å, $b = 17.641$ (6) Å, $c = 13.973$ (5) Å, $\alpha = 102.40$ (3)°, $\beta = 93.57$ (3)°, $\gamma = 93.15$ (3)°, and $Z = 2$ (with six toluene molecules of crystallization per unit cell) for $D_c = 1.27$ g cm⁻³. Least-squares refinement on the basis of 6427 observed reflections led to a final R value of 0.065. IIIa isomerizes to the *trans* isomer IIIb at room temperature in hours to days depending on sample concentration. IIIb crystallizes from toluene under hexane diffusion in space group $P2_1/n$ with unit cell dimensions $a = 14.678$ (2) Å, $b = 17.424$ (3) Å, $c = 28.736$ (4) Å, $\beta = 100.67$ (1)°, and $Z = 4$ for $D_c = 1.34$ g cm⁻³. Least-squares refinement on the basis of 8312 observed reflections led to a final R value of 0.051. In both IIIa and IIIb, $(\text{C}_5\text{Me}_5)_2\text{Sm}[\text{OP}(\text{C}_6\text{H}_5)_3]$ units are connected by a bridging $-\text{OCH=CHO}-$ moiety. The two C_5Me_5 ring centroids, the OPPh_3 oxygen atom, and the enediolate oxygen atom describe a distorted tetrahedral coordination geometry around each samarium center. The enediolate bridge is best resolved in the *cis* isomer IIIa and has the following bond distances (Å): Sm-O, 2.147 (10) and 2.179 (10); C-O, 1.319 (19) and 1.352 (18); C=C, 1.324 (22). O-C=C angles of 132.51 (18)° and 128.4 (18)° were observed. In the *trans* isomer IIIb there is an apparent rotational disorder of the bridging group about the Sm-O bonds.

Carbon monoxide is one of the most extensively investigated ligands in organometallic chemistry. In recent years, the desire to use CO as a feedstock has encouraged research on both the homogeneous and heterogeneous conversion of CO/H₂ mixtures

("syn-gas") to reduced, homologated oxygenates and hydrocarbons.⁴⁻¹² One reaction that has been studied to model hydrogen

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