is accompanied by a gross change in cluster geometry.[19]

$$2[Os_{10}C(CO)_{24}HgR]^- \rightarrow [Os_{20}C_2(CO)_{48}Hg]^{2-} + HgR_2 \tag{11}$$

We have sought evidence for the symmetrization reaction represented by eq 12. This reaction, however, has

$$2[Re_7C(CO)_{21}HgY]^{2-} \rightleftharpoons [\{Re_7C(CO)_{21}\}_2Hg]^{4-} + HgY_2 \tag{12}$$

not been observed. Furthermore, the symmetric cluster $[\{Re_7C(CO)_{21}\}_2Hg]^{4-}$ cannot be synthesized from 2:1 mixtures of $[Re_7C(CO)_{21}]^{3-}$ and HgX_2 (X = Cl, CN). $Hg(\eta^3\text{-}M_3)_2$ complexes are known in which a mercury atom is triply bridging two triangular faces,[16,20,21] but in all cases the triply bridged faces are sterically uncongested. The structures of $[Re_7C(CO)_{21}ML_n]^{2-}$ derivatives[1-3] show that six CO ligands are oriented markedly toward the capping metal center; thus, steric interactions around the Hg center may strongly disfavor formation of $[\{Re_7C(CO)_{21}\}_2Hg]^{4-}$. On the other hand, the high overall charge density (4–) on the symmetrization product would likely also be a barrier to its formation.

Acknowledgment. This work was supported by National Science Foundation Grants DMR 86-12860 to the Materials Research Laboratory and CHE 84-07233 to J.R.S.

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Communications

Scope of the Cobalt-Catalyzed [2 + 2 + 2] Homo-Diels–Alder Reaction

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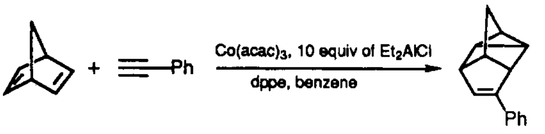
Summary: A cobalt-catalyzed homo-Diels–Alder reaction between norbornadiene and several acetylenes is described. Azeotropic drying of $Co(acac)_3$ is found to increase the reactivity of the catalyst such that sterically hindered and silylsubstituted acetylenes participate in the cycloaddition.

The discovery that metal catalysts can promote cycloadditions has become a powerful tool in organic synthesis.[2,3] The homo-Diels–Alder reaction,[4] in which two new rings are created in the deltacyclic product, is an example of a multi-ring-forming reaction, but one that thus far has found few applications in synthesis. This situation has arisen due to the lack of generality with respect to dienophiles that participate in the coupling and the competing [2 + 2] cycloadditions.[4h] In this letter we describe results that substantially increase the scope of [2 + 2 + 2] cycloadditions between norbornadiene and various acetylenes catalyzed by cobalt–phosphine complexes.

Simple unactivated acetylenes are notoriously poor dienophiles in cycloaddition reactions.[5] We were intrigued, therefore, by a report[6] which indicated that acetylenes react with norbornadiene in the presence of low-valent cobalt complexes to yield a mixture of cycloadducts in which the major product arises via a [2 + 2 + 2] coupling (eq 1). A severe limitation in the reported reaction was that substitution of an aryl group for a simple alkyl group resulted in low yields of the desired coupling products, the major adduct arising from a homocoupling of two norbornadienes.[6] This lack of reactivity and the resulting competitive side processes had to be overcome before the reaction could be sufficiently reliable for use in total synthesis.



1

(1)

In our initial experiments we isolated deltacyclene 1 in 75–80% yield when a benzene solution of norbornadiene and phenylacetylene was treated with a catalytic quantity (1–5 mol %) of commercially available $Co(acac)_3$ with added 1,2-bis(triphenylphosphino)ethane (1:1) which was reduced with Et_2AlCl. Any change in solvent, ligand, or the use of other acetylenes led to unacceptable yields and

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(1) NSERC (Canada) University Research Fellow, 1987–1992.

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(5) For a review of acetylenes as dienophiles see: DeLucchi, O.; Modena, G. *Tetrahedron* **1984**, *40*, 2585.

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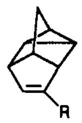
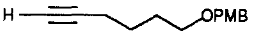
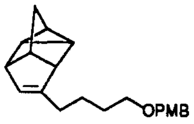
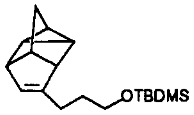
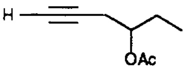
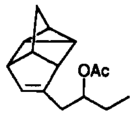
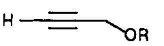
Table I. Cobalt-Catalyzed Coupling of Norbornadiene and Substituted Acetylenes

entry	acetylene	time, h	product[a]	yield,[b] %
1	H—≡—R			
a	R = butyl	1	2, R = butyl	10[c] 91[d]
b	R = isopropyl	24	R = isopropyl	50 58[e]
c	R = tert-butyl	16	R = *tert*-butyl	24[a] 50[e,f]
2		12		74[g]
3		2		90
4		4		82[h]
5			NR	

[a] 1–2 mol % of Co(acac)$_3$, 1 equiv of dppe, 4 equiv of Et$_2$AlCl in benzene. [b] Yield after flash chromatography or distillation. [c] Reaction with unactivated catalyst. [d] THF/benzene (1:1) as solvent. [e] 5 mol % of Co(acac)$_3$. [f] Contaminated with 5–10% 2-(3,3-dimethyl-1-butynyl)nortricyclane, see text. [g] 8 equiv of Et$_2$AlCl. [h] ca. 1:1 ratio of diastereomers.

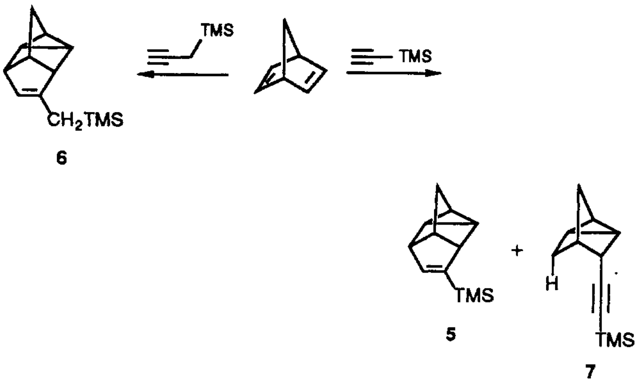
very slow reactions. For example, 1-hexyne gave less than 10% of cycloaddition product 2[7] even after prolonged heating (Table I).

We reasoned that adventitious moisture might interfere with the reduction step (perhaps explaining why 10 equiv of reducing agent were used). The reported preparation[8] of Ni(COD)$_2$ indicates that drying commercially available anhydrous Ni(acac)$_2$ before the reduction step is required. In an analogous manner, the Co(acac)$_3$ was first subjected to azeotropic drying.[9a] Reduction as before in benzene yielded cobalt complexes that had markedly enhanced activity in the cycloaddition process.[9b] THF/benzene (1:1) proved to be an effective solvent mixture and also minimized the homodimerization of norbornadiene.[10]

A examination of other acetylenes indicated that increasing substitution at the propargylic carbon diminished the rate of the reaction (Table I). This problem was overcome by simply increasing the amount of catalyst (5 mol %) and acetylene (1.5–2 equiv) (entries 1a–c). The decrease in reactivity is presumably a result of difficulty in achieving complexation of the acetylene to the metal, which must precede cycloaddition.

A variety of functional groups are compatible with this catalyst and the conditions under which it is generated. These include benzyl and silyl ethers and esters, all of which are frequently used as protecting groups (entries 2–4). We were surprised to find the location of the heteroatom with respect to the acetylene was crucial in achieving cycloaddition. Substrates with oxygen atoms in a propargylic position (entry 5) do not react, and addition of 1 equiv of methyl propargyl ether inhibits the reaction of hexyne with norbornadiene.

Silicon in the form of acetylenic and propargylic[11] silanes reacted smoothly with norbornadiene yielding vinyl- and allylsilane containing products 5 and 6 in 60 and 75% yields, respectively (TMS = trimethylsilyl). It is worth noting that 5 was obtained in <2% yield when unactivated catalyst was used to promote the cycloaddition under *refluxing* conditions. A disubstituted acetylene, bis(trimethylsilyl)acetylene, gave no cycloadduct under the usual conditions.



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(7) Satisfactory NMR, IR, and mass spectra and/or combustion analyses were obtained for all new compounds.

(8) Schunn, R. A. *Inorg. Synth.* **1974**, *15*, 5.

(9) (a) The color of the solid changed from brown to purple. (b) A typical procedure is as follows: Azeotropically dried Co(acac)$_3$ (1–5 mol %) was transferred to a flame-dried flask along with dppe (1 equiv). After the flask was flushed with argon, the solvent, norbornadiene, and the acetylene were added and the flask was placed in a water bath at room temperature. Diethylaluminum chloride was added dropwise over 2–10 min at a rate such that the temperature did not exceed 45 °C. (*Caution*: the reaction can be exothermic and there can be an induction period.) The reaction was stirred for the indicated time before removal of the solvent to yield an oil. Purification by bulb-to-bulb distillation or flash chromatography provided the product.

(10) The dimers of norbornadiene have been observed as products in the presence of rhodium catalysts. Acton, N.; Roth, R. J.; Katz, T. J.; Frank, J. K.; Maier, C. A.; Paul, I. C. *J. Am. Chem. Soc.* **1972**, *94*, 5446 and references therein.

(11) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678.

Organometallics **1989**, *8*, 2735–2737 2735

These cycloadditions tend to be very clean processes yielding a single product. However, in the reaction of trimethylsilylacetylene, a second product was isolated in ca. 5–10% yield. Analysis of the IR (2168 cm^{-1}) and ^{13}C NMR spectra (three cyclopropane resonances at 16.6, 11.4, and 9.8 ppm) indicated that the structure was that represented by 7. Close examination of the spectrum of the crude reaction mixture revealed a similar adduct was produced in the reaction with *tert*-butylacetylene. No trace of these adducts was observed in the other acetylene cycloadditions. Insertion into the terminal C–H bond[12] appears to be a competitive reaction in those cases where a bulky group hinders coordination of the acetylene to the cobalt.[13] Two possible stereochemical outcomes (exo and endo) are possible for the acetylenyl group in adduct 7. In this instance it is impossible to distinguish between the two since the products are *enantiomers*. It is nevertheless of mechanistic significance. Experiments using a labeled norbornadiene will resolve the issue and are presently underway in our laboratories. We favor coordination to the endo face of the olefin since exo complexation cannot lead to formation of a cyclopropane ring.[14]

Deltacyclene has proven to be useful in the synthesis of highly strained unnatural products of theoretical interest.[15] More highly substituted deltacyclenes are now readily available. The results presented demonstrate a much broader scope of homo-Diels–Alder cycloadditions than was previously indicated.

Acknowledgment. This research was supported by the Natural Science and Engineering Research Council (NSERC) of Canada, the Bickell Foundation, and the University of Toronto. We thank Louise Edwards for preliminary experiments and Professor G. L. Lange for the use of valuable equipment. We also thank a reviewer for bringing ref 4i and 14 to our attention.

Supplementary Material Available: Details of the preparation and spectral data for all new compounds (8 pages). Ordering information is given on any current masthead page.

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[12] Insertion into terminal acetylenes is presumably one of the steps in carbonylation of terminal alkynes catalyzed by palladium salts: Tsuji, J.; Takahashi, M.; Takahashi, T. *Tetrahedron Lett.* **1980**, 849.

[13] Ethylene is known to react with norbornadiene to yield vinylnortricyclane (see ref 6). The mechanism in this reaction is proposed to proceed via a metallacycle which seems unlikely in the present case.

[14] Nickel catalyzes the vinylation of norbornene and norbornadiene to give the exo product. Bogdanovic, B.; Henc, B.; Losler, A.; Meister, B.; Pauling, H.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 954. However, no cyclopropane formation accompanies C–C bond formation.

[15] (a) von R. Schleyer, P.; Leone, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 4164. (b) Coates, R. M.; Kirkpatrick, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 4883 and ref 5.

Mechanism of η^1-Pentadienyl Ligand Isomerization. First Structural Characterization of a 3-η^1-Pentadienyl-Metal Complex[1]

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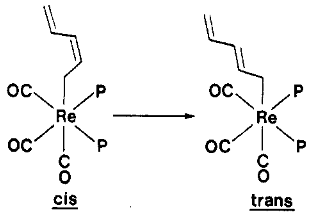
Summary: Treatment of (η^5-pentadienyl)Re(CO)$_3$ with 1 equiv of $Et_2PCH_2CH_2PEt_2$ (depe) produces (*cis*-η^1-pentadienyl)Re(CO)$_3$(depe) (**1**). Upon irradiation at 0 °C, **1** is converted to (3-η^1-pentadienyl)Re(CO)$_3$(depe) (**2**). This species rearranges thermally via a phosphine dissociation/association process to (*trans*-η^1-pentadienyl)Re(CO)$_3$(depe) (**3**). Compounds **1** and **2** have been structurally characterized.

Earlier, we reported cis → trans isomerization in the η^1-pentadienyl ligand of (η^1-pentadienyl)Re(CO)$_3$(PR$_3$)$_2$ (R = Me, Et) complexes.[2]



We now communicate new mechanistic information about this interesting ligand rearrangement, obtained from a study of the 1,2-bis(diethylphosphino)ethane (depe) system. Included in this report is an X-ray diffraction study of (3-η^1-pentadienyl)Re(CO)$_3$(depe), a key intermediate in the isomerization process. This represents the first structural characterization of a "3-η^1-pentadienyl" ligand, wherein the central carbon atom of the pentadienyl chain coordinates in a σ-fashion to the metal center.

Treatment of (η^5-pentadienyl)Re(CO)$_3$[3] with 1 equiv of 1,2-bis(diethylphosphino)ethane (depe) in diethyl ether leads to the formation of (*cis*-η^1-pentadienyl)Re(CO)$_3$(depe) (1).[4] The solid-state structure of 1, determined by X-ray crystallography, is shown in Figure 1.[5] The coordination geometry of 1 is octahedral with the three carbonyl ligands in a facial orientation. The *cis*-η^1-pentadienyl ligand exhibits an overall sickle shape with torsional angles of −0.5° and 178.0° for C1–C2–C3–C4 and C2–C3–C4–C5, respectively. The five pentadienyl carbon atoms are coplanar to within 0.02 Å, and the pentadienyl plane makes a dihedral angle of 29.7° with the complex's equatorial plane (Re/P1/P2/C11/C31).

Characteristic of the cis geometry about the internal double bond, C2–C3, is the relatively small coupling constant between H2 and H3 (11 Hz). A second distinguishing feature of the ^1H NMR spectrum of 1 is the downfield shift of H4's signal relative to that of H2 (δ 7.33 vs δ 6.42).

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[1] Pentadienyl-Metal-Phosphine Chemistry. 18. For the previous paper in this series, see: Bleeke, J. R.; Rauscher, D. J. *Organometallics* **1988**, *7*, 2328.

[2] Bleeke, J. R.; Rauscher, D. J.; Moore, D. A. *Organometallics* **1987**, *6*, 2614.

[3] Paz-Sandoval, M. A.; Powell, P. *J. Organomet. Chem.* **1981**, *219*, 81.

[4] **Synthesis of (*cis*-η^1-Pentadienyl)Re(CO)$_3$($Et_2PCH_2CH_2PEt_2$) (1).** 1,2-Bis(diethylphosphino)ethane (depe) (0.12 g, 6.0×10^{-4} mol) was added to (η^5-pentadienyl)Re(CO)$_3$ (0.20 g, 6.0×10^{-4} mol) in 40 mL of diethyl ether, and the resulting solution was stirred for 4 days at room temperature. Solvent was then removed under vacuum. The residue was redissolved in diethyl ether and filtered through Celite. Slow evaporation of the diethyl ether solvent at room temperature yielded 0.12 g (37%) of pale yellow crystals. Anal. Calcd for $C_{18}H_{31}ReP_2O_3$: C, 39.77; H, 5.76. Found: C, 39.82; H, 5.62.

Spectroscopic Data for 1. ^1H NMR (benzene-d_6, 20 °C): δ 7.33 (d of t, J_{H-H5_a} = 17 Hz, J_{H-H5_s} = 11 Hz, 1, H4), 6.42 (q, J_{H-H} = 11 Hz, 1, H2), 5.82 (t, J_{H-H} = 11 Hz, 1, H3), 5.22 (d, J_{H-H4} = 17 Hz, 1, H5$_a$), 5.08 (d, J_{H-H4} = 11 Hz, 1, H5$_s$), 1.48 (m, 4, phosphine bridge CH$_2$'s), 1.38 (m, 2, H1's), 1.32 (m, 4, phosphine ethyl CH$_2$'s), 0.92 (m, 4, phosphine ethyl CH$_2$'s), 0.80 (m, 12, phosphine CH$_3$'s). $^{13}C\{^1H\}$ NMR (benzene-d_6, 20 °C): δ 148.6 (t, J_{C-P} = 4 Hz, C2), 134.4 (s, C4), 116.8 (s, C3), 110.6 (s, C5), 24.0 (m, phosphine bridge CH$_2$'s), 21.2 (d, J_{C-P} = 29 Hz, phosphine ethyl CH$_2$'s), 15.0 (d, J_{C-P} = 26 Hz, phosphine ethyl CH$_2$'s), 8.5 (s, phosphine CH$_3$'s), 7.9 (s, phosphine CH$_3$'s), −4.2 (t, J_{C-P} = 7 Hz, C1). $^{31}P\{^1H\}$ NMR (benzene-d_6, 20 °C): δ 27.4 (s). IR (toluene, 22 °C, selected peaks): 2002, 1928, 1885 cm^{-1} (s, C—O stretches); 1620 cm^{-1} (w, C=C stretch); 1040, 1030 cm^{-1} (m, P—C stretches). UV (acetonitrile, 22 °C): λ_{max} = 282 nm (ϵ = 6500).

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