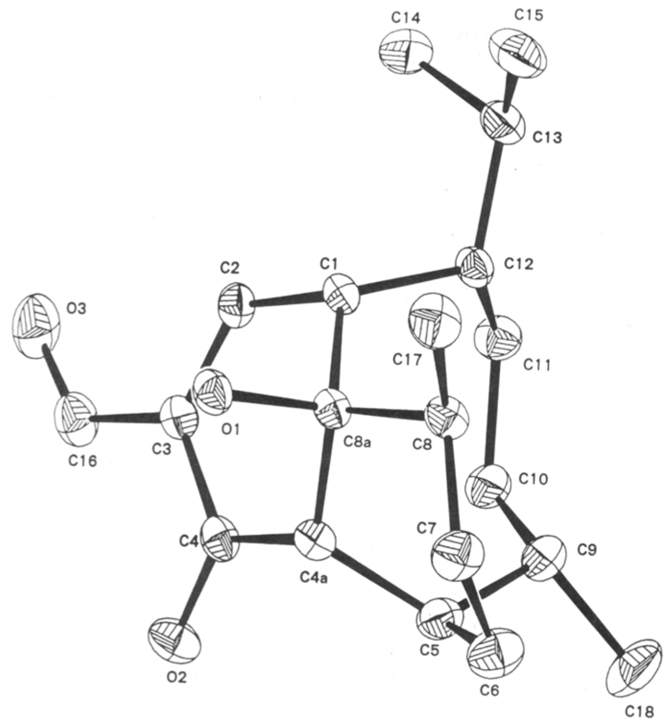


Figure 1. Molecular structure of **5** by an ORTEP drawing.

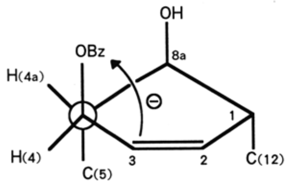


Figure 2. The presumed conformation of benzoate **7**.

reflections. A perspective drawing of the final X-ray model of **5** is given in Figure 1. The structure of the oxidation product was defined to be **5** and hence that of the natural product to be **1** except for the stereochemistry at C-4.

The relative configuration at C-4 of **1** was deduced as follows. In the ^{1}H NMR spectra ($CDCl_3$) of **1** and **2**, 4-Hs (**1**, δ 4.20; **2**, δ 5.48)[2,4] resonated as singlet without coupling to 4a-Hs (**1**, δ 2.23; **2**, 2.05),[2,4] respectively, indicating the dihedral angles of 4-Hs and 4a-Hs in **1** and **2** both to be close to 90°. As shown by a molecular model study (see, e.g., Figure 2), an interpretation was unambiguous as 4-H and 4a-H are in trans configuration. This assignment was further supported by the NOESY spectrum[5] of **2**. The spectrum showed, in addition to NOE's between 4-H and 4a-H and between 4-H and one (δ 4.65) of 16-H_2, that 4-H also brought about NOE's with two other protons at δ 1.89 and 1.22, which were assigned to 5-H and 10-H, respectively.[6] These phenomena are possible only when 4-H and 4a-H are trans and 4a-H and 5-H are cis.

The absolute structure was established by using the CD allylic benzoate method[7] as follows. After protection of the primary alcohol in **1** by silylation (t-$Bu(Me)_2SiCl$/imidazole), the resulting **6** was converted to benzoate **7**[8] (C_6H_5COCl/pyridine/DMAP). The CD spectrum of **7** exhibited a negative Cotton effect ($\Delta\epsilon$ −14.0 at 230 nm (MeOH)), indicating an anticlockwise relationship between the endocyclic double bond and the benzoate chromophore (Figure 2). Consequently, the absolute stereostructure of vinigrol was deduced to be as shown in **1**.

The decahydro-1,5-butanonaphthalene skeleton of vinigrol is unprecedented, and, as far as we are aware, vinigrol is the first example of this structural type. The activity of vinigrol as an antihypertensive and platelet aggregation-inhibiting agent[1b] is also of interest.

Supplementary Material Available: Experimental details and characterization data for **3–5** and details of the X-ray crystal analysis of **5** including tables of fractional coordinates, thermal parameters, interatomic distances, and interatomic angles (8 pages). Ordering information is given on any current masthead page.

---

[5] (a) Jeener, J.; Meier, B. H.; Bachnann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546. (b) Macura, S.; Huang, Y.; Suter, D.; Ernst, R. R. *J. Magn. Reson.* **1981**, *43*, 259.

[6] These protons were buried in the signals of δ 2.0–1.85 and 1.3–1.0 (see ref 4). The chemical shifts were determined by measurement of the frequencies showing the largest NOE values by irradiation in the NOE difference spectrum.

[7] (a) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy: Exiton Coupling in Organic Spectrometry*; University Science Books: Mill Valley, CA, 1983. (b) Harada, H.; Iwabuchi, J.; Yokota, Y.; Uda, H.; Nakanishi, K. *J. Am. Chem. Soc.* **1981**, *103*, 5590.

[8] FABMS, m/z 563 $(M + Na)^+$; ^{1}H NMR ($CDCl_3$) δ 8.04 (d, J = 8 Hz, 2 H), 7.58 (t, J = 8 Hz, 1 H), 7.46 (t, J = 8 Hz, 2 H), 6.10 (d, J = 6 Hz, 1 H), 5.71 (s, 1 H), 4.21 (s, 2 H), 2.52 (d, J = 6 Hz, 1 H), 2.24–2.17 (m, 2 H), 2.07–1.86 (m, 3 H), 1.70 (m, 1 H), 1.6–1.2 (m, 9 H), 1.04 (d, J = 7 Hz, 6 H), 1.00 (d, J = 7 Hz, 3 H), 0.98 (d, J = 7 Hz, 3 H), 0.90 (s, 9 H), 0.06 (s, 3 H), 0.04 (s, 3 H).

Itsuo Uchida, Takeshi Ando, Naoki Fukami
Keizo Yoshida, Masashi Hashimoto*
Exploratory Research Laboratories
Fujisawa Pharmaceutical Co., Ltd.
5-2-3 Tokodai, Toyosato-machi, Tsukuba-gun
Ibaraki 300-26, Japan

Toshiji Tada, Shigetaka Koda, Yukiyoshi Morimoto
Analytical Research Laboratories
Fujisawa Pharmaceutical Co., Ltd.
2-1-6 Kashima, Yodogawa-ku
Osaka 532, Japan

Received July 27, 1987

Catalysis of Diene Polymerization and Diels–Alder Reactions by an Octahedral Tungsten Nitrosyl Lewis Acid. X-ray Crystal Structure of the η^1-Acrolein Complex (cis-Me_3P)($trans$-NO)$(CO)_3$W—O=C(H)C(H)=CH_2

Summary: Cyclopentadiene and isoprene are polymerized by 0.1 mol % $(Me_3P)(CO)_3(NO)W{-}FSbF_5$ (**1**), and catalysis of the Diels–Alder reactions of cyclopentadiene or butadiene with α,β-unsaturated enones is also induced by as little as 0.1 mol % **1**; the X-ray structure of the adduct of **1** and acrolein, the presumed catalytic intermediate, reveals a simple Lewis acid interaction of the tungsten with the acrolein oxygen.

Sir: While catalysis of Diels–Alder reactions by non-transition-metal Lewis acids is well-known,[1] examples of transition-metal catalysis aside from those involving high oxidation state titanium compounds[1b,i] are rare.[2] Recent

---

[1] (a) Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436–4437. (b) Fray, G. I.; Robinson, R. *Ibid.* **1961**, *83*, 249. (c) Inukai, T.; Kojima, T. *J. Org. Chem.* **1967**, *32*, 872–875. (d) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16–33. (e) Houk, K. N.; Strozier, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 4094–4096. (f) Kelly, T. R.; Montury, M. *Tetrahedron Lett.* **1978**, 4311–4314. (g) Fringuelli, F.; Pizzo, F., Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 2802–2808. (h) Nugent, W. A.; McKinney, R. J.; Harlow, R. L. *Organometallics* **1984**, *3*, 1315–1317. (i) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876–889.

0022-3263/87/1952-5293$01.50/0 © 1987 American Chemical Society

Table I. Diels-Alder Reactions of Cyclopentadiene and Butadiene[a]

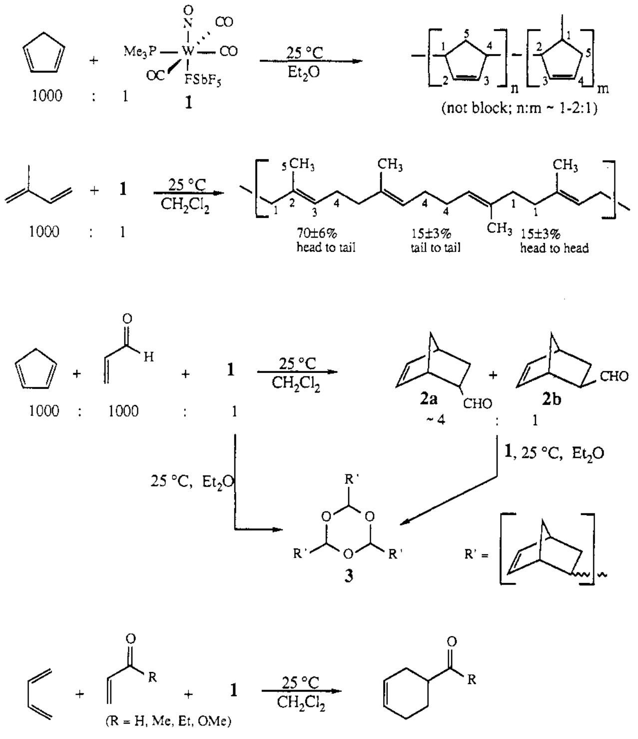
equiv							
C_5H_6	C_4H_6	$CH_2{=}C(H)C(O)R$	R	**1**	time, hr	**2a/2b**	% yield
203		200	H	1	0.5	81:19	100
100		100	H	1	0.5	77:23	33[b,c]
1061		1049	H	1	1.0	84:16	89
100		100	H	0	0.25		<3[c]
					4.5	76:24	45[c]
					68	80:20	92[c]
	110	100	H	1	0.25		100[c]
	1130	1000	H	1	17		77
	120	40	Me	1	42		73
	60	20	Et	1	12		47
	60	20	OMe	1	6		7[c]
					48		32[c]
					20 days		78[c]
	60	20	OMe	1	13		25[d]

[a] All reactions carried out in methylene chloride at room temperature except as noted. [b] −35 °C, CH_3CN quench. [c] NMR yield. [d] 41 °C.

reports of stoichiometric and catalytic reactions involving olefin isomerization, oligomerization, and polymerization by transition-metal Lewis acids[3] would suggest that such materials are too reactive to be Diels–Alder catalysts. We recently reported the synthesis of tungsten nitrosyl compound **1**, in which the mononitrosyl tungsten cation $(Me_3P)(CO)_3(NO)W^+$ is coordinated to the "noncoordinating" anion SbF_6^-.[4] While many neutral donor ligands immediately displace the coordinated SbF_6^- ligand from **1**,[5] simple olefins do not. With the expectation that this Lewis acid therefore might be less reactive than those cited above, we began a study of the reactions of **1** with dienes and dienophiles. We report here (1) catalysis of cyclopentadiene and isoprene polymerization, (2) catalysis of Diels–Alder reactions between dienes and α,β-unsaturated enones, and (3) isolation and the first X-ray crystal structure of a Lewis acid adduct of acrolein, the presumed catalytic intermediate.

Cyclopentadiene was found to undergo a remarkably rapid polymerization in the presence of 0.1 mol % of **1** (Scheme I).[6] The observation of a 2:1 ratio of aliphatic/olefinic hydrogens in the ^1H NMR clearly showed that the product was not a Diels-Alder polymer but was instead simply a mixture of 1,4- and 1,2-polycyclopentadiene. On the basis of ^1H NMR,[6,7] the polymer reproducibly consists of 50 ± 2% of 1,4-linkages, while on the basis of our analysis of the ^{13}C NMR,[6] it is 64 ± 3% 1,4-polycyclopentadiene. The discrepency is unlikely to be due to solubility problems of the 1,2-structure, since the bulk

Scheme I



---

[2] Transition-metal catalysts in low oxidation states are known for *homo*-Diels–Alder reactions involving norbornadiene (ref 2a–c) and for butadiene and isoprene dimerization (ref 2d–f); inefficient Mo(II) and W(II) catalysis (ref 2g), simultaneous allylic oxidation/Diels–Alder catalysis by Mn(IV) and Cr(VI) (ref 2h,i), and Cu(I) and/or Cu(II) catalysis (ref 2j–l) have been reported: (a) Schrauzer, G. N.; Glockner, P. *Chem. Ber.* **1964**, *97*, 2451–2462. (b) Mrowca, J. J.; Katz, T. J. *J. Am. Chem. Soc.* **1966**, *88*, 4012–4015. (c) Noyori, R.; Umeda, I.; Kawauchi, H.; Takaya, H. *Ibid.* **1975**, *97*, 812–820. (d) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 105–115. (e) Candlin, J. P.; Janes, W. H. *J. Chem. Soc. C* **1968**, 1856–1860. (f) Ballivet-Tkatchenko, D.; Riveccie, M.; Murr, N. E. *J. Am. Chem. Soc.* **1979**, *101*, 2763–2765. (g) Bailey, M. S.; Brisdon, B. J.; Brown, D. W.; Stark, K. M. *Tetrahedron Lett.* **1983**, *24*, 3037–3040. (h) Vig, O. P.; Trehan, I. R.; Kumar, R. *Indian J. Chem., Sect. B* **1977**, *15B*, 319–321. (i) Taber, D. F.; Gunn, B. P. *J. Am. Chem. Soc.* **1979**, *101*, 3992–3993. (j) Corey, E. J.; Weinshenker, N. M.; Schaaf, T. K.; Huber, W. *Ibid.* **1969**, *91*, 5675–5677. (k) Evers, J. Th. M.; Mackor, A. *Tetrahedron Lett.* **1978**, 2317–2320. (l) Moore, J. A.; Partain, E. M., III *J. Org. Chem.* **1983**, *48*, 1105–1106.

[3] (a) Ballivet, D.; Tkatchenko, I. *J. Mol. Catal.* **1975**, *1*, 319–322. (b) de Renzi, A.; Panunzi, A.; Vitagliano, A.; Paiaro, G. *J. Chem. Soc., Chem. Commun.* **1976**, 47. (c) Connelly, N. G.; Draggett, P. T.; Green, M. *J. Organomet. Chem.* **1977**, *140*, C10–C11. (d) Ballivet-Tkatchenko, D.; Billard, C.; Revillon, A. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1697–1706. (e) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627–4629. (f) Sen, A.; Lai, T.-W. *Organometallics* **1982**, *1*, 415–417. (g) Sen, A.; Thomas, R. R. *Ibid.* **1982**, *1*, 1251–1254. (h) Legzdins, P.; Martin, D. T. *Ibid.* **1983**, *2*, 1785–1791. (i) Ballivet-Tkatchenko, D.; Bremard, C. *J. Chem. Soc., Dalton Trans.* **1983**, 1143–1148. (j) Lennon, P. J.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Waterman, P. *J. Am. Chem. Soc.* **1980**, *102*, 7033–7038. (k) Lennon, P.; Rosenblum, M. *Ibid.* **1983**, *105*, 1233–1241. (l) Raab, K.; Beck, W. *Chem. Ber.* **1984**, *117*, 3169–3174. (m) Beck, W.; Raab, K.; Nagel, U.; Sacher, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 505–506.

[4] Hersh, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 4599–4601.

[5] Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1987**, *26*, 1826–1828.

[6] In a typical procedure (carried out at room temperature in an inert atmosphere glovebox), 35 mg (0.057 mmol) of **1** was suspended in 5 mL of ether, and 4.08 g (61.7 mmol, 1082 equiv) of cyclopentadiene was added dropwise, yielding a tacky white solid in 15 min. Solvent removal followed by dissolving in benzene, filtration, and precipitation of an aliquot in methanol gave 2.29 g (69% yield) of polycyclopentadiene as a brittle light brown solid. The use of CH_2Cl_2 as the reaction solvent gave only insoluble polymer. ^1H NMR ($CDCl_3$) δ 5.64 (2 H), 2.61, 2.41, 2.02 (3 H), 1.61 (1 H, CH_2, 1,4-polycyclopentadiene); ^{13}C NMR ($CDCl_3$) δ 134.2 (C_2, C_3), 50.5 (C_1, C_4), 32.0 (C_5)(1,4-polycyclopentadiene), 133.1 (C_3), 130.1 (C_4), 55.2 (C_2), 44.6 (C_1), 36.2 (C_5)(1,2-polycyclopentadiene); $[\eta]$ (benzene, before precipitation, 30 °C) = 0.21 ± 0.01 dL/g.

[7] (a) Yen, S.-P. S. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1963**, *4*, 82–86. (b) Aso, C.; Kunitake, T.; Ishimoto, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 1163–1174.

polymer is remarkably soluble (>2 g/dL), and the intrinsic viscosity $[\eta]$ = 0.21 dL/g is correspondingly low;[7] we presume the problem is due to difficulties in integrating the broad overlapping ^{1}H NMR bands. The reaction is obviously not regio- or stereospecific, and there is no reason to propose that the polymerization is metal-centered, rather than being cationic in nature. Isoprene was also polymerized by **1**, albeit in low yield;[8] analysis by ^{13}C NMR[9] indicated that the polymer has the all-trans 1,4-structure, but with substantial amounts of head-to-head and tail-to-tail linkages (Scheme I).

The use of cyclopentadiene in Diels–Alder reactions catalyzed by **1** was complicated by competitive polymerization when the reaction was carried out in ether as above, but *slow* addition of cyclopentadiene at 0 °C to an acrolein solution containing 0.1 mol % **1** gave rise to a 32% yield of Diels–Alder adduct **2** as well as a 49% yield of a mixture of diastereomeric trioxanes[10] **3** (Scheme I); no polycyclopentadiene was detected. The unexpected formation of **3** was found to be due to reaction of **2** with **1**, rather than to prior cyclotrimerization of acrolein.[11] Reaction of acrolein with **1** gave a 7% yield of a complex mixture of products, while a 56% yield of **3** was obtained by treatment of **2** with 0.13 mol % **1** for 1 h in ether at 20 °C. Lewis acid catalysis of aldehyde cyclotrimerization in nonpolar solvents is well-known,[12] and in fact use of methylene chloride rather than ether as the Diels–Alder solvent eliminated the cyclotrimerization side reaction (Scheme I).[13] The results, collected in Table I, show that while the rate enhancement over the thermal reaction is significant, enhancement of the endo/exo selectivity is surprisingly low.[1d,14] Uncatalyzed Diels–Alder reactions of butadiene, which is not polymerized by **1**, typically proceed at a reasonable rate only at temperatures near 130–140 °C.[1c,15] The results in the presence of **1** (Scheme I, Table I) show that reaction occurs at room temperature, that once again even a 1000:1 reactant/catalyst ratio gives a good yield, and that the reactivity order is aldehyde > ketone > ester. No reaction was observed at room temperature between butadiene and acrylic acid, acrylamide, crotonaldehyde,[1g] or 2-cyclohexenone.[1g] A key point is that the reactions are truly catalytic; many Lewis acid catalyzed Diels–Alder reactions employ a full equivalent of the "catalyst", and even those that are catalytic may require 20–50 mol % of the catalyst.[1a,g,i,16]

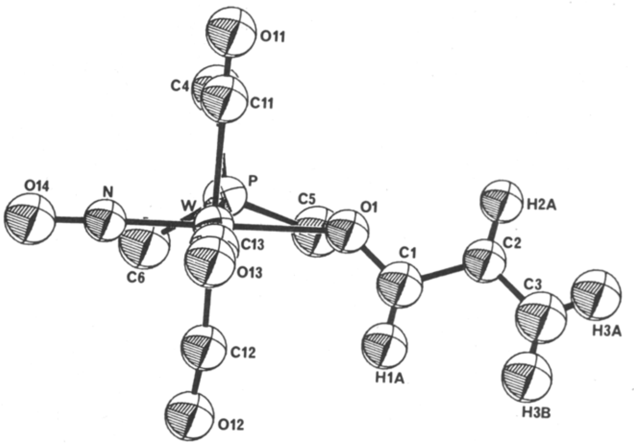


Figure 1. ORTEP drawing of **4** (cation only), viewed normal to the W–O(1)–C(1)–C(2) plane. Selected bond distances (Å) and angles (deg): W–O(1), 2.192 (18); O(1)–C(1), 1.228 (31); C(1)–C(2), 1.442 (37); C(2)–C(3), 1.336 (38); W–P, 2.512 (8), W–N, 1.775 (23); W–O(1)–C(1), 137.1 (1.9); O(1)–C(1)–C(2), 119.0 (2.6); C(1)–C(2)–C(3), 118.9 (2.6).

In order to probe the mechanism of the Diels–Alder catalysis, **1** was combined separately with butadiene and acrolein. While no interaction with butadiene was detected by either ^{1}H or ^{31}P NMR in CD_2Cl_2, immediate adduct formation with acrolein occurred to give **4**.[5,17] The low-field chemical shifts of the coordinated acrolein fragment in the ^{13}C NMR suggested that neither η^2-olefin coordination—which is typically seen in transition-metal enone complexes[18]—nor η^2-carbonyl coordination—which is typically seen in low oxidation state transition-metal ketone or aldehyde adducts[19]—was occurring here. However, both the ^{1}H and ^{13}C NMR spectra[17] were similar to those of protonated acrolein,[20] suggesting a simple Lewis acid interaction between the acrolein oxygen and the tungsten atoms. A single-crystal X-ray diffraction study of **4** showed that this presumed η^1 mode of coordination also is present in the solid state (Figure 1).[21] The acrolein fragment is nearly planar (O(1)–C(1)–C(2)–C(3) dihedral

---

(8) Isoprene (2.31 g, 33.9 mmol, 1028 equiv) was slowly added to a solution of **1** (20 mg, 0.033 mmol) in 5 mL of CH_2Cl_2. After the mixture was stirred overnight, the resultant gel was treated as described for cyclopentadiene, giving 0.30 g (13% yield) of soluble polymer and 0.62 g (27% yield) of insoluble polymer. No reaction occurred when ether was used as the reaction solvent. ^{13}C NMR ($CDCl_3$) δ 134.94 (C_2), 124.28 (C_3), 39.76 (C_1), 26.75 (C_4), 16.02 (C_5)(*trans*-1,4-polyisoprene), 38.55 (C_1, trans-4,1–1,4 linkage), 28.30 (C_4, trans-1,4–4,1 linkage).

(9) (a) Tanaka, Y.; Sato, H. *Polymer* **1976**, *17*, 113–116. (b) Sato, H.; Ono, A.; Tanaka, Y. *Ibid.* **1977**, *18*, 580–586. (c) Khatchaturov, A. S.; Dolinskaya, E. R.; Prozenko, L. K.; Abramenko, E. L.; Kormer, V. A. *Ibid.* **1977**, *18*, 871–877. (d) Beebe, D. H. *Ibid.* **1978**, *19*, 231–233.

(10) The *tri*meric structure was assigned on the basis of the molecular weight of 331 ± 26 measured by the freezing point depression of benzene (Shoemaker, D. P.; Garland, C. W.; Steinfeld, J. I.; Nibler, J. W. *Experiments in Physical Chemistry*, 4th ed.; McGraw-Hill: New York, 1981; pp 168–179); complete characterization of **3** is available in the supplementary material.

(11) (a) Bergman, E. U.S. Patent 3 274 162, 1966. (b) Jungnickel, J. L.; Reilly, C. A. *J. Mol. Spectrosc.* **1965**, *16*, 135–157.

(12) Hashimoto, K.; Sumitomo, H.; Kawase, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1609–1618.

(13) In a typical procedure, a solution of 2.39 g (36.1 mmol, 1061 equiv) of cyclopentadiene in 6 mL of CH_2Cl_2 was added dropwise under nitrogen to a solution of 2.00 g (35.7 mmol, 1049 equiv) of acrolein and 21 mg (0.034 mmol) of **1** in 4 mL of CH_2Cl_2 and stirred 10 min at 0 °C. After 1 h at room temperature, the reaction mixture was filtered through a silica pad to remove **1**, and the CH_2Cl_2 removed to give 3.89 g (89% yield) of **2**.

(14) (a) Sauer, J.; Kredel, J. *Tetrahedron Lett.* **1966**, 731–736. (b) Danishefsky, S.; Bednarski, M. *Ibid.* **1985**, *26*, 2507–2508.

(15) (a) Shortridge, R. W.; Craig, R. A.; Greenlee, K. W.; Derfer, J. M.; Boord, C. E. *J. Am. Chem. Soc.* **1948**, *70*, 946–949. (b) Alder, K.; Vogt, W. *Justus Liebigs Ann. Chem.* **1949**, *564*, 109–120. (c) Bailey, W. J.; Baylouny, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 2126–2129.

(16) Reetz, M. T.; Kyung, S.-H.; Bolm, C.; Zierke, T. *Chem. Ind.* (*London*) **1986**, 824.

(17) ^{1}H NMR (CD_2Cl_2) δ 9.23 (d, J = 8.5 Hz, 1 H), 7.19 (d, J = 12.6 Hz, 1 H), 7.12 (d, J = 19.7 Hz, 1 H), 6.51 (m, 1 H), 1.79 (d, J = 9.1 Hz, 9 H); ^{13}C NMR (CD_2Cl_2) δ 212.49 (br d, J_{PC} = 2.5 Hz, *C*HO; $^1J_{CH}$ = 182.9 Hz, $^{2,3}J_{CH}$ = 18.3, 11.6 Hz), 155.01 (*C*H_2, $^1J_{CH}$ = 165.8, 162.1 Hz, $^2J_{CH}$ = 1.1 Hz), 136.57 (*C*H, $^1J_{CH}$ = 169.0 Hz, $^2J_{CH}$ = 18.1, 3.0 Hz)(CH_2CHCHO), 200.34 (d, trans-J_{PC} = 39.65 Hz, *C*O), 199.72 (d, cis-J_{PC} = 7.56 Hz, (*C*O)$_2$), 16.05 (d, J_{PC} = 31.77 Hz, (*C*H_3)$_3$P). Full details may be found in the supplementary material.

(18) See, for instance: (a) Moriarty, R. E.; Ernst, R. D.; Bau, R. *J. Chem. Soc., Chem. Commun.* **1972**, 1242–1243. (b) Krüger, C.; Tsay, Y.-H. *Cryst. Struct. Commun.* **1976**, *5*, 219–222. (c) Herrmann, W. A. *Chem. Ber.* **1975**, *108*, 486–499. (d) Grevels, F.-W.; Lindemann, M. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1298–1309. (e) Einstein, F. W. B.; Jones R. H.; Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1986**, *5*, 2476–2480.

(19) See, for instance: (a) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353–362. (b) Clark, C. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *Ibid.* **1982**, *231*, 335–360. (c) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223–8227. (d) Fernândez, J. M.; Emerson, K.; Larsen, R. H.; Gladysz, J. A. *Ibid.* **1986**, *108*, 8268–8270.

(20) The ^{13}C NMR chemical shifts reported for $CH_2{=}CHC(H)OH^+$ are δ 211.8 (*C*HO), 176.8 (*C*H_2), 133.4 (*C*H): Olah, G. A.; Halpern, Y.; Mo, Y. K.; Liang, G. *J. Am. Chem. Soc.* **1972**, *94*, 3554–3561.

(21) Details of the X-ray diffraction study may be found in the supplementary material.

angle = 12.8°) and the W, O(1), C(1), and C(2) atoms are coplanar to within 0.001 Å, it is roughly perpendicular to the P–W vector (angle between the W–acrolein and P–N–C(13)–O(1)–W least-squares planes = 70.1°) and it is present in the s-trans conformation as would be expected on the basis of a recent theoretical study.[22] The acrolein C–C and C–O bond lengths are similar to those seen in other structures of Lewis acid adducts of α,β-unsaturated enones,[23] while the tungsten–oxygen bond length is relatively long,[18a,24] which is in accord with the catalytic activity of 1.

In conclusion, a novel transition-metal catalyst for the Diels–Alder reaction has been discovered. On the basis of a rare X-ray crystal structure of a Lewis acid–dienophile adduct, it is reasonable to suggest that the catalytic activity of 1 is due solely to its Lewis acidity. While the catalyst described here is achiral, chiral analogues may be envisioned readily. Chiral catalysis of the *hetero*-Diels–Alder reaction—which is not observed for acrolein here—is known,[25a–c] as is chiral Diels–Alder induction by stoichiometric amounts of chiral Lewis acids,[25d,e] but true Diels–Alder *catalysis* with high asymmetric induction remains unknown.[16,25] Work is in progress on the design and synthesis of such a catalyst.

Acknowledgment. We thank Professor M. E. Jung for several helpful discussions. Financial support from the UCLA Committee on Research, a Biomedical Research Support Grant, and Merck & Co. is gratefully acknowledged.

Supplementary Material Available: Characterization of 3 and 4 and tables of crystallographic data for 4 and details of the solution (15 pages). Ordering information is given on any current masthead page.

---

[22] Loncharich, R. J.; Schwartz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14–23.

[23] (a) Foxman, B. M.; Klemarczyk, P. T.; Liptrot, R. E.; Rosenblum, M. *J. Organomet. Chem.* **1980**, *187*, 253–265. (b) Lewis, F. D.; Oxman, J. D.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 466–468. (c) Poll, T.; Metter, J. O.; Helmchen, G. *Angew Chem.* **1985**, *97*, 116–118.

[24] (a) Sünkel, K.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1983**, *251*, 227–243. (b) Chisholm, M. H. In *Inorganic Chemistry: Toward the 21st Century*; Chisholm M. H., Ed.; ACS Symposium Series 211; American Chemical Society: Washington, DC, 1983; Chapter 16. (c) Cotton, F. A.; Schwotzer, W. *J. Am. Chem. Soc.* **1983**, *105*, 4955–4957.

[25] (a) Bednarski, M.; Maring, C.; Danishefsky, S. *Tetrahedron Lett.* **1983**, *24*, 3451–3454. (b) Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1983**, *105*, 6968–6969. (c) Quimpère, M.; Jankowski, K. *J. Chem. Soc., Chem. Commun.* **1987**, 676–677. (d) Kelly, T. R.; Whiting, A.; Chandrakumar, N. S. *J. Am. Chem. Soc.* **1986**, *108*, 3510–3512. (e) Narasaka, K.; Inoue, M.; Okada, N. *Chem. Lett.* **1986**, 1109–1112. (f) Hashimoto, S.-I.; Komeshima, N.; Koga, K. *J. Chem. Soc., Chem. Commun.* **1979**, 437–438.

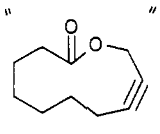
Robert V. Honeychuck, Peter V. Bonnesen
Judah Farahi, William H. Hersh*
Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024

Received September 9, 1987

Preparation of Medium-Ring Acetylenic Lactones Utilizing Metal-Promoted Alkyne Bending

Summary: Reaction of a variety of acetylenic hydroxycarbonyl compounds with $Co_2(CO)_8$ gives rise to readily isolated alkyne–$Co_2(CO)_6$ complexes in which lactonization, previously impossible due to geometric constraints, proceeds relatively smoothly due to "bending" of the alkyne moiety upon metal coordination.

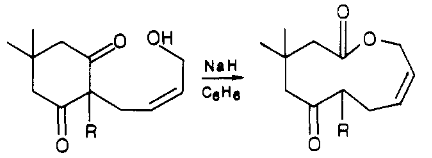
Sir: In connection with ongoing studies of intramolecular Pauson-Khand-type cyclization reactions,[1,2] we required access to 11-membered ring acetylenic lactones, e.g., 1.[3]



1

Four reports of 12-membered ring lactones containing triple bonds may be found in the literature.[4] In two cases, favorable conformational effects allow intramolecular oxygen bridging to occur leading to "highly strained" compounds with the triple bond in a 10-membered ether–lactone ring.[4a,c] Considering odd-size rings, the smallest lactone containing triple bonds is a 15-membered ether–lactone.[5]

A simple entry into 11-membered ring lactones (without a triple bond, of course), developed by Mahajan,[6] utilizes an intramolecular retro-Dieckmann reaction (eq 1). Direct application to an acetylenic analogue is geometrically impossible due to the linear nature of the butynyl unit. However, metal complexation of alkynes by reaction with $Co_2(CO)_8$ results in a substantial geometric change to a system with ca. 140° bond angles about the "alkyne" carbons.[7] It therefore seemed entirely reasonable that precomplexation with $Co_2(CO)_8$ would result in a system capable of the desired lactonization, provided that the complexed alkyne function survived the conditions required for the process.[8]



(1)

Several substrates for investigation were prepared by alkylation of cyclic ketones with $BrCH_2C{\equiv}CCH_2OSi\text{-}t\text{-}BuMe_2$[9] (Table I). Desilylation followed by reaction with

---

[1] General references for the Pauson-Khand reaction: (a) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, 977. (b) Pauson, P. L.; Khand, I. U. *Ann. N. Y. Acad. Sci.* **1977**, *295*, 2. (c) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855.

[2] Recent intramolecular examples: (a) Knudsen, M. J.; Schore, N. E. *J. Org. Chem.* **1984**, *49*, 5025. (b) Billington, D. C.; Willison, D. *Tetrahedron Lett.* **1984**, *25*, 4041. (c) Carceller, E.; Centellas, V.; Moyano, A.; Pericàs, M. A.; Serratosa, F. *Tetrahedron Lett.* **1985**, *26*, 2475. (d) Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851. (e) Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, *41*, 5861. (f) Simonian, S. O.; Smit, W. A.; Gybin, A. S.; Shashkov, A. S.; Mikaelian, G. S.; Tarasov, V. A.; Ibragimov, I. I.; Caple, R.; Froen, D. E. *Tetrahedron Lett.* **1986**, *27*, 1245. (g) Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128. (h) Hua, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 3835. (i) Schore, N. E.; Knudsen, M. J. *J. Org. Chem.* **1987**, *52*, 569.

[3] Portions of this work have been reported: Schore, N. E. *Abstracts of Papers*, 192nd Meeting of the American Chemical Society, Anaheim; American Chemical Society: Washington, DC, 1986; ORGN 80.

[4] Inanaga, J.; Katsuki, T.; Takimoto, S.; Ouchida, S.; Inone, K.; Nakano, A.; Okukada, N.; Yamaguchi, M. *Chem. Lett.* **1979**, 1021. (b) Ireland, R. E.; Brown, F. R., Jr. *J. Org. Chem.* **1980**, *45*, 1868. (c) Inanaga, J.; Kawanami, Y.; Yamaguchi, M. *Chem. Lett.* **1981**, 1415. (d) Guillerm, D.; Linstrumelle, G. *Tetrahedron Lett.* **1985**, *26*, 3811.

[5] Voitkevich, S. A.; Solov'eva, N. P.; Kizyakova, L. P.; Bel'fer, A. G. *Maslo-Zhir. Prom.* **1973**, 29; *Chem. Abstr.* **1974**, *80*, 27228u.

[6] Mahajan, J. R. *Synthesis* **1976**, 110.

[7] Dickson, R. S.; Fraser, P. J. *Adv. Organomet.* Chem. **1974**, *12*, 323.

[8] While this work was in progress, Schreiber and co-workers reported a similar use of alkyne complexation to form metal-complexed medium-ring acetylenic carbocycles via low-temperature alkylations.[2g]

0022-3263/87/1952-5296$01.50/0