

- (13) S.-I. Murahashi, T. Yano, and K. Hino, *Tetrahedron Lett.*, 4235 (1975).
 (14) The insertion of palladium into the C-N bond, leading to a five-membered chelating palladium complex,¹⁵ which would be a precursor of propylamine or allylamine, was suggested: S.-I. Murahashi, T. Yano, and K. Hino, *Symp. Organomet. Chem.*, 23rd, 1975, 46 (abstract page) (1975).
 (15) (a) M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, 16, 73 (1977); (b) W. G. Parrshall, *Acc. Chem. Res.*, 3, 139 (1970); (c) A. J. Carty, *Organomet. Chem. Rev.*, 18, 327 (1976); (d) J. Dihand and M. Pfeffer, *Coord. Chem. Rev.*, 18, 327 (1976).

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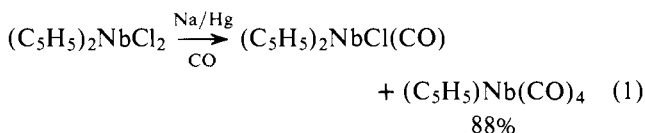
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Cyclopropene, Alkene, Alkyne, and Carbonyl Complexes of Cyclopentadienylniobium Species and Reduction of Cyclopropene

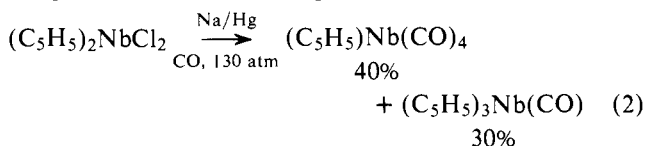
Sir:

Catalytic reduction of unsaturated hydrocarbons by homogeneous catalysis¹ and by biological² means have become subject of increasing interest. Mechanisms of such reactions have been elucidated by isolation of related stable metal-hydrocarbon complexes and careful investigation of their reduction chemistry.^{3,4} We wish to report a new series of complexes derived from a $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbCl}$ species and describe the reduction chemistry of a novel cyclopropene complex.

Generation of the $(\text{C}_5\text{H}_5)_2\text{NbCl}$ species seems to proceed smoothly when 200 mg of $(\text{C}_5\text{H}_5)_2\text{NbCl}_2$ ⁵ dissolved in 40 mL of toluene is stirred with sodium amalgam in the presence of a substrate molecule. The resulting air-sensitive solution can then be filtered and the solvent removed in vacuo and purified by sublimation. In this manner, treatment of $(\text{C}_5\text{H}_5)_2\text{NbCl}_2$ with carbon monoxide yields a new chlorocarbonyl complex, $(\text{C}_5\text{H}_5)_2\text{NbCl}(\text{CO})$ as well as the known $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4$:

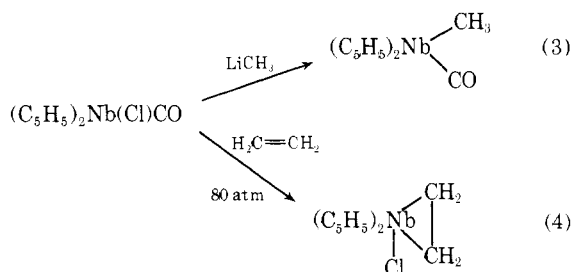


Niobocene chlorocarbonyl is characterized by a sharp singlet in its ¹H NMR at 5.01 ppm due to the cyclopentadienyl protons and a strong infrared absorption at 1900 cm⁻¹ due to the carbonyl group.⁶ $(\text{C}_5\text{H}_5)\text{Nb}(\text{CO})_4$ was identified by its mass spectrum and previously reported infrared spectrum.⁷ If the reduction of $(\text{C}_5\text{H}_5)_2\text{NbCl}_2$ is carried out under high pressure carbon monoxide, $(\text{C}_5\text{H}_5)\text{Nb}(\text{CO})_4$ is obtained in higher yields and by simpler procedures than previously reported⁷ and a new complex $(\text{C}_5\text{H}_5)_3\text{Nb}(\text{CO})$ is generated:



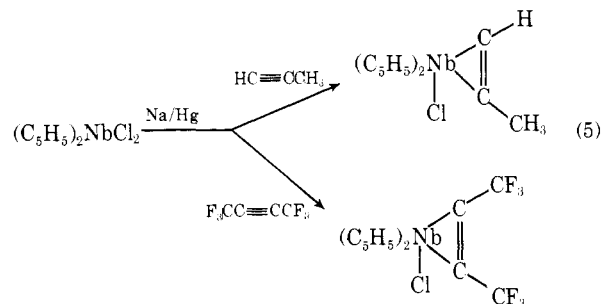
$(\text{C}_5\text{H}_5)_3\text{Nb}(\text{CO})$ is characterized by a strong carbonyl infrared absorption at 1890 cm⁻¹ and a ¹H NMR exhibiting singlet absorptions at 4.4 and 6.20 ppm integrating 10:4.8, suggesting two $\eta^5\text{-C}_5\text{H}_5$ and one $\eta^1\text{-C}_5\text{H}_5$ ligands.⁶

Niobocene chlorocarbonyl may be used to synthesize new carbonyl or alkene complexes (eq 3 and 4). $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)(\text{CO})$ is characterized by ¹H NMR absorptions at 4.67 and -0.38 ppm integrating 10:3 and a strong carbonyl infrared absorption at 1890 cm⁻¹.⁷ $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{Cl})(\text{C}_2\text{H}_4)$ is characterized by ¹H NMR absorptions showing a singlet at



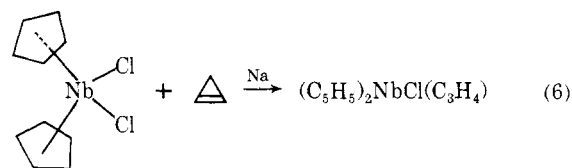
6.01 ppm due to cyclopentadienyl protons and broad overlapping multiplets at 1.33 and 1.45 ppm (integration 10:4.8) due to the inequivalent ends of the ethylene ligand.⁶ Related olefin complexes⁸ have displayed similar NMR spectra.

Coordination of alkynes by the niobocene monochloride fragment also proceeds smoothly under the conditions shown in eq 5. $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{CF}_3\text{C}\equiv\text{CCF}_3)\text{Cl}$ is characterized by a ¹H NMR absorption at 5.28 ppm due to cyclopentadienyl

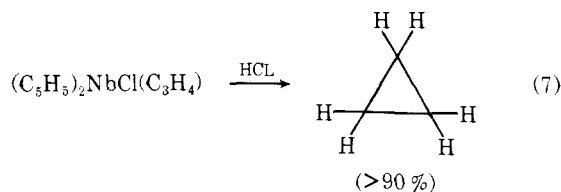


protons, a mass spectrum with $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{CF}_3\text{C}\equiv\text{CCF}_3)\text{Cl}^+$ as the present ion, and an infrared absorption at 1790 cm⁻¹ due to the C≡C stretch. $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{HC}\equiv\text{CCH}_3)\text{Cl}$ is characterized by a strong infrared absorption at 1740 cm⁻¹ due to the C=C stretch, a satisfactory mass spectrum, and a ¹H NMR spectrum with absorptions at 5.30, 2.83, 2.37, and 7.98 ppm integrating 10:1.25:1.67:0.9. The two methyl absorptions at 2.83 and 2.37 ppm are due to the two possible isomers of $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{HC}\equiv\text{CCH}_3)\text{Cl}$.⁶ Similar complexes of tantalum have been prepared, but only with disubstituted alkynes.⁹ Synthesis of $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{HC}\equiv\text{CCH}_3)\text{Cl}$ by displacement of carbon monoxide from $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{Cl})\text{CO}$ does proceed at 1 atm, although very slowly, as followed by NMR.¹⁰

Having demonstrated the ability of the $(\text{C}_5\text{H}_5)_2\text{NbCl}$ species to readily coordinate ordinary alkenes and alkynes, a new substrate of intermediate multiple bond character, cyclopropene,¹¹ was investigated. A moss-green cyclopropene complex was readily isolated (eq 6). This compound is char-



acterized by a ¹H NMR with a sharp singlet at 5.87 ppm due to cyclopentadienyl protons and a broad multiplet due to cyclopropene protons at 1.43 ppm integrating 10:4.9. The mass spectrum and infrared spectrum were in agreement with the proposed structure and treatment of the complex with HCl yielded almost pure cyclopropane, providing additional support for the structure (eq 7). This is the first reported reduction of cyclopropene via an isolable metal complex. One other monomeric cyclopropene complex has been reported,¹³ but no investigation of its chemistry was undertaken. Reduction of cyclopropene by the nitrogenase enzyme to a mixture of cyclopropane and propene has been recently reported.¹⁴ While our results do suggest that cyclopropane formation from



metal-coordinated cyclopropene is feasible, the formation of propene by a similar initial metal coordination has not yet been verified. Further examples of the reduction of cyclopropene by metal centers are being investigated to demonstrate the conditions necessary for both cyclopropane and propene formation. In addition, the seemingly extraordinarily rich chemistry of bis(cyclopentadienyl)niobium species is being more fully investigated.

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References and Notes

- (1) P. M. Maitlis, "The Organic Chemistry of Palladium", Academic Press, New York, N.Y., 1971; P. L. Rylander, *Org. Chem.*, **28**, 60 (1973).
- (2) (a) M. Kelly, *J. Biochem.*, **107**, 1 (1968); (b) R. W. F. Hardy and E. K. Jackson, *Fed. Proc.*, **26**, 725 (1967).
- (3) J. L. Thomas, *J. Am. Chem. Soc.*, **95**, 1838 (1973).
- (4) J. L. Thomas, *J. Am. Chem. Soc.*, **97**, 5943 (1975).
- (5) F. Siebert and H. S. De Liefde Meijer, *J. Organomet. Chem.*, **23**, 177 (1970).
- (6) Elemental composition of all new complexes have been verified by elemental analysis and/or a satisfactory mass spectrum. $(\text{C}_5\text{H}_5)_2\text{NbCl}(\text{CO})$ has been reported independently by D. A. Lemenovskii, T. V. Bankova, and V. P. Fedin, *J. Organomet. Chem.*, **132**, C14-16 (1977).
- (7) R. P. M. Werner, A. H. Filbey, and S. A. Manastyrskij, *Inorg. Chem.*, **3**, 298 (1964).
- (8) L. J. Guggenberger, P. Meakin, and F. M. Tebbe, *J. Am. Chem. Soc.*, **96**, 5420 (1974).
- (9) J. A. Labinger, J. Schwartz, and J. M. Townsend, *J. Am. Chem. Soc.*, **96**, 4009 (1974).
- (10) Increased pressures of $\text{HC}\equiv\text{CCH}_3$ were not investigated due to the possibility of explosion.
- (11) Cyclopropene was prepared as described by Closs.¹² Purification was accomplished by trap to trap distillations at -100°C , followed by low temperature fractionation.
- (12) G. L. Closs and K. D. Krants, *J. Org. Chem.*, **31**, 638 (1966).
- (13) J. P. Visser, A. J. Schipperijun, and J. Lukas, *J. Organomet. Chem.*, **47**, 439 (1973).
- (14) C. E. McKenna, M.-C. McKenna, and M. T. Higa, *J. Am. Chem. Soc.*, **98**, 4675 (1976).

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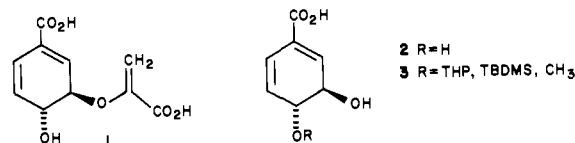
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Shikimate-Derived Metabolites. 2. 1 Synthesis of a Bacterial Natural Product Illustrating a Concerted $\text{Syn-S}_{\text{N}}2'$ Reaction

Sir:

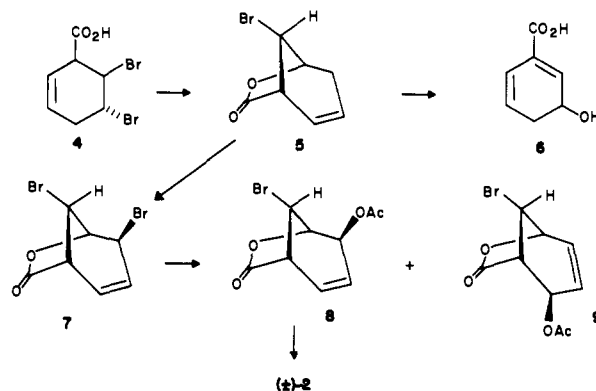
Chorismic acid (**1**) occupies a central position in the shikimate metabolic pathway since it is the first branch point intermediate governing the biosynthesis of aromatic amino acids, bacterial growth promoters, and the isoprenoid quinones essential to respiratory chain phosphorylation.² We have been interested in the chemistry of chorismic acid and in processes

which regulate metabolism at this juncture, specifically the partnership of chorismate mutase and complementary prephenate dehydratase/dehydrogenase enzymes. Among the many in vivo transformations of **1** in *Aerobacter aerogenes* is the cleavage of its enolpyruvyl side chain to produce *trans*-3,4-dihydroxy-3,4-dihydrobenzoic acid (**2**). This substance,



previously synthesized by Chiasson and Berchtold,³ may have some biochemical function directly or indirectly in controlling metal ion consumption, or as a weak growth promoter.⁴ This communication describes a five-step stereospecific synthesis of **2** and brings new information to bear on the mechanism and stereochemistry of the controversial $\text{S}_{\text{N}}2'$ reaction.⁵

Bromination of 1,4-dihydrobenzoic acid in CH_2Cl_2 furnishes a mixture of dibromo acids from which the major isomer **4** can be crystallized (62%, mp $98-102^\circ\text{C}$). Cyclization of **4** in aqueous NaHCO_3 affords **5** (65%, mp 52°C , IR λ_{max} 5.61μ).^{6,7} This olefinic bromolactone contains the requisite diene system for **1** and **2** in masked form; saponification of **5** ($\text{Ba}(\text{OH})_2$, EtOH) leads to **6** in good yield. Compound **5** is resistant to most allylic oxidizing agents but a slow reaction ensues with NBS (CCl_4 , $(\text{C}_6\text{H}_5\text{CO}_2)_2$, reflux, 18 h) which generates enedibromide **7** stereospecifically in 70% yield (mp $69-70^\circ\text{C}$) along with $\sim 10\%$ of an unidentified tribromide (mp 114°C). The structure of **7** was assigned on the basis of ^{13}C and ^1H magnetic resonance data, particularly the sharp singlet for the bridging hydrogen at δ 4.84 (CDCl_3), shifted 22 Hz downfield from the corresponding singlet in **5** (4.47). Dibromide **7** can be converted (4 equiv NaOAc, HMPA) to a 1:1 mixture of allylic acetates **8** and **9** (86%) which are readily



separated by column chromatography.⁸ Saponification of **8** (mp $74-75^\circ\text{C}$) using aqueous KOH (3.0 equiv) furnishes (\pm) -**2** in 77% yield. After recrystallization from acetone-pentane, pure **2** (56%) has mp $150-151^\circ\text{C}$, UV λ_{max} 273 nm as well as IR, NMR, and mass spectral data fully in accord with literature values.³

We have noticed during this work a remarkable preference for reactions to occur on the β face of these bicyclic lactones which suggests an efficient way to use allylic ester **9**, coproduced with **8** during the acetolysis of **7**. Acidic hydrolysis of **9** (1:2 10% H_2SO_4 -THF, reflux, 80%) affords the corresponding allylic alcohol **10** (mp $121-23^\circ\text{C}$, NMR (acetone- d_6) δ 4.94 (s, 1 H, bridging H)) with no trace of rearrangement product. Treatment of this alcohol with methanesulfonyl chloride (1.1 equiv, $\text{C}_5\text{H}_5\text{N}$, 0°C) furnishes mesylate **11** (85%, mp $155-156^\circ\text{C}$) which when stirred with LiOAc in HMPA is quantitatively converted to the rearranged *syn*-allylic acetate **8**. Under these homogeneous conditions, which cause no isomerization in the starting mesylate, the reaction follows