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 (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).
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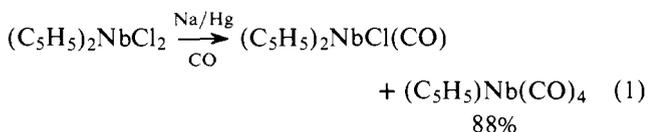
Received May 23, 1977

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

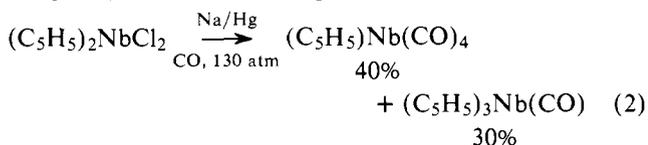
Sir:

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 $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4$:

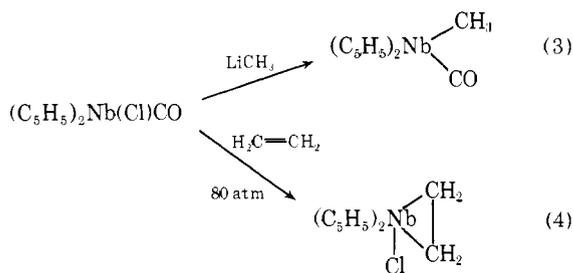


Niobocene chlorocarbonyl is characterized by a sharp singlet in its ¹H NMR at 5.01 ppm due to the cyclopentadienyl protons and a strong infrared absorption at 1900 cm⁻¹ due to the carbonyl group.⁶ $(\text{C}_5\text{H}_5)\text{Nb}(\text{CO})_4$ was identified by its mass spectrum and previously reported 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:



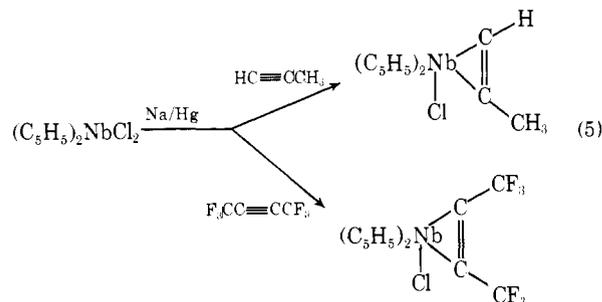
$(\text{C}_5\text{H}_5)_3\text{Nb}(\text{CO})$ is characterized by a strong carbonyl infrared absorption at 1890 cm⁻¹ and a ¹H NMR exhibiting singlet absorptions at 4.4 and 6.20 ppm integrating 10:4.8, suggesting two $\eta^5\text{-C}_5\text{H}_5$ and one $\eta^1\text{-C}_5\text{H}_5$ ligands.⁶

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



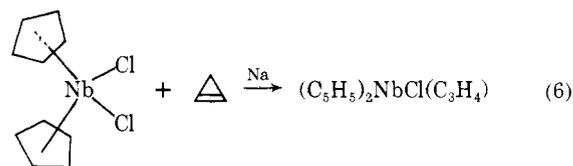
6.01 ppm due to cyclopentadienyl protons and broad overlapping multiplets at 1.33 and 1.45 ppm (integration 10:4.8) due to the inequivalent ends of the ethylene ligand.⁶ Related olefin complexes⁸ have displayed similar NMR spectra.

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