Isolation of η^2-(*C,C*) Ketene Complexes of Nickel from the Reactions of Nickelacyclobutane Complexes with Carbon Monoxide

Akira Miyashita,* Hiroaki Shitara, and Hiroyuki Nohira

Department of Applied Chemistry, Faculty of Engineering, Saitama University, Shimo-ohkubo, Urawa 338, Japan

The η^2-(*C,C*) ketene complex [Ni(CH_2=C=O)(PPh_3)$_2$], a model complex for homogeneous CO reduction, was isolated by carbonylation of nickelacyclobutane complexes or by the reaction of [Ni(PPh_3)$_4$] with CH_2Br_2 in the presence of Zn followed by carbonylation.

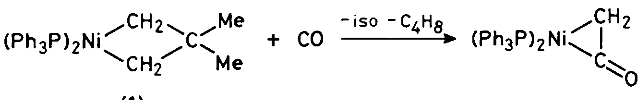
The current interest in transition metal ketene complexes[1] derives from the possible intermediacy of these materials in homogeneous carbon monoxide reduction related to the Fischer–Tropsch synthesis.[2] We now report isolation of novel unsubstituted ketene complexes of Ni from the reactions of nickelacyclobutane complexes with CO and demonstrate that their unique chemical properties are relevant to CO activation *via* carbene intermediates.

Treatment of bis(triphenylphosphine)nickelacyclobutane (**1**)[3] (0.77 mmol, 0.15 M) with CO (3 atm) in toluene below −50 °C (5 days) gave a deep red solution which was quickly passed through a short column of neutral alumina (Woelm N super I) at −65 °C. During the reaction, isobutene (84%) was formed, but no dimethylcyclobutanone was produced. Addition of diethyl ether to the orange-red eluant resulted in the precipitation of yellow crystalline [Ni(CH_2=C=O)(PPh_3)$_2$] (**2**) (17%) which was recrystallized from CO-saturated acetone–ether.† The i.r. spectrum of (**2**) contains ν(C=O) at 1750s and ν(C–H, saturated) at 2960m and 2830m cm^{-1}. The ^{1}H n.m.r. spectrum ([$^2H_6$]acetone, −48 °C) shows equivalent CH_2 proton resonances at δ 2.35 (2H, $J_{P\text{-}H}$ 7.5 Hz) and phenyl resonances at δ 7.45 (30H). The ^{13}C n.m.r. spectrum ([$^2H_8$]toluene, −46 °C) shows characteristic signals due to the ketene ligand at δ 38.4 (CH_2) and 176 (C=O). The spectroscopic data for (**2**) are fully consistent with the η^2-(*C,C*) ketene structure.[4]

The Ni-ketene complex (**2**) can also be obtained either by direct reaction of [Ni(PPh_3)$_4$] with ketene in toluene, or by carbonylation of the Ni-carbene complexes presumably formed from the reaction of [Ni(PPh_3)$_4$] and CH_2Br_2 in the presence of Zn.‡

The ketene complex (**2**) can be readily reduced with $LiAlH_4$ in tetrahydrofuran (thf) to afford quantitative amounts of EtOH, while treatment with MeOH resulted in the formation of AcOMe (76%).

Thermolysis of (**2**) in the solid state led to quantitative



(**1**) (**2**)

$$(2) \xrightarrow[55\ ^\circ C,\ acetone]{} CH_2=CH_2 + Ni(CO)(PPh_3)_n$$

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† Elemental analysis of (**2**) was unsuccessful owing to its extreme air- and moisture-sensitivity. Triphenylphosphine extracted with n-hexane after acidolysis of (**2**) was determined by u.v. spectroscopy, and Ni as its dimethylglyoxal complex; data were consistent with the formulation of (**2**).

‡ Methylene species formed from CH_2Br_2 and Ni^0 complexes are believed to be Ni-carbene complexes mainly on the basis of their reactivities. M. D. Cooke and E. O. Fischer, *J. Organomet. Chem.*, 1973, **56**, 279; S. Takahashi, Y. Suzuki, K. Sonogashira, and N. Hagihara, *Chem. Lett.*, 1976, 515; T. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1979, 1003; P. Gassman and T. H. Johnson, *J. Am. Chem. Soc.*, 1976, **98**, 6058.

decomposition to yield hydrocarbons such as C_2H_4 (83%), C_3H_6 (3%), and C_4H_8 (3%). Upon being heated at 55 °C in acetone, (**2**) extensively decomposed to give C_2H_4 (76%) and a Ni–carbonyl complex which was identified by i.r. analysis [strong terminal $\nu(CO)$ signal at 2065 cm^{-1}]. These results could be accounted for by C=C bond cleavage of the co-ordinated $CH_2=C=O$ of (**2**). This is in accord with recent studies on Os cluster complexes with a μ_2-CH_2CO ligand.[5]

These observations indicate that Ni-ketene complexes, formed from the reaction of the nickelacyclobutane complex (**1**) with CO, can be substantially converted into alcohol or hydrocarbons under mild conditions.

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