Isolation of η²-(*C,C*) Ketene Complexes of Nickel from the Reactions of Nickelacyclobutane Complexes with Carbon Monoxide

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The η²-(*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.

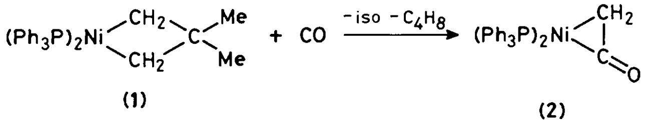
The current interest in transition metal ketene complexes[1] derives from the possible intermediacy of these materials in homogeneous carbon monoxide reduction related to the Fischer–Tropsch synthesis.[2] We now report isolation of novel unsubstituted ketene complexes of Ni from the reactions of nickelacyclobutane 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 η²-(*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



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

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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 ν(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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References

1 D. A. Straus and R. H. Grubbs, *J. Am. Chem. Soc.*, 1982, **104**, 5499; T. W. Bodnar and A. R. Cutler, *ibid.*, 1983, **105**, 5926; P. T. Barger, B. D. Santarsiero, J. Armantrout, and J. E. Bercaw, *ibid.*, 1984, **106**, 5178.

2 W. Keim, in 'Catalysis in C_1 Chemistry,' Reidel, Dordrecht, 1983, p. 5.

3 R. H. Grubbs and A. Miyashita, in 'Fundamental Research in Homogeneous Catalysis,' ed. M. Tsutsui, Plenum Press, New York, 1979, p. 51; A. Miyashita and R. H. Grubbs, *Tetrahedron Lett.*, 1981, 1255.

4 G. Fachinetti, C. Brien, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Am. Chem. Soc.*, 1978, **100**, 1921; W. A. Herrman, J. Plank, M. Ziegler, and K. Weidenhammer, *ibid.*, 1979, **101**, 3133; T. Mitsudo, Y. Watanabe, and Y. Takegami, *J. Chem. Soc., Chem. Commun.*, 1979, 265, and references cited therein.

5 A. J. Arce and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1982, 364; E. D. Morrison, G. R. Steinmetz, G. L. Geoffroy, W. C. Fultz, and A. L. Reingold, *J. Am. Chem. Soc.*, 1984, **106**, 4783.