J. Am. Chem. Soc. **1996,** *118,* 10305−10306 10305

A First Example of a "Wittig Reaction" on a Coordinated Carbon Dioxide Nickel Complex

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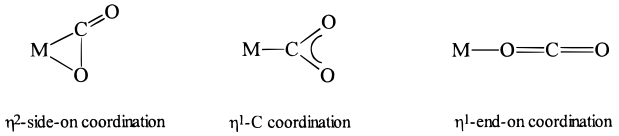
Received July 24, 1996

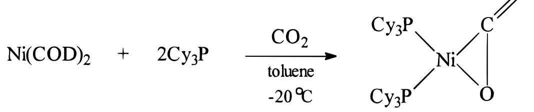
Carbon dioxide chemistry has been of great interest due to its fundamental importance and practical applications. Developing efficient catalytic processes in which carbon dioxide can be used as a carbon source is one of the main objectives of this research area.[1] Carbon−carbon coupling is the key to achieve C_2 or higher organic molecules. We are reporting the first example of a Wittig reaction on a coordinated carbon dioxide nickel complex.

Coordination of carbon dioxide to a transition metal is one of the initial steps in the catalytic conversion of carbon dioxide into useful organic molecules. The electronic structure of carbon dioxide is perturbed by bonding to a transition metal center. Different types and degrees of altered reactivities have been observed for different coordination modes of carbon dioxide. Two coordination modes, η^2 side-on coordination and η^1-C coordination, for mononuclear metal carbon dioxide complexes are well-known.[2] A third mode, η^1 end-on coordination, has been proposed as a result of calculations or as a proposed intermediate.[2,3]



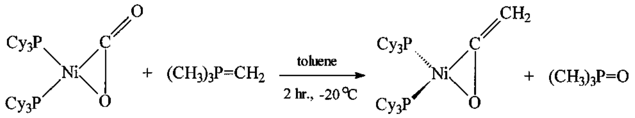
η^2-side-on coordination η^1-C coordination η^1-end-on coordination

The η^2 coordination of carbon dioxide to the nickel complex $(Cy_3P)_2NiCO_2$, where Cy = cyclohexane, is favored as starting complex with the ylide due to the electrophilic carbon of the coordinated CO_2. The complex was first prepared by Michele Aresta in 1974.[1a,4] On the basis of their literature procedures, the preparation was modified to a one-step procedure:



To a 100 mL Schlenk flask charged with 0.2 g (0.727 mmol) of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) and 2 equiv of Cy_3P (0.408 g) were added 20 mL of anhydrous toluene in a nitrogen atmosphere box. The reaction flask was immediately brought out of the box and placed into a −20 °C cooling bath. The reaction solution was bubbled with carbon dioxide gas through a syringe needle for 40 min. The product precipitated as a yellow crystalline solid. The reaction mixture was stirred for another 20 min and then filtered under vacuum. The yield is 89%. The spectral data agree with the literature values.[3] The C═O in coordinated CO_2 is characterized by a strong IR band at 1740 cm^{-1}.

Trialkyl phosphorus ylides $R_3P{=}CH_2$ are strong nucleophiles and react with organic ketones and aldehydes to form alkenes via a [2 + 2] cycloaddition mechanism (Witting reaction). Such ylides also react with the bridging carbonyl in $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$ (dppm = bis(diphenylphosphino)methane) and $[\eta^5\text{-}CpFe(CO)_2]_2$ to form μ-alkylidene complexes through the same C−C formation mechanism.[5] The carbon of η^2-CO_2 metal complexes has demonstrated some interesting reactivities toward nucleophiles.[6] When $(Cy_3P)_2NiCO_2$ is treated with an excess of trimethyl phosphorus ylide, a nickel ketene complex is formed:[7]



The nickel ketene complex obtained in the above reaction showed characteristic IR stretches of a η^2-(C,O) coordinated nickel ketene complex.[9] The band at 1570 cm^{-1} may be assigned to the C═O stretch of the ketene coordinating to the nickel with η^2-(C,O). The IR stretch at 1611 cm^{-1} could be assigned to the C═C double bond in the ketene ligand. These assignments are consistent with the literature data.[9] The only structurally characterized η^2-(C,O) nickel ketene complex, (dtbpm)Ni[η^2-(C,O)-Ph_2C_2O] (dtbpm, = bis(di-*tert*-butylphosphino)methane), was reported by Hofmann's group in 1992.[9a] The variable temperature (VT) $^{31}P\{^1H\}$ NMR spectra of our nickel ketene complex, $(Cy_3P)_2Ni[\eta^2\text{-}(C,O)\text{-}CH_2{=}CO]$, in toluene-$d_8$, show a singlet at δ 27.15 ppm at 298 and at 193 K,[7] which suggests that either the nickel atom has a tetrahedral geometry

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(7) The $^{31}P\{^1H\}$ NMR for $(Cy_3P)_2Ni[\eta^2\text{-}(C, O)\text{-}CH_2{=}CO]$ shows a singlet at δ 27.15 ppm. The coupled spectrum of the byproduct, $Me_3P{=}O$, shows a multiplet of 10 peaks centered at δ 37.98 ppm due to the coupling of phosphine to the nine protons in the three Me groups. The FTIR shows a strong 1611(s) cm^{-1} peak for C═C stretch. The ^1H NMR for the CH_2 group of the coordinated ketene is at δ 2.45 (br) ppm. The elemental analysis data are not quite consistent with the calculated results due to a trace amount of byproduct, $Me_3P{=}O$. The yield is 52%. The variable temperature studies were performed on a Bruker ARX-500MHz NMR spectrometer at the University of Missouri−St. Louis.

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S0002-7863(96)02547-4 CCC: $12.00

or the rotation of the ligand at 193 K has not been frozen out.[8k] The starting nickel CO_2 complex has a square planar environment for the nickel atom. The low temperature $^{31}P\{^1H\}$ NMR spectrum of $(Cy_2P)_2NiCO_2NiCO_2$ at 188 K (C_7D_8) reveals the presence of two doublets ($^2J_{P-P} = 39.6$) at 51.7 and 20.2 ppm, respectively.[3]

Free organic ketenes are very reactive molecules, and they can be stabilized by transition metal complexes. Transition metal ketene complexes are important intermediates in catalysis, such as in the Fischer–Tropsch process.[8] Ketenes can be bonded to transition metal complexes in a wide variety of ways.[8a] The two common bonding modes for mononuclear ketene complexes are η^2-(C, O) and η^2-(C, C). The η^2-(C, O) mode is considered to be favored by early transition metal complexes due to the electrophilic properties of the metals, while the η^2-(C, C) mode is preferred by late transition metals. Indeed, several nickel ketene complexes have been characterized spectroscopically to have the η^2-(C, C) bonding mode, and these ketene complexes have demonstrated much interesting chemistry.[8a] The coordinated ketene can be readily converted to various organic molecules such as alcohols, aldehydes, acetones, and acids.[8] In contrast, our preliminary investigation has shown that the η^2-(C, O) nickel ketene complex we isolated has its own characteristic reactivity which differs from the η^2-(C, C) species $(Ph_3P)_2Ni[\eta^2\text{-(C, C)-}CH_2{=}CO]$ reported in the literature.[10] For example, instead of reacting with nucleophiles, the η^2-(C, O) nickel ketene complexes we isolated can readily undergo electrophilic addition of H^+ to the ketene α-carbon to form acetaldehyde and $(Cy_3P)_2NiCl_2$. Detailed studies of these ketene complexes with electrophiles, such as HX and RX, and the ligand effects on the bonding modes of η^2-(C, C) and η^2-(C, O) to nickel complexes are currently under investigation.

Acknowledgment. We acknowledge Research Corporation for the Cottrell College Science Award (C-3394) and the GRFC of Southeast Missouri State University. C. A. Wright is grateful to the NASA JOVE scholarship. We are grateful to Janet Wilking at University of Missouri–St. Louis for the VT NMR experiment.

JA962547C

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