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Synthesis and Reactivities of Novel η^2-(C,O) Methylphenylketene Complex of Nickel

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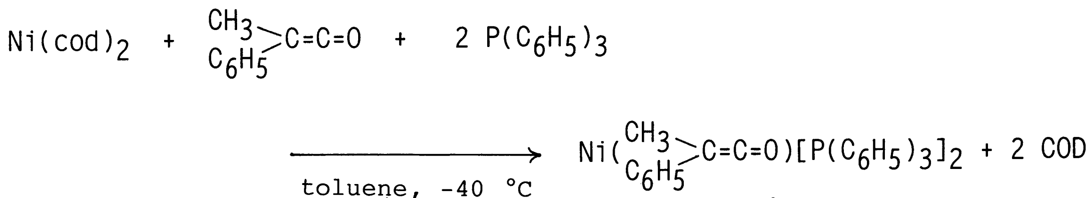
Bis(triphenylphosphine)(methylphenylketene)nickel complex (**1**) was cleanly isolated from the reaction of bis(1,5-cyclooctadiene)nickel with methylphenylketene in the presence of triphenylphosphine. The spectroscopic analyses of **1** suggest to be η^2-(C,O) ketene structure being close to oxanickelacyclopropane structure. Based on the chemical reactivities of **1**, it is proposed that the ketene moiety of **1** switches its coordination mode from η^2-(C,O) to η^2-(C,C) type prior to undergoing further reactions.

Transition metal-catalyzed reactions utilizing a variety of substituted ketenes have been extensively studied, particularly for synthetic application.[1,2] Despite of the ubiquitous use of ketenes in organic synthesis remains unexplored the reaction mechanism elucidating how the ketene ligand interacts with transition metal center to be activated and behaves in its coordination sites prior to undergoing further reactions with reagents. On relevance of our recent works on metal ketene complexes,[3] our interests have been extended to investigate the structures and the chemical behaviors of transition metal complexes of disubstituted ketenes. In this paper, we report the isolation of methylphenylketene complex of Ni and describe its unique chemical properties.

Treatment of bis(1,5-cyclooctadiene)nickel [$Ni(cod)_2$] (0.40 g, 1.5 mmol) and triphenylphosphine (0.83 g, 3.2 mmol) with methylphenylketene (0.30 g, 2.3 mmol) in toluene (10 ml) below -40 °C caused rapid color change of the yellow solution to result the formation of orange suspension. The resulting orange crystals of **1** were isolated by filtration, washed with ether, and then recrystallized from freshly distilled THF-ether below -30 °C (0.63 g, 61%).[4,5]



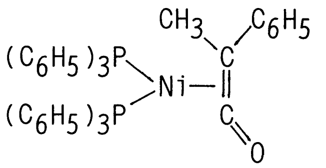
$$Ni(cod)_2 + \begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>\!C{=}C{=}O + 2\ P(C_6H_5)_3 \xrightarrow[\text{toluene, -40 °C}]{} Ni(\begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>\!C{=}C{=}O)[P(C_6H_5)_3]_2 + 2\ COD$$

1

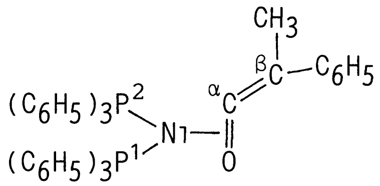
The isolated ketene complex **1** is found to be air-sensitive and thermally unstable, particularly in the solution. The coordination mode of the ketene ligand of **1** has been determined mainly by IR and NMR spectroscopies. The IR spectrum of **1** showed a characteristic strong band at 1590 cm^{-1} which could be assigned to the C=O stretching vibration of the ketene coordinating to the nickel through η^2-(C,O) manner.[6)] This is not inconsistent with that $\nu_{(C=O)}$ values of the η^2-(C,O) ketene complexes are well-documented to appear at the range of 1550-1650 cm^{-1},[7)] while those of the η^2-(C,C) ketene complexes at 1680-1790 cm^{-1}.[3c)]

The ^{1}H-NMR spectrum (CD_2Cl_2, -60 °C) revealed the methyl signal at δ 1.00 ppm (s, 3H) and the phenyl signals of the ketene ligand and the triphenylphosphine ligands at 7.12-7.41 (m, 35H). The gated-decoupled ^{13}C-NMR spectrum (CD_2Cl_2, -60 °C) exhibited the methyl carbon resonance at δ 16.3 ppm (q, J_{C-H}= 125 Hz), the β-carbon resonance at 72.9 (s), and the carbonyl carbon resonance at 166.9 (dd, J_{C-P^1}=39 Hz, J_{C-P^2}=8 Hz). These two different coupling constants of the carbonyl carbon with phosphorus atoms reflect that the complex **1** has a square-planar coordination geometry, in which the methyl and phenyl groups locate in-plane.

Interestingly, the carbonyl carbon resonated at higher magnetic field by 41 ppm compared with that of free methylphenylketene. These spectroscopic data are substantially consistent with the η^2-(C,O) ketene structure **B**.

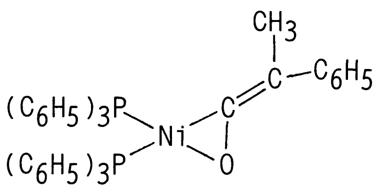


A



B

The large value of the coupling constant between the carbonyl carbon and P^1 could reflect an effective proof of the S character of the carbon hybrid orbital making up the Ni-C bonding property,[8)] suggesting that the complex **1** is nearly oxanickelacyclopropane structure **C**.

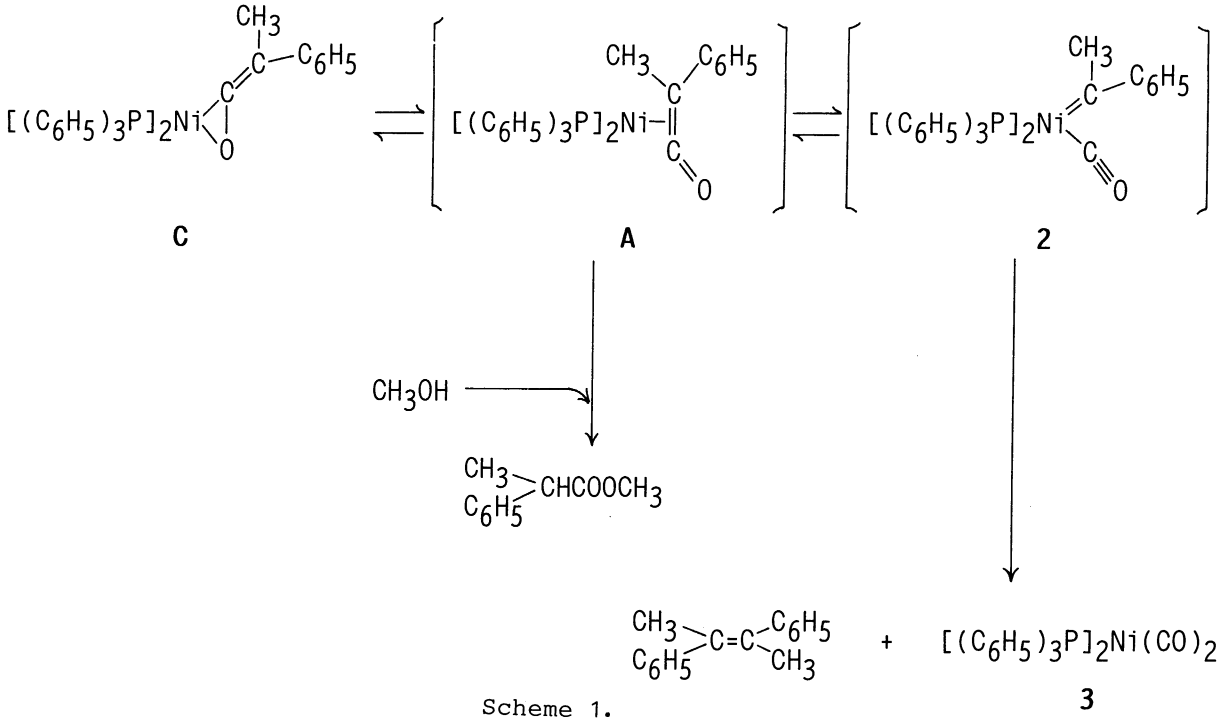


C

The ketene complex **1** was further characterized by its chemical reactivities. The reduction of **1** with $LiAlH_4$, treated initially at 0 °C by raising the temperature to 15 °C, gave 2-phenyl-1-propanol and 2-phenylpropanal with 49 and 6% yield based on Ni, respectively.

By the treatment of **1** with methanol initially at 0 °C, methyl 2-phenylpropionate was yielded (27%/Ni) in addition to styrene, ethylbenzene, (E)- and (Z)-2,3-diphenyl-2-butene with 17, 1, 7, and 2% yield, respectively. IR spectrum of the reaction residue isolated from the reaction solution, exhibited the two characteristic bands at 1950 and 2000 cm^{-1} which could be assigned to $\nu_{(C\equiv O)}$ of cis-$Ni(CO)_2[P(C_6H_5)_3]_2$ (**3**).$^{9)}$

Thermal decomposition reaction of **1** in toluene was carefully investigated by monitoring its spectral changes of IR. By raising the solution temperature from -30 °C to 20 °C, the initial strong signal at 1590 cm^{-1} started decreasing its intensity with color-change of the initial orange solution to dark brown, and a sharp signal at 1930 cm^{-1} compatible with $\nu_{(C\equiv O)}$ of $Ni(CO)[P(C_6H_5)_3]_3$ appeared instead.$^{10)}$ This signal increased its intensity gradually with the solution color deepened. After complete disappearance of the original signal at 1590 cm^{-1}, the signal at 1930 cm^{-1} started losing its intensity and new characteristic sharp signals at 1950 and 2000 cm^{-1} due to $\nu_{(C\equiv O)}$ of **3** came out at the same time.$^{9)}$ After complete decomposition of **1** in toluene, the dark brown solution was found to contain 2,3-diphenyl-2-butenes, styrene and unidentified products. These results can be presumably accounted for in terms of the conceivable formation of the metal-carbene carbonyl intermediate **2** involving the isomerization of **C** to **A**, although direct spectral observation on these novel interchanges was unsuccessful so far.$^{11)}$ Moreover, the carbene complex **2**, from which 2,3-diphenyl-2-butenes and styrene might form, may not be directly derived



Scheme 1.

from η^2-(C,O) ketene complex **C** as no precedent report has been made.[3c)] Previously, we described that η^2-(C,C) unsubstituted ketene complexes of Ni and Pt reacted stoichiometrically with methanol to give methyl acetate and thermally decomposed to give ethylene via the metal-carbene carbonyl complexes, while η^2-(C,O) ketene complexes did not react with alcohol directly.[3)] These observations are in favor of the assumption that the initial isomerization of **C** into the η^2-(C,C) ketene intermediate **A** appears to be required prior to undergoing methanolysis or thermolysis, and is followed by rapid decomposition to **2** as depicted in Scheme 1.

Further studies particularly on these unusual isomerization of **1** are now in progress.

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4) Elemental analysis for **1**: Found: C, 75.48; H, 5.37%. Calcd for $C_{45}H_{38}ONiP_2$: C, 75.55; H, 5.35%.

5) Similar nickel complex having diphenylketene ligand was reported to be prepared. H. Hoberg and J. Korff, J. Organomet. Chem., 152, 255 (1978).

6) IR(KBr) of **1**: 3100-3030 cm^{-1} (w, ν_{C-H}, aromatic), 2930-2860 cm^{-1} (w, ν_{C-H}, saturated), 1630 cm^{-1} (sh, $\nu_{C=C}$), 1590 cm^{-1} (s, $\nu_{C=O}$).

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11) No apparent line-shape change was observed by raising the measuring temperature from -60 °C to 5 °C in NMR spectrum. At the temperature above 5 °C, ^{1}H-NMR exhibited drastic spectral changes involving line-broadening before decomposition products appeared. Unfortunately, we were unable to attain the frozen spectrum owing to the rapid structure change during the time required to accumulate the spectrum.

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