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Synthesis and reactivities of novel η^2 -(C,O) alkylphenylketene complexes of nickel. Coordination-mode switching reaction of the ketene ligand *

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Abstract

A series of bis(tertiary phosphine)(alkylphenylketene)nickel complexes, $\text{Ni}[(\text{C}_6\text{H}_5(\text{R})\text{C}=\text{C}=\text{O})\text{L}]_2$ [R = CH_3 (a), C_2H_5 (b); L = $\text{P}(\text{C}_6\text{H}_5)_3$ (1), $\text{P}(\text{C}_6\text{H}_5)_2(p\text{-CH}_3\text{C}_6\text{H}_4)$ (2)], were isolated from the reaction of bis(1,5-cyclooctadiene)nickel with alkylphenylketene in the presence of the corresponding tertiary phosphines. The spectroscopic analyses of 1 and 2 suggest η^2 -(C,O) to be a ketene structure close to the structure of oxanickelacyclopropane. Based on their chemical reactivities and fluxional behaviors in ^1H and ^{13}C NMR, the ketene moieties of 1 and 2 switch their coordination-mode from η^2 -(C,O) to η^2 -(C,C) type via an associative process involving binuclear μ -ketene intermediates prior to undergoing further reactions.

Introduction

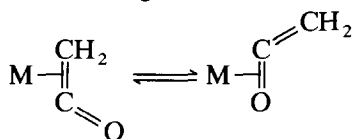
Transition metal-catalysed reactions utilizing a variety of ketenes have been extensively studied, particularly for synthetic applications [1]. In these reactions, transition metal ketene complexes are believed to play key roles in determining stereo- and regio-selectivities [2]. Despite the ubiquitous use of ketenes in organic synthesis, the reaction mechanism elucidating how the ketene ligand interacts with the transition metal center to be activated and its behavior in the coordination sites prior to undergoing further reactions with various reagents, remain unexplored.

One of the current topics for these ketene complexes, in which there are two types of the coordination-mode such as η^2 -(C,C) and η^2 -(C,O) [3], is whether the

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* Dedicated to Professor Akio Yamamoto upon his retirement from Tokyo Institute of Technology and in honour of his contributions to organometallic chemistry.

coordinating ketene molecule switches its coordination mode.

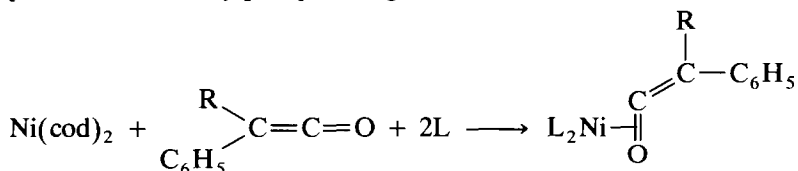


If so, a simple question how it does take place remains to be answered. Such basic studies may offer us fundamental information for understanding not only the factors governing the multifarious reaction modes of transition metal ketene complexes, but also the mechanism of CO reduction with H₂ via transition metal ketene intermediates as C₂-templates [3]. Further to our recent work on metal ketene complexes [4], our interests have been extended to investigate the structure and the chemical behavior of transition metal complexes of disubstituted ketenes. In this paper, we report on the isolation of alkylphenylketene complexes of Ni and describe its unique chemical properties involving the coordination-mode switching reaction of the ketene ligand from η²-(C,O) to η²-(C,C) type [5].

Results and discussion

Preparation of Ni[C₆H₅(R)C=C=O]L₂ [R = CH₃ (a), C₂H₅ (b); L = P(C₆H₅)₃ (1), P(C₆H₅)₂(p-CH₃C₆H₄) (2)]

A series of disubstituted ketene complexes of Ni **1** and **2** were cleanly isolated in moderately good yield from the reaction of Ni(cod)₂ with excess ketene in the presence of tertiary phosphine ligands as shown below.



L = P(C₆H₅)₃ (**1**)

L = P(C₆H₅)₂ (p-CH₃C₆H₄) (**2**)

R = CH₃ (a)

R = C₂H₅ (b)

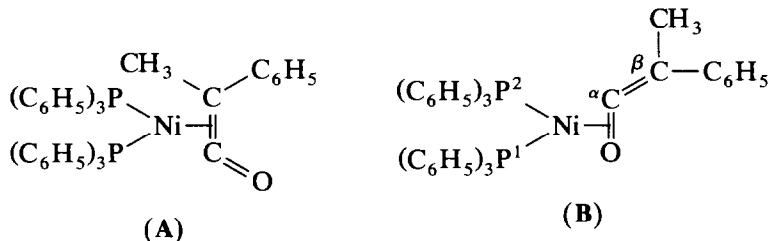
All these ketene complexes **1** and **2** were air- and moisture-sensitive and thermally unstable, particularly in solution. The coordination mode of the ketene ligands of **1** and **2** was determined mainly by IR and NMR spectroscopies. The IR spectrum of **1a** showed a characteristic band at 1590 cm⁻¹ which could be assigned to the C=O stretching vibration of the ketene coordinating to the nickel with η²-(C,O) [6*]. This is not inconsistent with the fact that ν(C=O) values of the η²-(C,O) ketene complexes are well documented to appear typically at the range of 1550–1650 cm⁻¹ [7], while those of the alternative η²-(C,C) ketene structure appear at 1680–1790 cm⁻¹ [3].

The ¹H NMR spectrum (CD₂Cl₂, -60°C) of **1a** revealed the methyl signal of the ketene ligand at δ 1.00 (s, 3H) and its phenyl signals at 7.12–7.41 (m, 35H) together with triphenylphosphine. The gated-decoupled ¹³C NMR spectrum

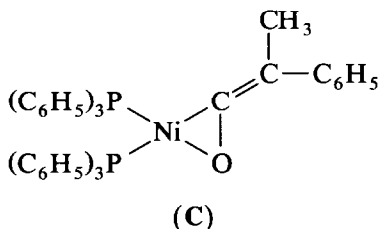
* Reference number with asterisk indicates a note in the list of references.

(CD_2Cl_2 , -60°C) exhibited a methyl resonance at δ 16.3 (q, $J_{\text{C-H}} = 125$ Hz), the β -carbon at 72.9 (s) in addition to the carbonyl α -carbon at 166.9 (dd, $J_{\text{C-P}^1} = 39$ Hz, $J_{\text{C-P}^2} = 8$ Hz). These two different coupling constants of the α -carbon with two phosphorus atoms reflect that the complex **1a** 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**.

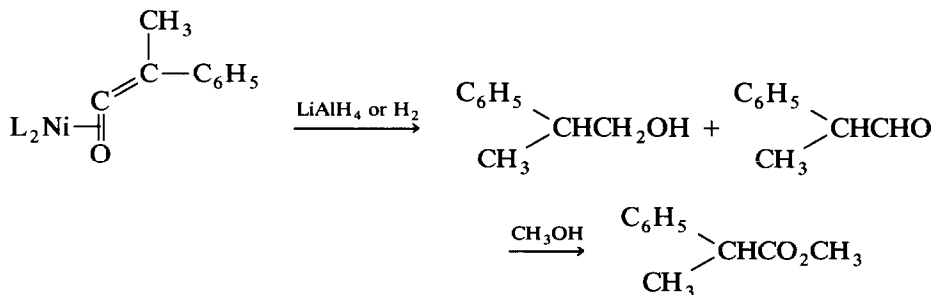


Furthermore, the large value of the coupling constant between the carbonyl carbon and P^1 could reflect an effective proof of the S-bonding character of the carbon hybrid orbital making up the Ni-C bonding properties [8], suggesting that the complex **1a** is the nearly oxanickelacyclopropane structure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



Chemical reactivities and thermal decomposition of **1** and **2**

The ketene complexes **1** and **2** readily reacted with reducing agent, nucleophile, and even with hydrogen. The reduction of **1a** with LiAlH_4 in THF, treated initially at 0°C by raising the temperature to 15°C , gave 2-phenyl-1-propanol (63% **1a**) and 2-phenylpropanol (16%), while its hydrogenolysis in THF (5 atm H_2 , 27°C , 20 h), afforded 2-phenyl-1-propanol (49%).



By the treatment of **1a** with methanol initially at 0°C , methyl-2-phenylpropanoate (37%) was yielded in addition with styrene (12%) and (*E*)-2,3-diphenyl-2-butene (8%).

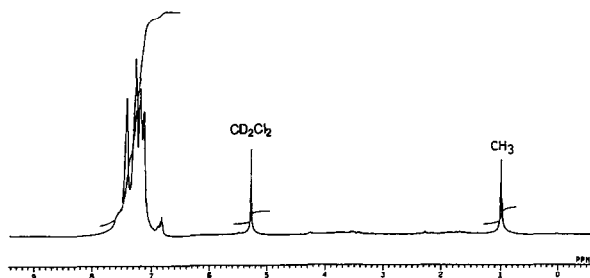
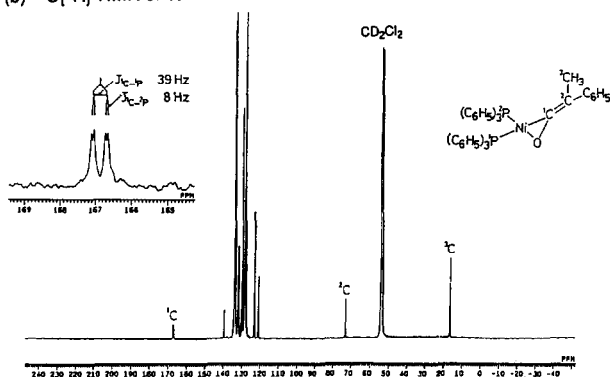
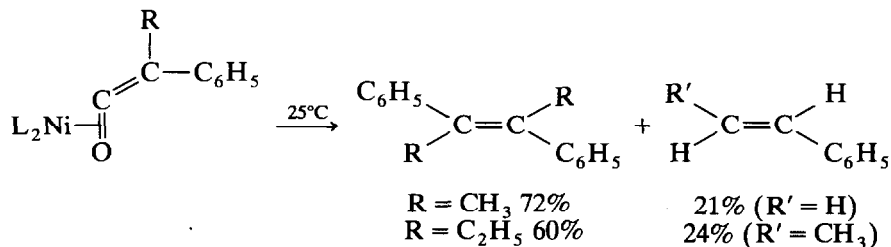
(a) $^1\text{H-NMR}$ of **1a**(b) $^{13}\text{C}\{^1\text{H}\}$ -NMR of **1a**

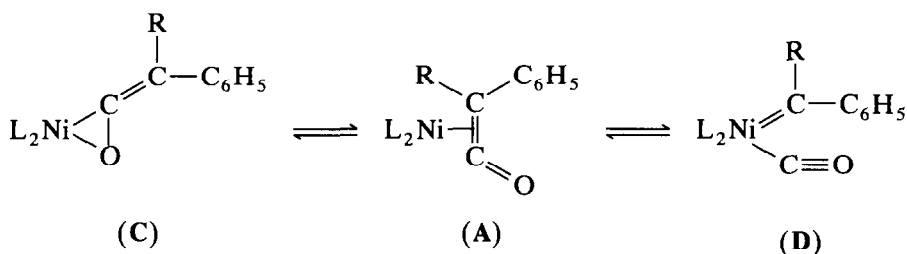
Fig. 1 NMR spectra of **1a**; (a) ^1H NMR, 400 MHz, CD_2Cl_2 , -60°C ; (b) $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CD_2Cl_2 , -60°C .

Interesting features of these complexes are their behaviors in solution. Although $\eta^2\text{-(C,O)}$ ketene complexes of transition metals are believed to be fairly stable in solution, **1** and **2** readily decomposed even at room temperature to afford olefins quantitatively together with $\text{Ni(CO)}_2\text{L}_2$. In toluene, **1a** completely decomposed to afford (*E*)-2,3-diphenyl-2-butene (72%, **1a**) and styrene (21%), while **1b** easily decomposed to yield (*E*)-3,4-diphenyl-3-hexene (60%, **1b**) together with (*E*)-1-phenyl-1-propene (24%).



To better define mechanisms by which **1** and **2** decomposed to yield olefins, thermal decomposition reaction of **1** in toluene was carefully investigated by monitoring its spectral changes of IR. By raising the solution temperature from -30 to 20°C , the initial strong signal at 1590 cm^{-1} started decreasing its intensity

with a color change from the initial orange solution to dark brown, and a sharp signal at 1930 cm^{-1} compatible with $\nu(\text{C}=\text{O})$ of $\text{Ni}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$ appeared instead [10]. This signal increased its intensity gradually with deepening of the color of the solution. After complete disappearance of the original signal at 1590 cm^{-1} , the signal at 1930 cm^{-1} started losing its intensity and a couple of new characteristic sharp signals at 1950 and 2000 cm^{-1} due to $\nu(\text{C}=\text{O})$ of $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ appeared [9]. These results can be presumably accounted for in terms of the initial bond hopping of the ketene ligand of **C** to form $\eta^2\text{-}(\text{C},\text{C})$ ketene species **A**. Then, **A** breaks the $\text{C}=\text{C}$ bond of the ketene ligand so as to yield the metal-carbene carbonyl intermediate **D** [4a,b], in which the carbene moiety likely undergoes β -hydrogen elimination and coupling reactions to afford olefins. Moreover, the carbene complex **D** may not be directly derived from $\eta^2\text{-}(\text{C},\text{O})$ ketene complex **C** as no precedent report has been made [2,7].



Previously, we showed that $\eta^2\text{-}(\text{C},\text{C})$ unsubstituted ketene complexes of Ni and Pt reacted rapidly and stoichiometrically with methanol to give methyl acetate, and thermally decomposed to give ethylene via the metal-carbene carbonyl complexes **D**, whereas $\eta^2\text{-}(\text{C},\text{O})$ ketene complexes did not react with alcohol directly [2,7]. These observations are in favor of the assumption that the initial isomerization of **C** into the $\eta^2\text{-}(\text{C},\text{C})$ ketene intermediate **A** takes place prior to undergoing methanolysis or thermolysis and is followed by rapid decomposition to nickel carbonyl complexes.

Temperature-dependent NMR studies of 1a

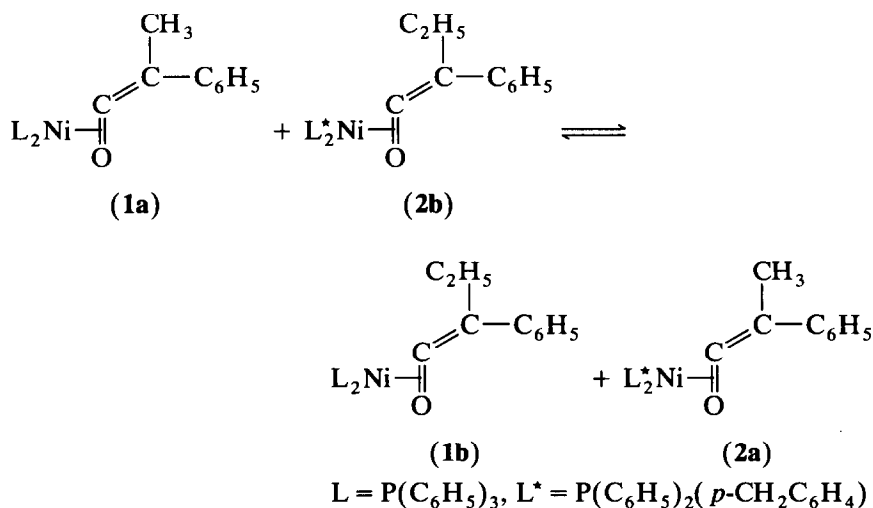
The coordination-mode switching reaction of the ketene ligand can be directly observed by analysing spectral changes of **1a** in CD_2Cl_2 by a variable-temperature NMR technique in ^1H and ^{13}C NMR [11]. Apparent line-broadening of the methyl signal in ^1H NMR, and α - and β -carbon on the ketene ligand in ^{13}C NMR were observed by lowering the solution temperature down to -90°C . These lineshape analyses of **1a** at the temperature range between -20 and -90°C suggested that apparent fluxionality of the ketene ligand occurred, although the frozen spectrum could not be attained owing rapid processing. The structure assignable to $\eta^2\text{-}(\text{C},\text{C})$ species may presumably change during the time required to accumulate its spectrum. Activation energy for this transformation was calculated as 14 kcal/mol , while activation entropy was obtained as -40 eu . This dynamic behavior of **1a** was not affected by the addition of 2-fold free ketene, while no exchange reaction of the original phenylmethylketene ligand with the added phenylethylketene was observed. Based on ^{31}P NMR of **1a**, no coordinating phosphine ligand was proved to be dissociated in the temperature range between -20 and -90°C , but the phosphine ligands apparently exchanged with added free phosphine via an associa-

tive mechanism since its exchange rate was largely affected by the concentration of the added phosphine.

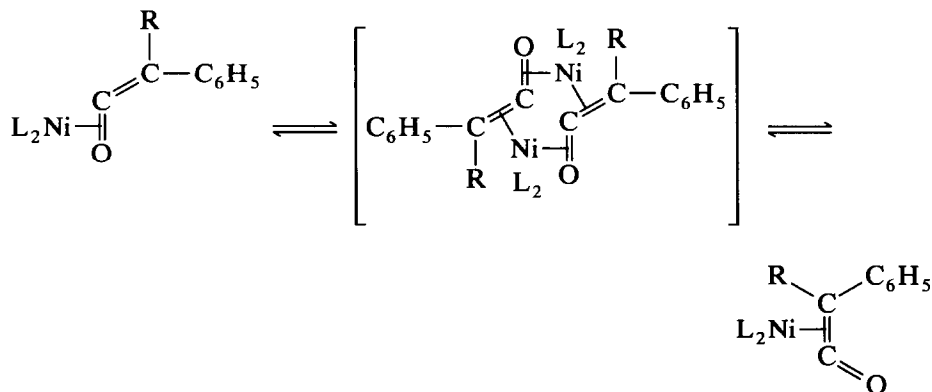
Consequently, these reversible lineshape changes of the ketene ligand can be accounted for by the two plausible pathways such as intramolecular double-bond hopping of the coordinated ketene, or coordination-mode change via a multi-metal center.

Crossover experiment for exchange reaction of the ketene ligands of 1a and 2b

To test for the possibility of an exchange reaction of the ketene ligand via the multi-metal center, a stoichiometric amount of **1a** and **2b** were dissolved and mixed in toluene at -20°C . After 5 h reaction at -20°C , ^{31}P NMR at -74°C exhibited two additional sets of signals assignable to **1b** and **2a** with almost the same signal intensities.



It should be noted that the only ketene ligands mutually exchanged, although no scrambling of the phosphine ligands yielding NiLL^* species was observed. Based on these experimental results that the ketene ligand exhibited the intermolecular crossover-exchange reaction, we assume an associative process involving binuclear μ -ketene intermediates for the coordination-mode switching reaction of the ketene ligand as depicted in the following scheme [12*]:



Experimental

General procedure

All reactions and other manipulations were carried out by standard Schlenk technique under an atmosphere of prepurified nitrogen or welding-grade argon purified over BASF catalyst and a molecular sieve (4 Å) before use. Solvents were freshly distilled from Na/benzophenone ketyl under an Ar atmosphere before use. Methylphenylketene and ethylphenylketene were prepared by dehydrochlorination of the corresponding acid halides as described previously [13].

Methylphenylketene: yellow liquid (b.p. 45–47°C/3.0 Torr) ^1H NMR (CDCl_3): δ 1.97 (s, CH_3 , 3H), 6.93–7.39 (m, C_6H_5 , 5H). ^{13}C NMR (CDCl_3): 8.5 (s, CH_3), 33.7 (s, C=), 123.5–133.3 (C_6H_5), 205.2 (s, C=O). IR $\nu(\text{C}=\text{C}=\text{O})$: 2090 s cm^{-1} . Ethylphenylketene: yellow-orange liquid (b.p. 68–69°C/5 Torr), ^1H NMR: 1.20 (t, CH_3 , $J = 7$ Hz, 3H), 2.40 (q, CH_2 , $J = 7$ Hz, 2H), 6.94–7.38 (m, C_6H_5 , 5H). ^{13}C NMR (CDCl_3): 12.9 (CH_3), 17.0 (CH_2), 41.7 (C=), 124.1–132.8 (C_6H_5), 205.2 (C=O). IR $\nu(\text{C}=\text{C}=\text{O})$: 2060s. Diphenyl(*p*-tolyl)phosphine was obtained by the treatment of diphenylphosphinous chloride with *p*-tolylmagnesium bromide, Colorless crystals. ^1H NMR (CDCl_3): 2.37 (s, 3H), 7.20–7.39 (m, 14H). ^{31}P NMR (CD_2Cl_2), –6.34 (upfield relative to external H_3PO_4). MS (70 eV, EI), 276 (M^+). Bis(1,5-cyclooctadiene)nickel was prepared by the literature procedure [14]. Proton and carbon-13 chemical shifts are referenced with TMS. ^{31}P chemical shifts are reported relative to external 85% phosphoric acid. ^1H and ^{13}C NMR were recorded with a Bruker AM-400 and Jeol GX-400. ^{31}P NMR spectra were obtained with the AM-400 instrument operating at 161.9 MHz. Mass spectra were recorded on a Jeol JMS-DX-303 at an Perkin-Elmer 1600 series FTIR. GC analyses were performed on Ohkura GC-103 and GC-802 with a 2-m column packed with 7% OV-1 on Chromosorb W equipped with a Shimadzu CR-3A data processing system. Elemental analyses were performed by the Chemical Analysis Center at Saitama University and the Institute of Physical and Chemical Research.

η^2 -(*C,O*) bis(triphenylphosphine)(methylphenylketene)nickel (**1a**)

Treatment of bis(1,5-cyclooctadiene)nickel [$\text{Ni}(\text{cod})_2$] (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 resulting in the formation of an orange suspension. The resulting orange crystals of **1a** were isolated by filtration, washed with ether, and then recrystallized from freshly distilled THF ether below –30°C (0.63 g, 61%) [4,5].

^1H NMR (CD_2Cl_2 , –60°C): δ 1.07 (s, CH_3 , 3H), 7.19–7.48 (m, C_6H_5 , 35H). ^{13}C NMR (CD_2Cl_2 , –60°C): 1.63 (CH_3 , q for gated-decoupled, $J(\text{C}-\text{H}) = 125$ Hz), 72.9 ($\text{CH}_3-\text{C}-\text{C}_6\text{H}_5$), 166.9 (dd, $J(\text{C}-\text{P}^1) = 39$ Hz, $J(\text{C}-\text{P}^2) = 8$ Hz, C=O), 123–138 (C_6H_5). ^{31}P NMR (CD_2Cl_2 , –74°C): 23.7, 49.5 (dd, $J(\text{P}-\text{P}) = 31$ Hz). IR (KBr) 2930, 2860 w ($\nu(\text{C}-\text{H}, \text{saturated})$) 16030 m ($\nu(\text{C}=\text{C})$), 1590s ($\nu(\text{C}=\text{O})$) cm^{-1} . Anal. Found: C, 75.48; H, 5.37. $\text{C}_{45}\text{H}_{38}\text{ONiP}_2$ calc.: C, 75.55; H, 5.35%.

η^2 -(*C,O*) Bis(triphenylphosphine)(ethylphenylketene)nickel (**1b**)

A mixture of $\text{Ni}(\text{cod})_2$ (0.48 g, 1.8 mmol) and $\text{P}(\text{C}_6\text{H}_5)_3$ (0.97 g, 3.7 mmol) was dissolved in toluene (10 ml) under nitrogen. After the mixture was stirred at –40°C for 1 h, ethylphenylketene (0.34 ml, 2.6 mmol) was added to give an orange

solution. After 5 h reaction, the resulting orange crystalline solid was isolated by filtration, washed with either below -30°C , and recrystallized from THF ether below -40°C (0.81 g, 63%). ^1H NMR (CD_2Cl_2 , -40°C): 0.14 (t, CH_3 , $J(\text{H}-\text{H}) = 7$ Hz; 3H), 1.73 (q, CH_2 , 2H), 7.20–7.52 (m, C_6H_5 , 35H). ^{13}C NMR (CD_2Cl_2 , -40°C): 13.1 (CH_3), 18.6 (CH_2), 80.0 ($\text{C}_2\text{H}_5-\text{C}-\text{C}_6\text{H}_5$), 166.4 (d, $J(\text{C}-\text{P}) = 49$ Hz, $\text{C}=\text{O}$), 125–138 (C_6H_5). ^{31}P NMR (CD_2Cl_2 , -30°C): 23.7, 48.1 (dd, $J(\text{P}-\text{P}) = 31$ Hz). IR (KBr): 2950, 2910 w ($\nu(\text{C}-\text{H}, \text{saturated})$), 1625 m ($\nu(\text{C}=\text{C})$) 1583s ($\nu(\text{C}=\text{O})$). Anal. Found: C, 75.54; H, 5.73. $\text{C}_{46}\text{H}_{40}\text{ONiP}_2$ calc.: C, 75.71; H, 5.54%.

$\eta^2-(\text{C},\text{O})$ Bis[diphenyl(*p*-tolyl)phosphine](methylphenylketene)nickel (**2a**)

Into a toluene solution of $\text{Ni}(\text{cod})_2$ (0.20 g, 0.73 mmol) and diphenyl(*p*-tolyl)phosphine (0.42 g, 1.51 mmol) was added a toluene solution of methylphenylketene (1.3 mmol) at -40°C . After 2 h reaction, a deep red solution was obtained, and concentrated to dryness to yield an orange solid which was recrystallized from THF/ether below -60°C (0.38 g, 69%). ^1H NMR (CD_2Cl_2 , -30°C): 1.14 (s, CH_3 , 3H), 2.39 (s, $\text{CH}_3-\text{C}_6\text{H}_4$, 3H), 7.21–7.52 (m, C_6H_5 , C_6H_4 , 33H). ^{31}P NMR (CD_2Cl_2 , -34°C): 23.2, 48.8 (dd, $J(\text{P}-\text{P}) = 31$ Hz). IR (KBr) 1628m ($\nu(\text{C}=\text{C})$), 1587s ($\nu(\text{C}=\text{O})$).

$\eta^2-(\text{C},\text{O})$ Bis[diphenyl(*p*-tolyl)phosphine](ethylphenylketene)nickel (**2b**)

Treatment of $\text{Ni}(\text{cod})_2$ (0.25 g, 0.92 mmol) and diphenyl(*p*-tolyl)phosphine (0.52 g, 1.90 mmol) with ethylphenylketene (0.18 ml, 1.3 mmol) in toluene (5 ml) below -60°C resulted in the formation of a deep orange solution. After concentrating the solution by 60%, the addition of ether at -40°C caused the precipitation of orange crystals which were isolated by filtration, washed with ether, and then recrystallized from freshly distilled THF/ether below -60°C (0.28 g, 39%). ^1H NMR (CD_2Cl_2 , -34°C): 0.12 (t, CH_3 , $J(\text{H}-\text{H}) = 7$ Hz, 3H), 1.68 (q, CH_2 , 2H), 2.39 (s, $\text{CH}_3-\text{C}_6\text{H}_4$, 3H), 7.23–7.55 (m, C_6H_5 , C_6H_4 , 33H). ^{31}P NMR (CD_2Cl_2 , -34°C): 23.1, 47.5 (dd, $J(\text{P}-\text{P}) = 31$ Hz). IR (KBr): 1625m ($\nu(\text{C}=\text{C})$), 1585s ($\nu(\text{C}=\text{O})$).

Thermal decomposition studies

Chemical reactions and thermal decomposition were carried out using a 3.0×10^{-3} M solution of **1** or **2** in toluene or other solvent as noted. In a 25 ml Schlenk tube equipped with a gas-tight serum cap was placed 2.0 ml of the sample solution which had been cooled to below -30°C . After complete reaction, the products in the solution were analysed by GC and identified by GC-MS and ^1H NMR on GC purified samples by comparison with the standard samples.

Reaction of 1a with hydrogen

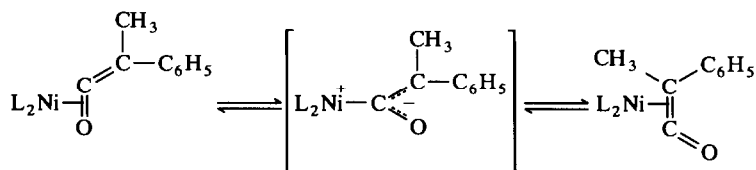
A glass pressure bottle (275 ml) containing a solution of **1a** (0.352 g, 0.492 mmol) in toluene was connected to a vacuum line and degassed through three freeze-thaw cycles. Hydrogen (5 atm) was then added at -30°C and the reaction mixture was allowed to warm to ambient temperature. After the reaction was completed (24 h), the products were analysed by GC and identified by GC-MS and ^1H NMR for GC purified samples.

Acknowledgements

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