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Preparation and properties of metallacyclobutanes of nickel and palladium

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Abstract

Bis(phosphine)-3,3-dimethylnickela- and palladacyclobutanes have been prepared by intramolecular C–H insertion reaction of the corresponding dineopentyl metal complexes. Nickelacyclobutane complexes decompose when heated thereby undergoing competitive carbon–carbon bond cleavage to give isobutene and ethylene, with reductive elimination affording 1,1-dimethylcyclopropane and skeletal isomerization of the metallacyclic ring yielding 3-methyl-1-butene, whereas the palladium analog gave no significant amounts of C–C bond cleavage products. Added phosphine was seen to have an effect on C–C bond scission of nickelacyclobutane complexes. Nickelacyclobutane complexes in solution are thought to be in equilibrium with olefin-coordinated nickel-carbene complex on the basis of available experimental evidence from hydrogenolysis, carbene-trap reactions with olefins and reaction with carbon monoxide.

Introduction

The formation and fragmentation of metallacycle complexes are believed to be involved in a number of important catalytic transformations. In particular, metallacyclobutane complexes are suggested to be significant intermediates for metal-catalyzed olefin metathesis [1], cyclopropanations [2], polymerizations [3], a variety of processes involving metal-carbenes [4], and hydrocarbon cracking and isomerization reactions [5]. An important aspect for these reactions is that the metal-carbene species, derived from the facile cleavage of carbon–carbon bonds in the metallacyclobutane ring [1], is presumed to play key roles in directing the product selectivity and even the reaction pathway. Although a number of metallacyclobutanes have been prepared [6–11], fundamental studies on their thermal decomposition reactions involving C–C bond cleavage remain unexplored.

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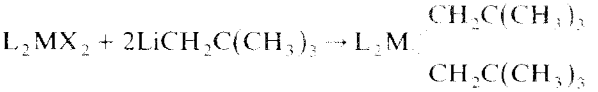
In this paper, we report on the preparation of nickela- and palladacyclobutane complexes by the thermal decomposition of the corresponding dineopentyl metal complexes, and describe their unique chemical properties involving competitive carbon–carbon bond cleavage, skeletal isomerization of metallacyclic ring and reductive elimination [1,7,8].

Results and discussion

Preparation of nickela- and palladacyclobutane complexes II

Bis(triphenylphosphine)-3,3-dimethylnickelacyclobutane (IIa) and [bis(diphenylphosphino)ethane]-3,3-dimethylnickelacyclobutane (IIb) were isolated in 12 and 18% yields, respectively, as thermally unstable and air-sensitive yellow to yellow-orange crystalline solids. The palladium analog IIc was isolated also in 31% yield as moderately stable off-white crystalline solids. Bis(phosphine)metal dihalides of Ni and Pd were treated with neopentyllithium at low temperature to yield the corresponding dineopentylmetal complexes (I), which were purified by recrystallization and characterized by spectroscopic methods and chemical reactions.

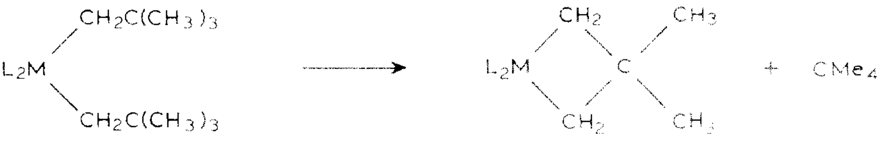


$$L_2MX_2 + 2LiCH_2C(CH_3)_3 \rightarrow L_2M\begin{array}{l}CH_2C(CH_3)_3\\ \\ CH_2C(CH_3)_3\end{array}$$

(Ia, $M = Ni$, $L = PPh_3$,
Ib, $M = Ni$, $L_2 =$ dpe;
Ic, $M = Pd$, $L = PPh_3$)

These dineopentylmetal complexes (I) decomposed to produce 3,3-dimethylmetallacyclobutane complexes (II) together with an equimolar amount of neopentane and traces of 1,1-dimethylcyclopropane. The metallacyclobutanes isolated were characterized by the combination of ^1H NMR spectroscopy, elemental analysis, and chemical reactions. The data are fully consistent with the proposed structures of II.

The nickel complexes Ia and Ib underwent intramolecular metal insertion reaction into the γ-C–H bond of neopentyl group to produce nickelacyclobutane complexes IIa and IIb and affording neopentane stoichiometrically. Because of the thermal instability of nickelacyclobutanes, these reactions had to be carried out below −20 °C for a long period of time. In contrast, the palladium complex Ic underwent competitive metal insertion to yield IIc, and reductive elimination to give 2,2,5,5-tetramethylhexane, which appears to be a decomposition model of dialkylpalladium complexes [12].

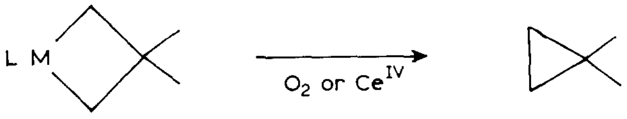


(I)

(IIa, $M = Ni$, $L = PPh_3$;
IIb, $M = Ni$, $L_2 =$ dpe;
IIc, $M = Pd$, $L = PPh_3$)

The nickel-alkyl in bis(phosphine)dineopentylnickel complexes I are stabilized because the alkyl has no β-hydrogen atoms as is well-documented. In these cases, however, metal insertion into the γ-C–H bonds of the alkyl group readily takes place to give metallacyclobutanes [6–10]. This cyclometallation was also observed for γ-C–H bond insertion in nickel and palladium neopentyl complexes I.

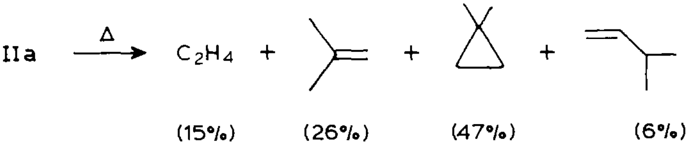
Complexes II were initially characterized by their chemical reactivities. Protonolysis of IIa, IIb and IIc with DCl in toluene resulted in the formation of quantitative amounts of 2,2-dimethylpropane-1,3-d_2, (by GC/MS). Treatment with Br_2 gave 1,3-dibromo-2,2-dimethylpropane (IIa, 49%; IIb, 52%; IIc, 67%) and oxidative decomposition of IIa, b, and c with O_2 or Ce^{IV} resulted in the formation of 1,1-dimethylcyclopropane with 80, 87, and 84% yield, respectively.



These chemical properties of II are fully consistent with the structure of II, proposed as metallacyclobutanes.

Facile carbon–carbon bond cleavage of metallacyclobutanes

Nickelacyclobutane complex IIa thermally decomposed to give a variety of hydrocarbons as shown in eq. 1. In addition to 1,1-dimethylcyclopropane and 3-methyl-1-butene (vide infra), isobutene and ethylene which resulted from the metathesis type carbon–carbon bond cleavage reaction of IIa were obtained in moderate yields.

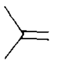
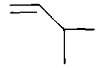


(1)

Addition of excess PPh_3 to a toluene solution of IIa appeared to promote C–C bond cleavage; the amount of ethylene and isobutene increased twice as much

Table 1

Decomposition reactions of the metallacyclobutane complexes [a]

Complex	Temp. (°C)	Time (h)	Products [b] (mol%)				
			C_2H_4				CMe_4
IIa	24	15	15	26	47	6	6
IIa + 5PPh_3	24	15	28	52	11	7	2
IIb	60	5	14	27	51	3	5
IIc	85	25	5	12	74	4	5

[a] Decomposition reactions were carried out in toluene solution. [b] Product gases in and over the solution were analyzed by GLC and identified by GC/MS and NMR spectroscopy.

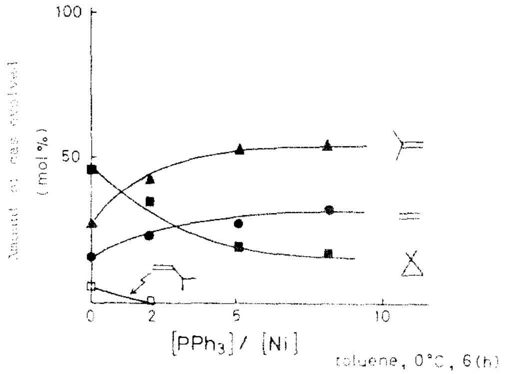


Fig. 1. The effect of added phosphine on the decomposition of IIa.

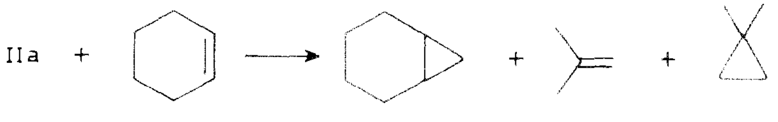
(Table 1). It is apparent from Table 1 that the C–C bond cleavage in nickelacyclobutanes IIa and IIb is a more facile process than that for the palladium analog. Platinacyclobutane complexes yield reductive elimination products only on thermal decomposition [10].

It has been reported that the decomposition modes of nickelacycle complexes were drastically changed by varying the number of coordinating phosphines [13]. The composition of the gas resulting from the decomposition of IIa as a function of added phosphine is shown in Figure 1. It has been found that the product yield due to C–C bond cleavage apparently increased with the amount of free phosphine added. This can be accounted for by the formation of a five-coordinate nickelacyclobutane complex which may play a key role in C–C bond cleavage of the metallacycle ring [13].

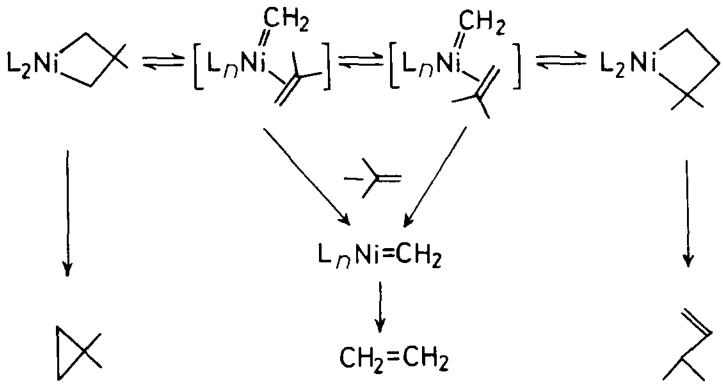
The addition of excess triphenylphosphine to the palladium complex IIc did not significantly alter the yield of decomposition products, as reported in the case of platinacyclobutane complex [10].

All of the reaction products can be rationalized as in Scheme 1. The observed reaction of the nickel complexes IIa and IIb which is favorable for C–C bond cleavages suggest that there is intermediate formation of a methylene-Ni complex which then dimerizes to give ethylene. 3-Methyl-1-butene, resulting from the isomerization of IIa, is important in establishing the reversibility of the metallacyclobutane with a metal-olefin-methylene complex.

Chemical evidence for the generation of nickel-methylene complexes was obtained mainly by trapping methylene with olefin, to give cyclopropane compounds, or by hydrogenation to give methane. Decomposition of IIa in the presence of excess cyclohexene resulted in the formation of norcarane (8% per Ni).



The methylene complex could also be trapped with hydrogen to give methane. Treatment of IIa with H_2 (5 atm) in toluene gave methane (38% per Ni), isobutane (32%) and dimethylcyclopropane (51%) as summarized in Table 2. When this

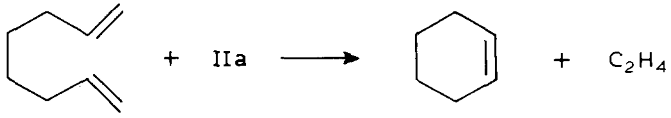


Scheme 1. Possible pathway for the interconversion of IIa into 2,2-dimethylnickelacyclobutane via nickel-carbene-isobutylene intermediate.

reaction was carried out under deuterium, methane-d_2 (82% isotopic minimum) and isobutane-d_2 (92% isotopic purity) were produced in similar yields (by GC/MS).

In contrast, the dominant products from the hydrogenolysis of the palladium analog IIc were neopentane (69%) and dimethylcyclopropane (14%) with small amounts of methane (4%) and isobutane (6%).

Further chemical evidence for the nickel-methylene intermediate was obtained by the reaction with 1,7-octadiene resulting in a catalytic metathesis. Treatment of IIa with excess 1,7-octadiene in toluene resulted in the formation of cyclohexene (380% per Ni), while the palladium analog IIc gave no detectable metathesis products.

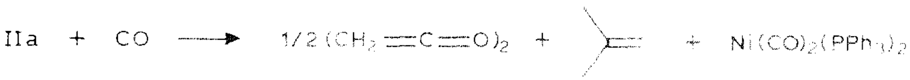


Interestingly, carbon monoxide (4 atm) reacted with IIa to give a low yield (8%) of ketene dimer [8] and no detectable amount of 3,3-dimethylcyclobutanone.

Table 2

Reaction products of the hydrogenation with H_2 of IIa and IIc

Product	Yield (%) of product from:	
	IIa	IIc
CH_4	53	4
C_2H_6	7	–
i-C_4H_{10}	62	6
i-C_4H_8	2	–
	32	14
i-C_5H_{12}	2	6
neo-C_5H_{12}	10	69



Although the fluxional behavior of IIa in toluene-d_8 was observed by the line-broadening of the signals due to metallic ring protons in the ^{1}H NMR spectrum, we were unfortunately unable to obtain the equilibrated spectrum. Further detailed study is required for spectroscopic observation on equilibrium of metallacyclobutanes with olefin-metal-methylene species.

The results of these metallacyclobutane complexes of Ni and Pd bear on a number of important catalytic processes involving olefin metathesis reactions for which the favored mechanism requires a facile equilibrium between metallacyclobutane and metal-olefin-methylene intermediate. Furthermore, we believe that these observed results provide multifarious information to understanding the mechanism for hydrocarbon isomerization and cracking, a process which could be of low activation energy and could occur at one metal center.

Experimental

General procedure

All reactions and other manipulations were carried out under an atmosphere of prepurified nitrogen or welding-grade argon purified over BASF catalyst and 5 Å molecular sieves before use. Solvents were freshly distilled from Na/benzophenone ketyl under an Ar atmosphere before use. Neopentyllithium and the starting metal complexes were prepared by standard procedures [14]. Hydrocarbons were analyzed by GLC on Ohkura GC-103 and 802 FID instruments attached to a Shimadzu computing integrator CR-1 equipped with a 2 m × 0.3 cm column with n-octane on Porasil-C and with Silicone SE-30 (10%) on Celite 545. ^{1}H NMR spectra were recorded with a JEOL JNM-FX-90Q and mass spectra were recorded on a JEOL JMS-D-300 equipped with a JMA-2000 data processing system at an ionizing voltage of 70 eV. Elemental analyses were performed by the Kyoto University and Wako Chemical Company microanalytical facilities.

Dineopentyl[bis(triphenylphosphine)]nickel(II) (Ia)

To a suspension of $NiCl_2(PPh_3)_2$ (1.6 g, 3.0 mmol) in toluene (30 ml) at −70 °C was slowly added a 3-molar excess of neopentyllithium/ether solution (0.68 *M*). The mixture was maintained below −60 °C with stirring for 6 h until the olive green Ni starting complex had dissolved. The pale yellow solid which precipitated from the deep red solution on addition of n-hexane was isolated by filtration using a glass fritted with cooling jacket. The solid was dissolved in a minimum amount of toluene (10 ml) below −65 °C, purified by rapid chromatography over neutral alumina (Woelm N-Super I, 5 cm × 2 cm diameter) at −55 °C. Addition of n-hexane to the eluate resulted in the yellow crystalline solid, Ia (38%).

Ia: ^{1}H NMR (−58 °C, C_7D_8) δ 1.14 ppm (s, 18H), 0.91 (m, 4H), 7.60 (broad m, 30H). Hydrolysis of Ia with sulfuric acid (at −10 °C) yielded neopentane (93%), and bromination gave neopentyl bromide (87%), (by GLC). In the solid state, Ia was stable enough to handle at −10 °C for short periods, but was extremely air sensitive. These properties made it unsuitable for elemental analysis.

Dineopentyl[bis(diphenylphosphino)ethane]nickel(II) (Ib)

A suspension of $NiCl_2$(dpe) (2.0 g, 3.8 mmol) in ether (50 ml) was treated with a 3-molar excess of neopentyllithium in ether at −50 °C. After the reaction mixture had been kept below −45 °C for 6 h, an orange-yellow crystalline solid precipitated from the red-brown solution. The compound was isolated by filtration and recrystallized from toluene/hexane mixtures to yield orange-yellow crystals Ib (42%) which were stable enough to handle in the solid state at room temperature for short periods. Protonolysis with gaseous hydrogen chloride in a toluene solution gave neopentane (96% per Ni).

Anal. Found: C, 72.36; H, 7.68; Ni, 9.52. $C_{36}H_{46}NiP_2$ calc: C, 72.10; H, 7.75; Ni, 9.80%.

Dineopentyl[bis(triphenylphosphine)]palladium(II) (Ic)

A mixture of $PdCl_2(PPh_3)_2$ (2.0 g, 2.9 mmol) and neopentyllithium (3-molar excess) in ether (50 ml) was slowly warmed to −20 °C. The off-white solid, which precipitated from the yellow solution was isolated and recrystallized from toluene (54%). Hydrolysis of Ic in a toluene solution yielded neopentane (98% per Pd) and bromination gave neopentyl bromide (89%). Ic: ^{1}H NMR (−20 °C, C_7D_8) 1.12 ppm (s, 18H), 0.88 (m, 4H), 7.41 (m, 30H).

Anal. Found: C, 71.68; H, 6.72. $C_{46}H_{52}P_2Pd$ calc: C, 71.43; H, 6.80%.

Bis(triphenylphosphine)-3,3-dimethylnickelacyclobutane (IIa)

A solution of Ia (2.0 g, 2.8 mmole) in toluene (20 ml) was maintained at −35 °C for 70 h using a constant low temperature bath. The yellow solid was precipitated by the addition of hexane and recrystallized from toluene/hexane to yield 0.22 g of IIa (12%). IIa: ^{1}H NMR (−30 °C, C_7D_8) 0.90 ppm (s, $-CH_3$, 6H), 1.07 [t, $-CH_2$, 4H, $J(^{31}P-^1H)$ 6 Hz], 7.65 (m, -Ph, 30H).

Anal. Found: Ni, 8.84; $(C_6H_5)_3P$, 79.8. $C_{41}H_{40}NiP_2$ calc: Ni, 8.99; $(C_6H_5)_3P$, 80.3%.

After IIa had been separated off, the gas and solution phase was found to contain 2.3 mmol of neopentane (83% per Ia) and 0.20 mmol of dimethylcyclopropane (7.3%).

Complex IIa (0.417 g) in toluene was treated with oxygen to give 1,1-dimethylcyclopropane in 78% yield (GLC, n-pentane internal standard). The dimethylcyclopropane was identified from its ^{1}H NMR spectrum after purification by preparative GLC: 1.06 (CH_3, 6H), 0.23 (CH_2, 4H).

Deuterium chloride, generated from D_2SO_4 and dry NaCl, reacted with IIa to produce a quantitative yield of neopentane-1,3-d_2, which was identified by GC/MS (35 eV), and by ^{1}H NMR spectroscopy on a GLC-purified sample.

Bromine reacted with IIa in toluene at −20 °C, to produce a 54% yield of 1,3-dibromoneopentane, identified from its ^{1}H NMR spectrum of a GLC purified sample: 1.16 (CH_3, 6H), 3.38 (CH_2Br, 4H).

[Bis(diphenylphosphino)ethane]-3,3-dimethylnickelacyclobutane (IIb)

An ether (30 ml) solution of Ib (1.0 g, 1.7 mmol) was maintained at −20 °C for 12 h before hexane was added. The resulting yellow orange solid was recrystallized from toluene/hexane mixtures to yield 0.16 g (18%) of IIb. IIb: ^{1}H NMR (−20 °C, C_7D_8) 0.86 (s, CH_3, 6H), 1.14 (t, CH_2, 4H, $J(^{31}P-^1H)$ 6 Hz], 2.08 (t, CH_2–P, 4H), 7.37 (m, C_6H_5, 20H).

Anal. Found: C, 69.52; H, 6.53; Ni, 11.5. $C_{30}H_{34}NiP_2$ calc: C, 69.90; H, 6.67; Ni, 11.40%.

Reaction of IIb with Br_2 produced 1,3-dibromoneopentane (52%), with gaseous DCl, a quantitative yield of neopentane-1,3-d_2, and with O_2, an 87% yield of 1,1-dimethylcyclopropane.

[Bis(triphenylphosphine)]-3,3-dimethylpalladacyclobutane (IIc)

A suspension of Ic (2.0 g, 2.6 mmol) in toluene (50 ml) was slowly heated from room temperature to 60 °C and maintained at this temperature for 1 h. The resulting yellow solution was filtered by passage through a Celite pad. The filtrate was cooled to give off-white crystals of IIc which were recrystallized from toluene to yield 0.95 g of IIc (31%). The organic products of the reaction were 2.0 mmol of neopentane and 0.96 mol of 2,2,5,5-tetramethylhexane. IIc: ^1H NMR (-10 °C, C_7D_8) 0.87 (s, CH_3, 8H), 0.85 [t, CH_2, $J(^{31}P-^1H)$ 3 Hz, 4H], 7.38 (m, C_6H_5, 30H).

Anal. Found: C, 69.82; H, 5.57. $C_{41}H_{40}P_2Pd$ calc: C, 69.77; H, 5.87%.

Thermal decomposition studies

Thermal decompositions were carried out using 2.0×10^{-4} *M* solutions of IIa 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. The tube was connected to a vacuum line (– 0.003 Torr) and degassed through three freeze-thaw cycles and then placed in a thermostated bath. After complete decomposition, the gaseous products in and over the solution were analyzed by GLC (n-octane on Porasil C 2 m, 80 °C).

1,1-Dimethylcyclopropane and 3-methyl-1-butene were identified by ^1H NMR on GLC purified samples, and other lighter hydrocarbons were identified by comparison of their retention time and with that of coinjected standard samples.

Reaction of IIa and IIc with hydrogen or deuterium

A pressure bottle (275 ml) containing a solution of IIa (0.748 g, 1.15 mmol) in toluene (10 ml) was connected to a vacuum line and degassed at dry-ice temperature. Hydrogen or deuterium (5 atm) was then added and the reaction mixture was allowed to warm to ambient temperature. After the reaction was completed (2 h at 52 °C), the products identified by GLC are listed in Table 2. Mass spectral analysis of the deuterated hydrocarbons was performed at 30 eV and 70 eV. Reaction of IIa with D_2 gave CH_2D_2 and i-$C_4H_8D_2$ or 82 and 92% isotopic purity, respectively.

Reactions of IIa and IIc with carbon monoxide

The same procedure was carried out as above, but under carbon monoxide (5 atm) gas instead of hydrogen. After 1 h at 50 °C, the solution turned black and a grayish-white solid separated. Analysis of the resultant solution by GLC (SE-30 Celite 545, 2 m) showed, with xylene as internal standard, that ketene dimer had formed in 8% yield. The product was identified by GC/MS and from its ^1H NMR spectrum of a GLC purified sample [$CH_2{=}C$, 4.84 ppm, 1H and 4.48 (d), 1H; $C{-}CH_2{=}C$ 3.84, 2H].

The white solid, isolated by filtration, was identified as $Ni(CO)_2(PPh_3)_2$ in 83% yield: m.p. 209–213 °C; IR(KBr), 2008, 1955 cm^{-1}.

Acknowledgments

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