# The Preparation and Reactions of Nickelocyclopentanes
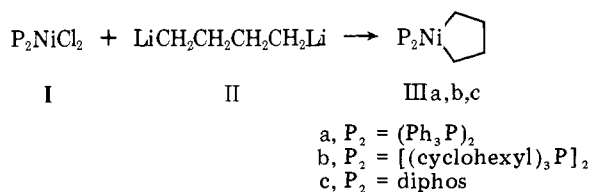
Sir:

Metallocyclopentanes have been suggested as intermediates in a number of transition metal catalyzed [2 + 2] cycloadditions of olefins.[1] They have been trapped from such reactions[2] and prepared as stable complexes.[3] The isolated complexes are more stable than acyclic analogues.

We now report the preparation and reactions of a series of phosphine nickelocyclopentanes which undergo competitive β-*carbon–carbon bond cleavage,* the reverse of the first step of the [2 + 2] cycloaddition reaction, *reductive elimination,* the required second step of the [2 + 2] cycloaddition reaction, and β-*hydride transfer,* the normal reaction of metal alkyl complexes.[4]

$$P_2Ni \langle \rangle \xrightarrow{9\ °C} CH_2{=}CH_2 + \square + 1\text{-butene}$$
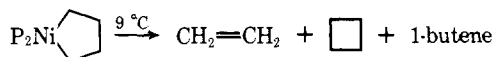
The complexes were prepared by the addition of 1,4-dilithiobutane[5] to the appropriate dichlorobisphosphinenickel(II) complex in ether at −78 °C. The temperature was slowly raised

$$P_2NiCl_2 + LiCH_2CH_2CH_2CH_2Li \longrightarrow P_2Ni \langle \rangle$$

| I | II | IIIa,b,c |

a, $P_2 = (Ph_3P)_2$
b, $P_2 = [(cyclohexyl)_3P]_2$
c, $P_2 = diphos$

to −20 °C and the resulting yellow solid formed at this temperature was isolated by filtration.

The solid was dissolved in toluene, filtered, and mixed with hexane. The solution yielded pure, yellow crystals of III (~40% yield) on cooling to −78 °C overnight.[6] Excess II or higher temperatures produced a brown solid, which could also be prepared from III + II, that analyzed for a 1:1 nickelate complex of III and II.[7] The analysis and molecular weights[8] of IIIa–c are given in Table I. The solid complexes decompose with smoke evolution in the air and all manipulations must be carried out under deoxygenated argon. The NMR spectra of IIIa were examined in detail. The ¹H spectrum of IIIa at −10 °C in toluene-d_6 showed multiplets at δ 1.67 and 1.87. A single ³¹P peak was observed for IIIa at −42.4 ppm (from H₃PO₄) over the temperature range of −10 to −90 °C. When a 20 mol excess of triphenylphosphine was added to IIIa a new set of multiplets appeared in the ¹H spectrum at δ 1.88 and 2.17. The ³¹P[9] spectrum of IIIa in the presence of a 2.7 molar excess of triphenylphosphine, singlets were observed for triphenylphosphine at 5.9 ppm (1.4), for IIIa at −42.3 ppm (1) and a new peak at −27.5 ppm (0.55). As the temperature was raised, the −27.5 ppm peak averaged with the free phosphine peak while the *signal for IIIa remained sharp.* The peak at −27.5 ppm is assigned the structure tris(triphenylphosphine)tetramethylenenickel(II), IVa,[10] on the basis of the following chemical and spectral evidence. When a toluene solution of IIIa was treated with an excess of Ph₃P at −10 °C, the bright yellow solution deposited golden brown crystals of IVa. The com-

Table I

Phosphine	% yield	Mol wt[8]	P/Ni[8]	C₄/Ni[8]
Ph₃P IIIa	36	626 (calcd 639)	2.0 (2.0)	0.98 (1.0)
(Cyclohexyl)₃P IIIb	43	343 (calcd 675)	2.04 (2.0)	0.97 (1.0)
Diphos IIIc	25	512 (calcd 513)	2.0	0.96
Ph₃P IVa	67 (from IIIa)		2.98 (3.0)	0.98 (1.0)
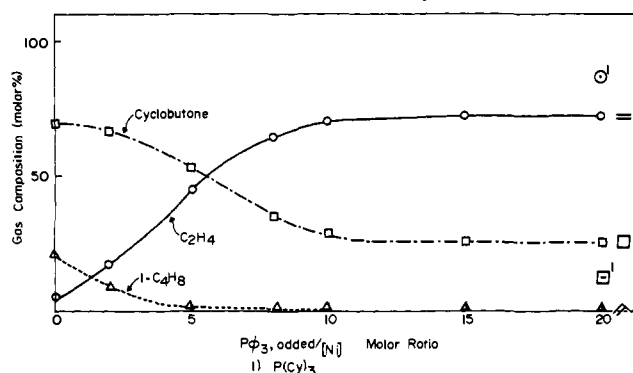
Figure 1.
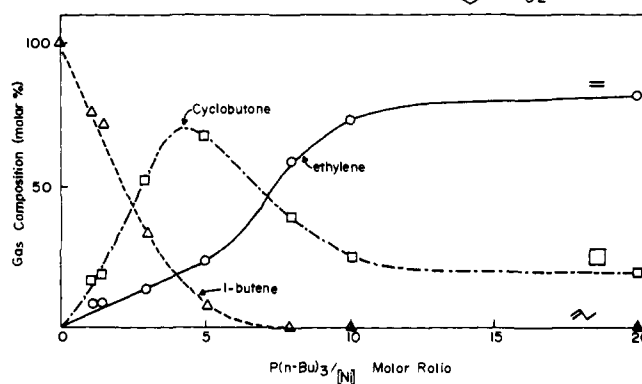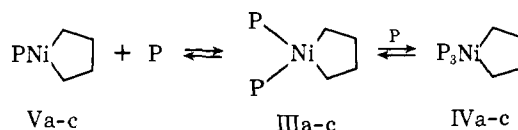

Figure 2.

pound was recrystallized at −50 °C from toluene that had been saturated with triphenylphosphene at −60 °C. The analysis is presented in Table I. A ³¹P signal at −27.5 ppm was observed at −90 °C for this compound. Oxidation of IVa (O₂) produced cyclobutane (93%) and hydrolysis with sulfuric acid (at −20 °C) produced butane (98%). This demonstrates that the C₄ ring remained intact.

The above NMR spectral and the molecular weight information is most consistent with the following equilibration scheme for the phosphine complexes.

$$PNi \langle \rangle + P \rightleftharpoons \overset{P}{\underset{P}{>}}Ni \langle \rangle \overset{P}{\rightleftharpoons} P_3Ni \langle \rangle$$

| Va-c | IIIa-c | IVa-c |

The molecular weight of IIIb suggests that in solution it is completely disassociated to Vb and the NMR firmly established the III → IV step.

Since the coordination number of the complexes was a function of the structure and concentration of the phosphine (Table I), the ratios of the decomposition products as a function of the phosphine structure and the P/Ni ratio were determined. This is the only way to determine the electronic and steric effects of the phosphine since comparisons can only be made between complexes of the same coordination number. The gas composition resulting from the decomposition of IIIa–c as a function of added phosphine is shown in Figures 1, 2, and 3. From the molecular weights in solution, IIIa and IIIc are present as the P₂ species whereas IIIb disassociated to a P₁ species (Vb). Cyclobutane is the predominate product for both P₂ species at P/Ni = 0. The disassociated IIIb produces 1-butene as the major product. As trialkyl phosphine is added to the tricyclohexylphosphine complex (IIIb) the amount of cyclobutane increases to a maximum at a P/Ni of
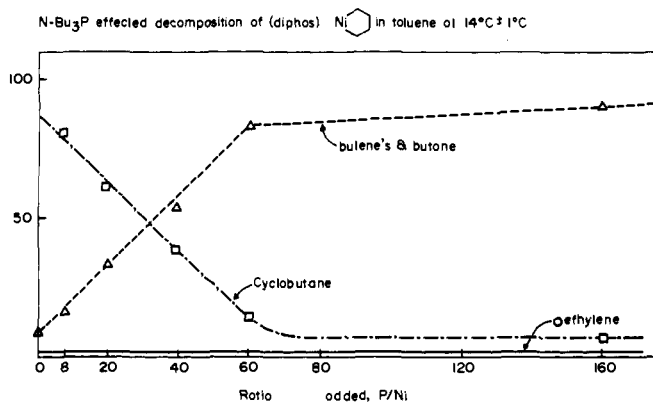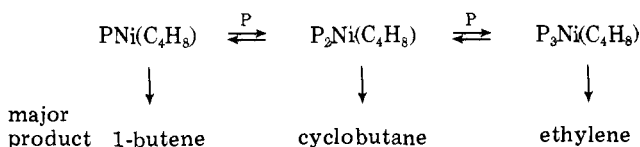
Communications to the Editor

N-Bu₃P effected decomposition of (diphos) Ni⬭ in toluene ol 14°C ± 1°C

Figure 3.

References and Notes

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(5) R. Grubbs and T. Brunck, *J. Am. Chem. Soc.*, **94**, 2538 (1972); R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 1739 (1953).
(6) All manipulations must be carried out under deoxygenated argon and the temperature must be maintained below −10 °C.
(7) D. G. Morrell and J. K. Kochi, *J. Am. Chem. Soc.*, **97**, 7262 (1975).
(8) The molecular weights were determined by freezing point depression of benzene. The complexes were decomposed with acid and peroxide. The gases were determined by GLC, the phosphine as the phosphine oxide and the nickel as the dimethylglyoxal complex.
(9) A. D. English, P. Meakin, and J. P. Jesson, *J. Am. Chem. Soc.*, **98**, 422 (1976); P. Meakin, A. D. English, and J. P. Jesson, *ibid.*, **98**, 414 (1976).
(10) P. Meier, A. Merbach, M. Dartiguenave, and Y. Dartiguenave, *J. Am. Chem. Soc.*, **98**, 6402 (1976).
(11) The complexes were decomposed at 9 ± 1 °C as 3 × 10⁻³ M solutions in toluene in reaction vessels attached to a gas manifold. As the reactions progressed those reactions which produced 1-butene as a major product also showed 2-butene as a secondary product.
(12) The diphos complex IIIc in the presence of an excess of (*n*-Bu)₃P showed no signals in the region between the signal for IIIc −44.8 ppm and the signal for the free phosphine (+33.1). The phosphine apparently acts as a base to induce the β-hydride elimination.
(13) Sloan Foundation Fellow and a Camille and Henry Dreyfus Foundation Grantee.

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4. At this point and at higher P/Ni ratios the decomposition ratios are very similar to those resulting from the triphenylphosphine complex at P/Ni = 0 and larger values and only for IIIc at P/Ni = 0. A sample of the pure trisphosphine complex, IVa, was decomposed under similar conditions. The major product (>90%) was ethylene. The yields of the gaseous products were close to quantitative and the ratios of the products were independent of the concentration of the starting complex. All of the low molecular weight hydrocarbons were transferred and collected at reduced pressure and analyzed by GLC.[11] These results combined with the NMR data are most consistent with the following scheme:

$$PNi(C_4H_8) \underset{\longleftarrow}{\overset{P}{\rightleftharpoons}} P_2Ni(C_4H_8) \underset{\longleftarrow}{\overset{P}{\rightleftharpoons}} P_3Ni(C_4H_8)$$

major
product   1-butene   cyclobutane   ethylene

Since the chelating phosphine does not form a five-coordinate species on mixing with excess phosphine, the phosphine effect, Figure 3, was very different than that observed for the nonchelating phosphines which form five-coordinate complexes.[12]

It is surprising that the high coordination number complex produced ethylene as the major decomposition product. An isomeration of a metallocycle to a bisolefin–metal complex reduces the oxidation state and retains the same coordination number of the metal. Since the trisphosphine metal complexes are coordinately saturated, the conversion to a lower oxidation state would require the loss of a ligand. The unexpected phosphine exchange of IVa with free phosphene independent of IIIa may provide the key to understanding this apparent inconsistency. Since the β-hydride elimination reaction requires an increase in coordination number, it is reasonable that this is the favored mode of decomposition for the low coordination number complexes.[3]

The only possible comparison of electronic effects which can be made are between the two trisphosphine complexes, IVa and b. It appears as though the better σ donor, poorer π acceptor favors an increase in the production of ethylene over cyclobutane. However, this effect may be associated with the III to IV equilibrium.

Experiments designed to sort out the pieces of this intriguing puzzle are presently in progress.

Total Synthesis of Humulene. A Stereoselective Approach

Sir:

The salient structural features of humulene (**1**), a fundamental monocyclic sesquiterpene, include the three olefinic linkages 2E, 6E, 9E, all of which are situated on the cycloundecane ring. Ever since the distinguished but *nonstereoselective* synthesis of humulene accomplished by Corey and Hamanaka in 1967,[1] virtually no synthesis has been reported for this interesting structure. A *highly stereoselective* synthesis of this unique compound is the subject of the present communication.

While humulene and the related sesquiterpenes are derived biologically from farnesol by anti-Markovnikov cyclization (eq 1),[2] the laboratory synthesis of these terpenes by such a cyclization has not yet been realized and represents a distinct challenge to the organic chemists. The simplicity of this scheme as a synthetic pathway led to the development of the present efficient synthesis.[3]

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