be readily blocked yielding a protected peptide suitable for further synthetic operations.

The preparation of the peptide γ-benzylglutaminyl-N^G-nitroarginine is described here to serve as an example of the reaction conditions used in the cleavage procedure. A solution of cyanogen bromide (1.85 g, 18.5 mmol) in propionic acid (7 ml) was added to the peptide-resin (0.37 mmol) and the mixture was shaken at room temperature for 24 hr. The propionic acid solution was collected and the resin was washed with the following solvents (each with three washes of 10 ml), trifluoroacetic acid, ethanol, and chloroform. The cleaved peptide (0.34 mmol) was then obtained by removal of solvent and excess reagent under reduced pressure. After purification by gel filtration on a polyacrylamide column (P_2), the peptide (0.28 mmol; amino acid analysis: $Arg_{1.0}$, Glu and $Hse_{1.8}$ Hse $lactone_{0.18}$) was digested with carboxypeptidase A (0.2 mg) dissolved in 5 ml of 0.2 *M* *N*-ethylmorpholine acetate, pH 8.5 at 31°. The digestion was followed by high voltage electrophoresis and showed that the release of homoserine with conversion of tripeptide into the desired dipeptide was complete after 2 hr. No other products could be detected even after a 24-hr digestion. The dipeptide (0.3 mmol) was purified by gel filtration and was shown to be homogeneous by high voltage electrophoresis at pH 2.1 and 5.6 (R_f 0.48 and 1.0, respectively, Gly = R_f 1.0), TLC (R_f 0.81, 1-butanol-acetic acid-diethylamine-H_2O (10:10:2:5), 0.58, 1-butanol-acetic acid-water (4:1:1)), and amino acid analysis (Arg, 1.0; Glu, 0.95).

These results show that a cyanogen bromide cleavage reaction allows the convenient preparation of peptides protected by many of the more stable groups such as carbobenzoxy, nitro, benzyl, etc., which should prove very useful in the semisynthesis of proteins.[14] At present the cleavage method is limited to peptides with C-terminal amino acids which are not readily cleaved by carboxypep idase A. It is anticipated that peptides containing methionine can be synthesized by this approach by incorporation of the methionine residue protected as the sulfoxide which is resistant to cyanogen bromide. Current investigations of Scheme B indicate that a peptide containing any C-terminal amino acid can be isolated in a homogeneous state by utilizing the marked specificity of carboxypeptidase B for basic residues (ref 15, see Scheme B, Figure 1).

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Heterogenized Rhodium Chloride Catalyst for Ethylene Dimerization

Sir:

A new catalyst system, rhodium chloride supported on silica gel, with high activity for ethylene dimerization has been found. As is well known, rhodium chloride is an active homogeneous catalyst for ethylene dimerization.[1-3] The new heterogeneous catalyst is more active than homogeneous rhodium chloride. Here, some characteristics of the catalyst are reported.

Carrier (5 g) (calcined at 300°C for 3 hr in vacuo before use) was impregnated with 20 ml of a methanol solution of rhodium trichloride trihydrate (rhodium content = 25%) (catalysts 1 and 2 in Table I, concentration 0.019 mol/l., catalysts 3-6, concentration 0.025 mol/l., respectively) for 2.5 hr at room temperature, followed by evacuation at 35°C for 6 hr without decantation. The solid was washed with 300 ml of methanol on a glass filter, and then evacuated at 35°C for 6 hr. The rhodium content of the catalyst was found by atomic absorption spectrophotometric analysis of rhodium from catalyst dissolved in hydrofluoric acid. Ethylene dimerization was carried out in a fixed bed type glass-made apparatus (200 ml). Reacting gas was circulated through the catalyst bed. A small amount of reacting gas was collected periodically through a sampling stopcock, and analyzed by gas chromatography. Propene hydrogenation was also carried out in the same apparatus with an equimolar mixture of propene and hydrogen at 25°C.

Preliminary experiments showed that hydrogen chloride remarkably enhanced the catalytic activity for ethylene dimerization, as is known in the case of homogeneous catalysis. In the absence of hydrogen chloride, the initial rate of butene formation with catalyst 1 was pretty low, 0.1×10^{-4} mol/(g-catalyst min). Thus, the dimerization was carried out in the presence of hydrogen chloride (2×10^{-4} mol). The activity was independent of hydrogen chloride amount as long as it exceeds 0.6×10^{-4} mol. 1-Butene was formed predominantly at the initial stage. The molar fraction of 1-butene decreases with time as it isomerizes to 2-butene. The molar ratio of *trans*- to *cis*-2-butene was 2.9. The rhodium content of the catalysts and the initial rate of butene formation are summarized in Table I with those of the other rhodium catalysts reported. Under the same conditions of catalyst preparation, the amount of rhodium supported on the carriers depended on the sort of carrier and increased in the order, silica gel (catalyst 3) < silica-alumina (catalysts 4,5) < alumina (catalyst 6). However, the dimerization activity per unit weight of catalyst increased in the reverse order, silica gel > silica-alumina > alumina. The catalytic activities per unit amount of rhodium are also summarized and

Table I. Comparison of the Activity of Various Rhodium Catalysts[a]

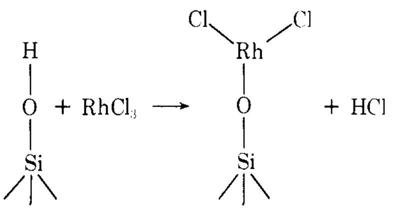
Catalyst	Initial rate ×10⁴ (mol g-catalyst^{-1} min^{-1})	Rh content ×10⁶ (g-atom g-catalyst^{-1})	Activity (mol g-atom-Rh^{-1} min^{-1})	Activation energy (kcal mol^{-1})
1 SiO_2	5.3	3.3	160	7
2 SiO_2 without washing	5.8	45	13	7
3 SiO_2	7.0	4.0	175	—
4 SiO_2–Al_2O_3 (13 wt % Al_2O_3)	1.6	33	4.8	—
5 SiO_2–Al_2O_3 (23 wt % Al_2O_3)	1.3	33	4.0	—
6 Al_2O_3	0.03	63	0.04	—
7 Rh-Y zeolite[4]	0.8	250	0.3	—
8 $RhCl_3$ (in EtOH)	—	—	~10^{-2}	13.6[3]
9 $[(C_2H_4)_2RhCl]_2$ (in EtOH)	—	—	~10^{-2}	17.2,[1] 14.7[3]

[a] Experimental conditions: catalysts 1–6, initial ethylene pressure = 460 Torr at 25°C; catalyst 7, 200 Torr at 20°C; catalysts 8~9,[3] 3000 Torr at 35°C or catalyst 9,[1] 1100 Torr at 50°C.

compared in Table I, which shows that silica gel has a high promoting effect. The activity of rhodium chloride supported on silica gel is much higher than that of Rh–Y zeolite,[4] and it corresponds to about 10^4-fold increase from that found with homogeneous rhodium chloride catalysts.[1,3]

A comparison of catalyst 1 and catalyst 2, which were prepared with and without washing by methanol, gives important information about the catalyst. As can be seen from Table I, catalyst 2 and catalyst 1 have almost the same activity, although the rhodium content of the former is much higher. From ESCA spectroscopic study, it was found that most of the rhodium content of catalyst 2 is free rhodium chloride. This part, the free rhodium chloride, which is removed by washing, may not be effective in the dimerization. The effect of heat treatment of these two catalysts (in vacuo for 3 hr) on their activity for dimerization and propene hydrogenation was examined. The dimerization activity of both catalysts decreased rapidly on heating at about 150°C, and the color of the catalysts changed from red-orange to dark brown or black. However, the hydrogenation activity of the catalysts exhibited a different temperature dependence. Catalyst 2 was active for the hydrogenation at temperatures higher than 200°C, whereas catalyst 1 was inactive even at 400°C, in spite of its sufficient rhodium content. The ESCA spectrum of the hydrogenation active catalyst 2 showed a considerable amount of metallic rhodium, which was responsible for the hydrogenation activity. When carbon monoxide was introduced into the reaction system the initial rate of the dimerization decreased linearly with the amount of carbon monoxide introduced. The amount of carbon monoxide needed for complete inhibition was estimated as 3.5 × 10^{-6} (mol/g-catalyst), which is almost the same as the rhodium content of catalyst 1, 3.3 × 10^{-6} (g-atom/g-catalyst). Accordingly, the active rhodium species can be considered as highly dispersed in molecular form, not in clusters. The observed activation energy of the dimerization was 7 kcal/mole, which is about one-half of that obtained with the homogeneous catalysis. Silica gel, which had been treated with γ-aminopropyltriethoxysilane,[5] a strong reagent for surface hydroxyl of silica gel, did not show any promotional effect in the dimerization.

From these results, we have concluded that the active rhodium species of the supported catalysts is the surface compound (I) formed from rhodium chloride and the surface silanol according to the equation



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and the high dimerization activity is due to the ligand effect of Si-O- on Rh. The latter effect may be found in the enhancement of catalytic activity of silica supported transition metal complexes.[6,7]

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Formation of Tetra- and Trinuclear Cluster Complexes from Tetracarbonylnickel and Hexafluorobut-2-yne. The Molecular Structures of $[Ni_4(CO)_4(CF_3C_2CF_3)_3]$ and $[Ni_3(CO)_3(CF_3C_2CF_3)(C_8H_8)]$

Sir:

There is considerable interest in fluxional and chemically active metal cluster complexes in relation to their ability to provide multinuclear sites for the bonding of alkenes or alkynes. We wish to report the first example of a complex in which a triangular array of metal atoms is able to stabilize a planar cyclooctatetraene ligand.

Removal of carbon monoxide in the reaction (50°) of tetracarbonylnickel with hexafluorobut-2-yne (HFB) affords (see Scheme I) hexakistrifluoromethylbenzene and a colorless volatile liquid complex $[Ni(CO)_2(CF_3C_2CF_3)]$ (**1**) (ν_{CO} (hexane) 2122 m, 2076 s, $\nu_{C\equiv C}$ 1905 w cm^{-1}; ^{19}F

Scheme I