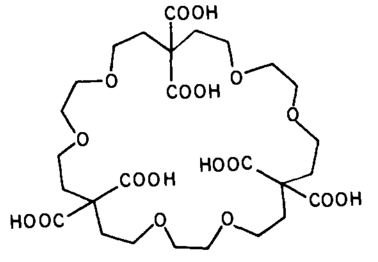

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absorptions due to the competitive formation of the **3b**-UO_2^{2+} complex.[9] From this competitive binding, a relative formation constant, $K_{rel} = K_{3b-UO_2^{2+}}/K_{CO_3^{2-}-UO_2^{2+}}$, was estimated to be $10^{-5.1}$, giving a log $K_{3b-UO_2^{2+}}$ value of 16.4 at 25 °C. The value is the largest among the hosts ever reported to bind uranyl ion, an example of which is a macrocyclic β-diketone reported by Cram (log $K = 12.5$ in aqueous dioxane).[4c] The large stability constant observed for the present macrocyclic hosts seem to be due to appropriate ligand arrangement as well as to the strong ligation of carboxylate anion.

High selectivity of the present host to uranyl was ascertained also by competition with other metal cations. An ethereal solution of **3b** (4.2×10^{-4} M, 1 mL) was stirred with a dilute solution of uranyl acetate (3.2×10^{-5} M, 5 mL) in the presence of a large excess of a competing cation such as Na^+ (0.469 M), Mg^{2+} (7.82×10^{-2} M), pH 8, Ni^{2+} (1.70×10^{-4} M), or Zn^{2+} (3.06×10^{-4} M), pH 6. Selectivity factors $K_{M^{m+}}/K_{UO^{2+}}$ for these metal ions were determined from the decrease of uranyl complexation by competition, and their values are $Na^+ < 1/180000$, $Mg^{2+} < 1/31000$, $Ni^{2+} = 1/210$, and $Zn^{2+} = 1/80$.

These results portend the efficient extraction of the uranyl ion from sea water with the present hexacarboxylic acid ligand attached to a polymer completely insoluble in water. Thus, 100 mg of cross-linked polystyrene-bound hexacarboxylic acid **3b**[10] (capacity: 630 μg of uranium/100 mg of polymer) was stirred with 5 L of sea water (Pacific Ocean) for 4 days. The polymer beads were separated, and uranyl ion was liberated by treatment with 15% ammonium bicarbonate solution (10 × 6 mL). The amount of uranium liberated was determined to be 6.85 μg, which corresponds to 41.5% of the total uranium present in the sea water treated.

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[9] It is a slow rate process requiring several hours for equilibration, but too long of a reaction often caused precipitation.

[10] Styrene was copolymerized with 3 mol % of triethylene glycol dimethacrylate. The resulting copolymer was chloromethylated and reacted with *N*-(ω-hydroxyoctyl)phthalimide, followed by the hydrolysis of phthalimide. The amino function was reacted with the mixed anhydride of hexacarboxylic acid prepared from ethyl chloroformate and triethylamine.

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Selective Homogeneous Catalytic Hydrogenation of Polynuclear Aromatics

Sir:

In a preliminary report, we recently described the synthesis and characterization of $(Ph_3P)_2(Ph_2P\overline{C_6H_4)Ru}H_2^+K^+\cdot C_{10}H_8\cdot(Et_2O)$ (**1**). This anionic hydride complex was found to be particularly useful for the hydrogenation of organic compounds containing polarized multiple bonds, for example, ketones, esters, and nitriles.[1]

Table I. Hydrogenation of Polynuclear Aromatics[a]

catalyst	substrate	% conversion[b]	solvent
$(Ph_3P)_3RuHCl$	naphthalene	0	THF
1	naphthalene	67	THF
1	naphthalene	70	toluene
1 + 18-crown-6	naphthalene	65	toluene
1	2-methylnaphthalene	35	THF
1	anthracene	99	THF[c]
1	phenanthrene	2	THF

[a] Typical conditions: complex 1 (0.035 mmol); aromatic substrate (3.9 mmol); solvent (5 mL); hydrogen (620-kPa gauge); 100 °C; 20 h. [b] Conversions were determined by gas chromatography with a 2 m × 3.2 mm stainless-steel column containing 1.5% BMBT on Chromosorb WHP 100/120 mesh; 150 °C 1 min, 4 °C/min to 220 °C. Products were identified by GC/MS techniques, and by comparison with authentic samples. [c] This reaction was stopped after 2-h reaction time.

In the preparation of **1**, we found that it could be isolated as the naphthalene or toluene adducts. X-ray structural work presently in progress indicates that the naphthalene in **1** is present only as a molecule of crystallization. Because of the apparently high affinity of **1** for aromatic compounds, we decided to investigate it as a possible catalyst for the hydrogenation of arenes. It was found that tetrahydrofuran (THF) solutions of **1** catalyzed the hydrogenation of polynuclear aromatics, predominantly to their tetrahydro derivatives, at 100 °C and 620-kPa gauge of hydrogen. Thus, naphthalene was found to be hydrogenated exclusively to tetrahydronaphthalene. Anthracene was hydrogenated to tetrahydroanthracene (98% selectivity) and 1,2,3,4,5,6,7,8-octahydroanthracene (2% selectivity). Anthracene was hydrogenated at a much faster rate than naphthalene (see Table I). Phenanthrene, which was hydrogenated much more slowly than anthracene and naphthalene, gave tetrahydrophenanthrene (96% selectivity) and 9,10-dihydrophenanthrene (4% selectivity). 2-Methylnaphthalene was found to be hydrogenated predominantly to 5,6,7,8-tetrahydro-2-methylnaphthalene (89% selectivity) and 1,2,3,4-tetrahydro-2-methylnaphthalene (9% selectivity). As can be seen from Table I, the relative ease of hydrogenation of the polynuclear substrates by using complex **1** as the catalyst is as follows: anthracene ≫ naphthalene > 2-methylnaphthalene > phenanthrene.

Under the same conditions, isolated aromatic rings such as benzene, toluene, tetralin, and pyridine were not hydrogenated. The precursor to **1**, $(Ph_3P)_3RuHCl\cdot C_6H_5CH_3$, under the same conditions was found to be inactive for the hydrogenation of naphthalene.

Other transition-metal complexes have recently been shown to homogeneously catalyze the hydrogenation of arenes,[2-7] but only one other, $Co_2(CO)_8$, has been reported to selectively hydrogenate naphthalene to tetrahydronaphthalene.[7] Complex **1** offers an advantage over the cobalt catalyst since the latter requires 13 000-kPa gauge of carbon monoxide/hydrogen and 200 °C whereas **1** is active at 620-kPa gauge of hydrogen and 100 °C. Moreover, with anthracene, $Co_2(CO)_8$ yields exclusively 9,10-dihydroanthracene whereas **1** gives predominantly 1,2,3,4-tetrahydroanthracene. The soluble metal complex catalyst $[C_5(CH_3)_5RhCl_2]_2$ in the presence of triethylamine has been reported to hydrogenate anthracene to tetrahydroanthracene (70%) and octahydroanthracene (22%).[4] Its reactivity with naphthalene,

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however, was not given. In the hydrogenation of phenanthrene, $\mathrm{Co_2(CO)_8}$[7] and **1** behave similarly in that phenanthrene is hydrogenated very slowly in comparison to anthracene. However, **1** gave predominantly 1,2,3,4-tetrahydrophenanthrene in contrast to $\mathrm{Co_2(CO)_8}$ which yields mainly 9,10-dihydrophenanthrene.

The $\mathrm{Co_2(CO)_8}$-catalyzed hydrogenation of polynuclear aromatics has been postulated by Feder and Halpern to proceed via a free-radical mechanism.[8] The various features of the $\mathrm{Co_2(CO)_8}$ system which implied the presence of radical intermediates are not seen in the hydrogenation of polynuclear aromatics with the ruthenium complex **1**. In fact, the product selectivities for the hydrogenation of anthracene and phenanthrene with **1**, as well as the relative hydrogenation rates for naphthalene and 2-methylnaphthalene, are in direct contrast to those observed for the cobalt catalyst (cf. Table I and ref 8).

The catalytic activity of **1** toward organic substrates containing polarized multiple bonds was attributed to its anionic hydride character.[1] For example, the rate of hydrogenation of acetone with **1** is sensitive to the polarity of the solvent medium, and particularly to the addition of potassium-complexing crown ethers. However, the rate of hydrogenation of naphthalene with **1** does not show such a dependence and thus appears to be unrelated to the anionic character of the catalyst. The hydrogenation of polynuclear aromatics with **1** most likely proceeds via a conventional π-coordination mechanism.

Acknowledgments. We thank Jeff Corsi and Richard Crissey for assistance in the preparation of **1**.

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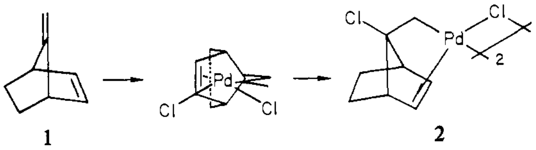
Molecular Structure of Dichloro(5-methylenecycloheptene)platinum(II). "In-Plane" Coordination of the Exocyclic Olefin

Sir:

The geometric requirements of olefins coordinated to Pt(II) have been of considerable recent interest. In two publications in this journal, Hoffmann and co-workers have utilized extended Hückel theory, first to model olefin insertion into Pt-H bonds,[1] and second to model olefin rotation about the Pt-olefin bond axis.[2] Thorn and Hoffmann[1] concluded that the olefin "insertion" process in *cis*-$\mathrm{L_2Pt(H)(olefin)}$ proceeds with the lowest activation barrier when the olefinic carbons, Pt, and ligated hydrogen all lie in the square plane of coordination. It was noted that such a coordination geometry has not been observed to date in stable d^8 square-planar olefin complexes.[3] In the second paper, Hoffmann and co-workers concluded that the olefin prefers to bind perpendicular to the coordination plane, primarily as a result of unfavorable steric interactions with the cis ligands in the "in-plane" orientation.[4] This view was presented earlier by Lewis and co-workers,[5] as well as by Ziegler and Rauk.[6]

We have been interested in the synthesis of stable "in-plane" coordinated olefins for many years. We have reported[7] our results with 7-methylenenorbornene (**1**), which was expected to bind $\mathrm{PdCl_2}$ as a diene, as shown in eq 1. The coordinated diene was not observed but was postulated to be an intermediate in the formation of the chloropalladated σ,π-chelate **2**. In unpublished work done even earlier,[8] we found that 5-methylenecycloheptene (**3**) reacted in a complex manner with $\mathrm{PdCl_2(PhCN)_2}$ in aprotic, nondonor solvents. Concurrent with our studies of **3** and Pd(II), Anderson and Michalowski reported[9a] the synthesis and spectral characteristics of the complex $\mathrm{PtCl_2}$-**3**, to which they assigned the monomeric structure **4**. Chelated **3** in the Pt(II) complex would seemingly require an "in-plane" or near "in-plane" geometry for the exocyclic olefin.



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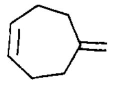

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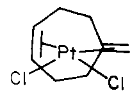

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In the Hoffmann paper on olefin binding and rotational barriers, doubt was raised concerning the actual (monomeric?)[9b] structure of the adduct of **3** with $\mathrm{PtCl_2}$. Since this complex is likely to be prototypal of the "in-plane" geometry for the coordinated olefin, we decided to synthesize the complex and determine the molecular structure by X-ray diffraction.

The title compound was prepared by direct reaction of sodium tetrachloroplatinate(II) with 5-methylenecycloheptene[10] in 1-propanol. The crystalline product was filtered after standing for 24 h and was recrystallized from $\mathrm{HCCl_3}$, yielding clear yellow needles. An orthorhombic prism, 0.25 × 0.21 × 0.15 mm, was selected for X-ray analysis. Cone-axis and zero-level precession photographs clearly gave the space group $P2_12_12_1$, and least-squares refinement of 12 carefully centered reflections with $2\theta \geq 40°$ [$\lambda_{\mathrm{Mo}\,K\alpha_1} = 0.70926$ Å] results in cell dimensions of $a_0 = 11.881$ (3), $b_0 = 7.094$ (2), and $c_0 = 11.344$ (3) Å.[11] One octant of data collected to a 2θ limit of 60° on an automated Picker FACS I diffractometer with the θ-2θ scan method (scan = 1.8 + 0.692 tan θ) yielded 1386 intensities greater than 2σ. An empirical absorption correction was made for the data on the basis of the intensity variation observed during rotation about the diffraction vector of five 00*l* reflections.[12] The maximum to minimum absorbance ratio was 4.1:1.

Due to disorder about a pseudo-twofold axis bisecting the ClPtCl angle, great care was taken in selection of refinement models. Two such models are relevant to the following discussion.

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(9) (a) C. B. Anderson and J. T. Michalowski, *J. Chem. Soc., Chem. Commun.*, 459 (1972). (b) Note that this ligand need not chelate to a metal. Indeed, the lowest energy conformation of 5-methylenecycloheptene is probably a chair form which is incapable of chelation and which would have a strain energy on the order of 4-5 kcal/mol less than the boat or twist-boat conformations required for chelation. It is not unusual, in our experience, for dimer or polymer formation to occur via bridging diolefin under the circumstances.

(10) 5-Methylenecycloheptene was prepared in four steps, starting from cycloheptene-5-carboxylic acid (see ref 8).

(11) A careful search for evidence indicating the need to double the unit cell was made at the suggestion of referee II. No such evidence was found after long-exposure cone-axis and oscillation photographs were examined.

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