of the corresponding diamine in 150 mL of dry hexane was then introduced. This mixture was kept under agitation at 55 °C during 48 h. The organolithium compound precipitate was filtered off and washed five times with anhydrous hexane. It appeared as a pale yellow fine powder (overall yield 50–60%).

5,5′-Bis[(*N*,*N*-dimethyl-2-aminophenyl)lithium]methane. Preparation A. The diamine (10^{-2} mol) and *n*-BuLi (2×10^{-2} mol) were mixed in dry *n*-hexane (150 mL) and heated to 60 °C during 48 h with agitation.

B. In a dry flask a solution of *n*-BuLi (2×10^{-2} mol) in 25 mL of *n*-hexane was stirred and heated to 60 °C. Then a solution of the amine (10^{-2} mol) in 100 mL of hexane was added dropwise over a period of 24 h. This addition was followed by an additional 48 h of heating to 60 °C.

C. The same conditions as in B were used, but the addition of the amine solution was done over a period of 72 h followed by an additional 48 h of heating at 60 °C.

D. The mixture obtained in A was heated with a solution of *n*-BuLi (2×10^{-2} mol) at 60 °C during 48 h.

In all cases, after reaction the mixture was cooled to room temperature and the organolithium precipitate was filtered off and washed with anhydrous hexane. The product appeared as a pale yellow powder. Its molar composition was as follows: method A, RLi_1 = 65% and RLi_2 = 35%; method B, RLi_1 = 60% and RLi_2 = 40%; method C, RLi_1 = 33% and RLi_2 = 67%; method D, RLi_1 = 20% and RLi_2 = 80%. The overall yield was 25–35% based on initial amine.

Synthesis of the Carbinols from Metalated Amines. General Procedure. A 10^{-2}-mol amount of the organolithium product was added to an excess of benzophenone (3×10^{-2} mol) dissolved in 20 mL of ether. The resulting mixture was stirred for 4 h and then acidified with 0.1 N HCl. The organic layer was extracted with ether; the aqueous layer was made basic with 0.1 N sodium hydroxide and extracted with ether. The latter extract was dried over magnesium sulfate, and the ether was distilled. The solid residue was fractionated by chromatography on a silica gel column (silica gel 60, Merck) with a hexane/ethyl acetate (9:1) mixture. The analytical data are given with Table I.

Kinetic Apparatus. The kinetic study has been done under vacuum (10^{-5} mmHg) in a series of sealed U-tubes (Figure 2). Amine, BuLi, solvent, and internal standard (*n*-pentane) were mixed in a. Every 2 h the solvent, pentane, and the butane which is formed during metalation are distilled from a to b cooled with liquid nitrogen. After sealing c and separation of tube b, the mixture was analyzed by gas chromatography with a Perkin-Elmer F 17 chromatograph under the following conditions: column (120 in.) was filled with Chromosorb AW, 80–100 mesh, impregnated with 3% OV 17 stationary phase; column temperature 25 °C; injection temperature 150 °C; detection temperature 200 °C.

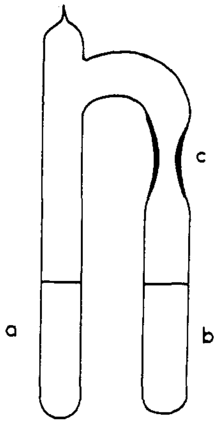

Figure 2. Kinetic apparatus.

Registry No.—(*N*,*N*,*N*′,*N*′-Tetramethyl-2,3-diaminophenyl)lithium, 68317-82-8; (*N*,*N*,*N*′,*N*′-tetramethyl-2,5-diaminophenyl)lithium, 68317-83-9; 5,5′-bis[(*N*,*N*-dimethyl-2-aminophenyl)lithium]methane, 68317-84-0; benzophenone, 119-61-9.

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Versatile Polymer-Bound Hydrogenation Catalysts. Rhodium(I)-Catalyzed Hydrogenation

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The bidentate ligand anthranilic acid has been anchored to polystyrene beads (Amberlite XAD-4) and the Rh(I) complex has been prepared. The polymer is a hydrogenation catalyst of exceptional activity, long-term stability, and considerable insensitivity to poisoning. Hundreds of catalytic cycles per metal atom are demonstrated without substantial loss of activity. The rhodium catalyst reduces a variety of olefinic and aromatic hydrocarbons and carbonyl, nitrile, and nitro functional groups. Catalytic activity depends upon retention of beads; if fragmentation occurs, the activity is considerably diminished. ESCA studies clearly demonstrate the rhodium to have a +1 formal oxidation state.

Anchoring ligands to insoluble polymeric supports, followed by complexation with transition metals, results in polymers having catalytic potential.[1-3] These metal complexes, hybrids of homogeneous and heterogeneous approaches, are attractive because they often permit the activity of soluble catalysts and the ease of product separation inherent in heterogeneous catalysts. In referring to this class of catalysts the names "polymer bound", "hybrid phase", or "supported" are common.

The choice of the ligand to be anchored is usually based on attempts to create environments analogous to those in the most active homogeneous catalysts. Because of the preponderance of phosphine complexes in homogeneous catalysts, most polymer-bound catalysts to date have involved these

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ligands. There are, however, two serious problems with this class of ligand: one, phosphines are easily oxidized[4,5] and, two, the metal, in certain cases, may elute from the support at a moderate rate.[6] One method to avoid these problems is to change the ligands which are attached.[7]

Our interest in anchoring anthranilic acid to chloromethylated polystyrene was predicated on the series of homogeneous catalysts defined by Avilov, Khidekel, and their associates.[8] These workers found, for example, that the Rh(I) complex of *N*-phenylanthranilic acid displayed exceptional hydrogenation activity with aromatic hydrocarbons. Furthermore, the catalyst was not highly oxygen sensitive and tolerated water. Since *N*-phenylanthranilic acid functions as a multidentate ligand it seemed attractive, with respect to catalyst longevity, to prepare a structurally similar polymer-bound catalyst. In a previous report we found that anchoring *N*-phenylanthranilic acid to chloromethylated polystyrene did not result in an active catalyst but that anchoring anthranilic acid, followed by complexation with Rh(III) and then reduction to Rh(I), led to a hydrogenation catalyst of exceptional activity.[9] In this report a more complete description of our findings is presented.

Experimental Section

Materials. Amberlite XAD-4 was a gift of the Rohm and Haas Co. It was obtained as hard, insoluble 20–50 mesh spheres. The polymer was received wet and was dried in a rotary evaporator at 50 °C for 12 h before being used. Chloromethylation was performed according to the procedure of Pepper et al.[10] In one batch the chlorine content was 10.02% (2.82 mequiv/g) and in another it was 11.31% (3.19 mequiv/g).

Anthranilic acid was anchored to the beads by stirring the beads with an excess of anthranilic acid in ethyl ether, acetone, or DMF. The following procedure was typical. To 1.00 g of the chloromethylated beads suspended in 50 mL of ethyl ether was added 0.5 g of anthranilic acid. This was stirred for 20 h, filtered, and washed with 200 mL of absolute ethanol. Anal. 0.42% N, 0.30 mequiv/g; 6.17% Cl.

Reagent grade chemicals were generally used without purification. Duplicate runs were made with bulk grade benzene and no noticable initial rate differences were observed.

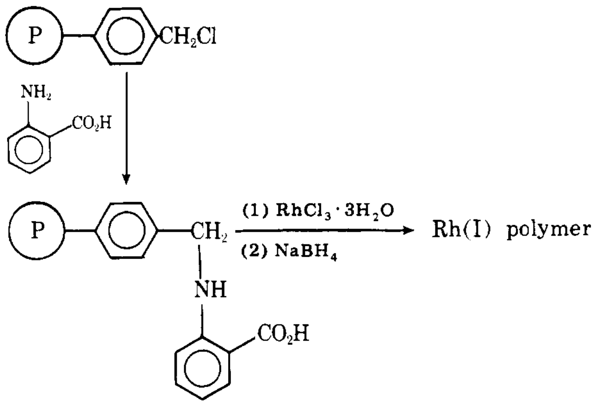
Rh(I)–Anthranilic Acid Polymer. A mixture of 1.00 g of the anthranilic acid anchored beads (0.30 mequiv/g of N) was stirred for 24 h with 0.10 g of rhodium trichloride trihydrate in 5 mL of absolute ethanol. After filtration, the beads were washed with 200 mL of absolute ethanol, suspended in 5 mL of absolute ethanol, and treated with 0.1 g of sodium borohydride. The color immediately changed to a dark brown. After filtration and washing with ethanol, the beads were dried under vacuum for 1 h. Anal. Rh, 0.96% (0.093 mequiv/g); N, 0.40%; ratio anthranilic acid/Rh = 3.0/1.0

Instruments and Hydrogenation Procedure. Low-pressure hydrogenations were carried out in a standard, catalytic apparatus (Parr Instrument Co., Model 3911). In a typical run a 500-mL reactor was charged with unsaturated compound and catalyst and the system was sealed, purged three times with hydrogen, and then pressurized to 60 psig. For high-pressure hydrogenation, the reactants were added to the 300-mL reaction vessel of an Aminco Shaking Assembly (No. 44-13106). The reaction vessel was flushed three times with hdyrogen. For room temperature reactions the pressure was then adjusted to the desired level. For higher temperature reactions, the reactor was partially pressurized and then heated, with shaking, to the desired temperature. The pressure was then adjusted to the desired level. The reactions were not considered to have begun until the system was at the desired temperature and pressure, and all reaction times were measured from this point. Termination of several experiments at early stages revealed that a low percentage of hydrogenation had occurred.

Infrared absorption spectra were recorded on a Perkin-Elmer 457 spectrophotometer. GLC data were acquired on a Varian Aerograph 1700, using 10% Carbowax or 20% SE-30 columns. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. ESCA studies were recorded on a AEI ES200 spectrometer.

Results and Discussion

Functional Group Studies. Anchoring anthranilic acid to chloromethylated polystyrene is accomplished through the reaction sequence shown in eq 1. There are two lines of evidence favoring nitrogen alkylation: (1) benzyl chloride and anthranilic acid yield the *N*-alkylated product and (2) infrared studies of the polymer reveal the carbonyl absorption (1690 cm^{-1}) to be more in accordance with a hydrogen-bonding carboxylic acid than an ester.



The metal is attached to the polymer by suspending the polymer-anchored anthranilic acid in a small volume of ethanol and adding $RhCl_3 \cdot 3H_2O$; the anhydrous metal chloride is unsatisfactory because of its low solubility. After stirring for several hours, the polymer is filtered and washed with copius amounts of ethanol. The metal is then reduced by treatment with sodium borohydride.

Examination of the data in Table I reveals that the rhodium catalyst is active in the hydrogenation of a variety of functional groups. The breadth of activity in this respect is significantly greater than one finds for individual homogeneous catalysts. The turnover rates (cycles/atom h) should be viewed only qualitatively since some experiments were permitted to proceed through several half-lives of the substrate, whereas other experiments were terminated before the elapse of a single half life.

Even with the intense recent interest in polymer-supported catalysts there are no reports of phosphine-anchored polymers capable of hydrogenating arenes. In fact the *only* extant report of a polymer-bound catalyst exhibiting activity with arenes is the initial report of our catalyst.[9] Not only does the catalyst display activity, but it is attractive in comparison with homogeneous and heterogeneous catalysts capable of hydrogenating arenes.[8,11] Consider, for example, a recent report by Muetterties[11a] concerning the homogeneous catalyst η^3-$C_3H_5CO[P(OCH_3)_3]_3$. The turnover rate for benzene at room temperature and 1–3 atm is less than one molecule per hour per metal atom. In Table I it is seen that the turnover rate for the rhodium polymer, under the same conditions, is comparable.

Performing the hydrogenation of benzene under a variety of temperatures reveals that the catalyst is stable up to 160 °C. This is comparable to stabilities displayed by phosphine catalysts. The rate of arene hydrogenation decreases in the order naphthalene > benzene > toluene > *p*-xylene.

Alkenes are rapidly reduced at 40–50 psig and room temperature. In the case of cyclohexene the average rate of hydrogenation over an 8-h period was 130 cycles/atom h. As the degree of substitution and steric hindrance increases the rates of reaction decrease according to 1 hexene $\simeq$ *trans*-3-hexene > cyclohexene ≫ 2, 3-dimethylbutene. The similarity in rates for 1-hexene and *trans*-3-hexene indicates that the catalyst is not especially sensitive to steric effects.[12] Since anthranilic acid is a small ligand, in comparison with triphenylphosphine, it is not surprising that lesser steric sensitivity is demonstrated than is seen in the phosphine-anchored polymers. Deactived olefins (entries 7–9) react slowly.

The hydrogenation of cyclohexene is largely independent of solvent,[13] as the data in Table II demonstrate. Two effects

Table I. Hydrogenation with Rh(I) Polymer

entry	registry no.	substance	mmol of substance	mmol of cat.[a]	time, h	pressure, psig	temp, °C	products yield (%)	products registry no.	cycles/atom h
1	110-83-8	cyclohexene	200	0.075	8.00	30	rt	cyclohexene (40)		130
2	592-41-6	1-hexene	16	.007	.50	30	rt	hexane (47)	110-54-3	2100
3	13269-52-8	*trans*-3-hexene	16	.007	.66	30	rt	hexane (69)		2400
4	563-79-1	2,3-dimethyl-2-butene	16	.007	3.40	30	rt	NR		
5	1700-10-3	1,3-cyclooctadiene						cyclooctane (1)	292-64-8	
			80	0.030	3.00	50	rt	cyclooctene (15)	931-88-4	150
6	111-78-4	1,5-cyclooctadiene						cyclooctane (1)		
			80	0.030	3.00	50	rt	cyclooctene (6)		70
								1,3-cyclooctadiene (6)		
7	104-54-1	cinnamyl alcohol	30	0.015	18.00	50	rt	3-phenyl-1-propanol (20)	122-97-4	20
8	140-10-3	*trans*-cinnamic acid	30	0.015	24.00	50	rt	3-phenylpropanoic acid (10)	501-52-0	8
9	930-68-7	2-cyclohexen-1-one	90	1.000	18.00	60	rt	cyclohexanone (100)	108-94-1	5
10		corn oil (9.2g)		0.20	20.00	50	rt	no detectable hydrogenation		
11		corn oil (9.2g)		0.030	1.00	500	70	60% hydrogenated		
12	71-43-2	benzene	230	3.0000	18.00	50	rt	cyclohexane (99)	110-82-7	4.2
13		benzene	230	0.35	18.00	1000	rt	cyclohexane (12)		4
14		benzene	230	0.35	5.00	1000	100	cyclohexane (25)		30
15		benzene	230	0.35	3.00	1000	180	cyclohexane (10)		20
16		benzene	115	0.044[b]	6.00	600	70	cyclohexane (9)		40
17	108-88-3	toluene	90	0.20	18.00	50	rt	methylcyclohexane (15)	108-87-2	3
18	106-42-3	*p*-xylene	160	0.20	14.00	1000	100	10% hydrogenation		5
19	93-89-0	ethyl benzoate	90	0.20	20.00	1000	100	trace hydrogenation		
20	91-20-3	naphthalene	70	0.20	3.00	1000	70	1,2,3,4-tetrahydronaphthalene[c]		120
		benzene	110					(100), cyclohexane(80)		150
21	98-95-3	nitrobenzene	100	0.20	2.00	800	70	aniline (100)	62-53-3	250
22		nitrobenzene	100	0.20	4.00	60	rm	no detectable hydrogenation		
23	100-47-0	benzonitrile	100	0.20	17.00	1000	100	$\mathrm{PhCH_2NHC(NH)Ph}$ (40)	15421-92-8	
								$\mathrm{PhCH_2N{=}CPh}$ (20)	780-25-6	
24	111-71-7	heptanal	75	0.20	17.00	1000	100	heptanol (25)	111-70-6	
								aldol aldehyde (60)	68332-36-5	
25	67-64-1	acetone (dry)	130	0.025	4.00	800	100	isopropyl alcohol (1)	67-63-0	13
26		acetone (1% H_2O)	130	0.025	4.00	800	100	isopropyl alcohol (2)		26

[a] Based on Rh. [b] Beads stored under air 1.5 years. [c] Registry no. 119-64-2.

should be considered in interpreting this data: bead swelling and the role of solvation during the course of hydrogenation. For catalysts bound to 1 and 2% cross-linked polystyrene, bead swelling is highly visible and important in the catalytic process because hydrogenation is considered to occur within the beads.[1] XAD-4 beads, on the other hand, are highly cross-linked (>50%) and do not visibly swell in any of the solvents listed; thus, swelling is not viewed as a major factor in catalyst activity. The small solvent effect is more likely related to solvation.

Since anthranilic acid was anchored to the beads in non-swelling solvents, the metal is more likely to be concentrated at or near the surfaces of the macroreticular bead structure. (The low metal analysis of the catalyst indicates that only 3% of the chloromethylated sites have been converted ultimately to metal complexes.) One consequence of surface sites is that the catalyst should not readily differentiate between unsaturated molecules of disparate sizes. The observation that corn oil is readily hydrogenated provides confirmation for the possibility of hydrogenating large molecules.

The rate of hydrogenation of 1,3-cyclooctadiene is 150 cycles/atom h; that of 1,5-cyclooctadiene is 70 cycles/atom h. Thus, conjugated dienes are reduced more rapidly than isolated ones; this trend is consistent with soluble rhodium catalysts. Isomerization is quite significant in the case of 1,5-COD because termination of the reaction at an early stage revealed equal concentrations of the 1,3-COD and cyclooctene. Direct hydrogenation of the 1,5-diene must be occurring, at least to some extent, because the rate of hydrogenation of the low concentration of 1,3-diene which would be present is not sufficient to account for all of the alkene.

This catalyst demonstrates selectivity. Hydrogenation of 2-cyclohexen-1-one, entry 9, produces the saturated ketone as the sole product.

Homogeneous catalysts, in general, have not proven to be very effective for the hydrogenation of nitro compounds.[14] The most thoroughly investigated catalyst[14a] is derived from $RuCl_2(PPh_3)_3$; normally hydrogenation conditions involve 50–100 atm and 90–130 °C. *Our catalyst readily converts nitrobenzene to aniline (entries 21 and 22).*[15] The fact that aniline does not destroy the catalyst is a tribute to the tenacity of the metal–polymer bonding. The filtered and washed catalyst retains its activity, so the metal is not eluting from the support and serving as a homogeneous catalyst.

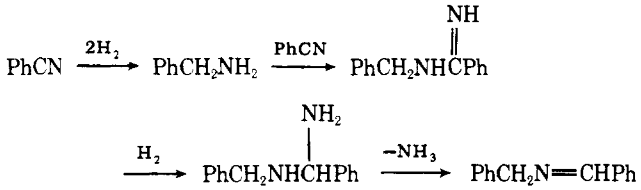
Hydrogenation of nitriles, using homogeneous catalysts, has been rather unsuccessful.[16] Muetterties,[17] using the nickel cluster $Ni_4[CNC(CH_3)_3]_7$, has recently reported the turnover rate for the hydrogenation of an isocyanide to be ~0.1/h at 90 °C and 1–3 atm and then indicated that the rate of hydrogenation of acetonitrile was "very low". The rhodium–polymer, however, does hydrogenate benzonitrile (entry 23) and at a rate of several molecules/hour. *This experiment represents*

Table II. Relative Rate of Hydrogenation as a Function of Solvent[a]

solvent	relative rate
acetonitrile	1.8
dimethylformamide	1.5
ethyl ether	1.0
cyclohexane	1.0

[a] 20% cyclohexene solutions hydrogenated at room temperature and 50 psig.

the first demonstration of hydrogenation of a nitrile using a polymer-bound catalyst. Benzylamine is not the product and the overall transformation follows that of other heterogeneous catalysts operating under "nontrapping" conditions.[18] The products may be envisioned to arise via the sequence shown in eq 2.



$$PhCN \xrightarrow{2H_2} PhCH_2NH_2 \xrightarrow{PhCN} PhCH_2NH\overset{NH}{\overset{\|}{C}}Ph \xrightarrow{H_2} PhCH_2NH\overset{NH_2}{\overset{|}{C}}HPh \xrightarrow{-NH_3} PhCH_2N{=}CHPh$$

In general, homogeneous catalysts which hydrogenate olefins either reduce carbonyl groups sluggishly or not at all.[12] One exception to this is $[H_2Rh(PPh_3)_2(Me_2CO)]PF_6$, which reduces both alkenes and ketones rapidly.[19] The conditions for high activity with each functional group differ however: alkenes are hydrogenated most rapidly in an anhydrous medium and ketones in solvents containing 1% water. It is evident (entries 26 and 27) that the rhodium catalyst slowly reduces ketones and that the rate of acetone hydrogenation doubles when 1% water is present. The reduction of the aldehyde is somewhat faster than the rate for ketones. (The main product of the aldehyde reaction derives from aldol condensation, a reaction known to be catalyzed by supported rhodium amines.[20]) Unlike $RhCl(PPh_3)_3$ the polymeric catalyst does not decarbonylate the aldehyde.[21]

Air Stability. This hybrid-phase catalyst is highly air stable. Beads stored under air for 1.5 years were nearly as active as the freshly prepared ones (entry 16). No special precautions were taken in these experiments to exclude either oxygen or nitrogen.[22] Generally reagent grade chemicals were used without purification. Dry, distilled benzene was hydrogenated, within the limits of detection, at the same initial rate as unpurified, bulk benzene.

Longevity. To examine the lifetime of the catalyst and determine if it is deactivated as rapidly as the phosphine catalysts apparently are, we undertook an examination of activity over the course of several runs.[23] Starting with 1.0 g of beads and 10 mL of benzene, the mixture was hydrogenated at 90 °C and 400 psig for 15 h and then cooled and filtered. The catalyst was washed with 20 mL of acetone and air dried for a few minutes. The process was repeated indentically twice. The activity of the catalyst during the third run was 77% of its original value. A total of approximately 300 benzene-to-cyclohexane cycles were completed, on the average, by each rhodium atom during this study.

The active lifetime of a catalyst is a function of the substrate being hydrogenated. Using unpurified (*p*-methoxyphenol stabilizer) cyclohexene, it was observed that after 1000 cycles the activity is 12% of its original level. If dry, distilled cyclohexene is used, the same level of deactivation was not reached until after 3000 cycles/atom. On the basis of these two sets of experiments this catalyst has a lifetime somewhat less than that of some other polymer-bound catalysts.

Four mechanisms could most reasonably contribute to this loss of activity. One, poisoning does occur, as just shown in the cyclohexene experiment. Two, rhodium could elute from the catalyst. This does not appear to be a particularly important factor, at least under the conditions presently considered, because the rhodium levels in the pre- and postmarathon benzene hydrogenations revealed very similar metal contents (0.96 vs. 0.89% Rh, respectively). Observation that the metal does not elute from the support has utmost importance in the quest for a practical catalyst. Three, sloughing[24] of polymer is well known for polystyrene. Since the metal appears to be concentrated at or near the surface of the bead, a low degree of sloughing could alter catalyst activity substantially. Four, rearrangement of the ligands may occur. There is direct evidence for this, especially in connection with an analogous palladium catalyst.[25] When it is considered that for these highly stable beads the rate of catalyst deactivation exceeds the rate of metal loss, it appears that this fourth mechanism predominates.

Bead Integrity. Additional comments should be made concerning the preparation of the rhodium catalyst. All experiments performed thus far have shown that bead size is highly important in the functioning of the catalyst. Chloromethylated Amberlite XAD-4 beads are 20–50 mesh spheres and if they are fragmented during derivatization with anthranilic acid, activity is reduced severely. Anthranilic acid was anchored to the beads by slurrying chloromethylated beads with anthranilic acid in a solvent. Several solvents (ethyl ether, acetone, dimethylformamide) appear to give similar results in terms of ultimate catalyst activity and susceptibility to bead fragmentation. Bead fragmentation can be avoided by short reaction times with anthranilic acid. Fragmented beads do not become very dark upon treatment with $RhCl_3 \cdot 3H_2O$ followed by reduction with $NaBH_4$.

Metal Oxidation State. The oxidation state of the rhodium appears to be +1.[8] Direct evidence for this comes from ESCA studies; narrow scan resolution of the Rh(3d) lines revealed a broad spectrum peaking at 308 eV and a shoulder at 312 eV. These binding energies are in agreement with those observed for the $3d_{5/2}$ and $3d_{3/2}$ lines observed in several other Rh(I) complexes.[26] There is further, though less conclusive, evidence.

When impregnating the beads with Rh(III), if one does not wash the beads thoroughly but intentionally leaves a small amount of rhodium in the ethanolic solution, addition of sodium borohydride causes the suspension to immediately turn black. This product has a different appearance than the one formed when the beads are thoroughly washed with ethanol—small particles are visible and the beads are darker. Upon hydrogenation with this material, extraordinary activity is evident for a few minutes, then activity diminishes. This change was particularly vivid when the powdered support was used. The black powder caused a very rapid hydrogenation of benzene for about 20 min, then virtually all activity ceased. Termination of the experiment, followed by filtration, revealed that the rhodium had separated from the white support, but the properly prepared beads to not lose their color even after many hours of catalytic activity and, in fact, they become darker.

Upon treatment of the Rh(III)-impregnated beads with sodium borohydride the beads darken instantly. In our first report of this catalyst we described the color as black, but a better description would be a very dark brown. In any event, when the catalyst is employed in hydrogenation the color irreversibly darkens. This color change is substrate dependent—it is faster for benzene, for example, than for mono- or dienes. It also occurs faster as the temperature is raised. The progress of darkening, however, does not monitor bead activity because "dead" beads from cyclohexene hydrogenation re-

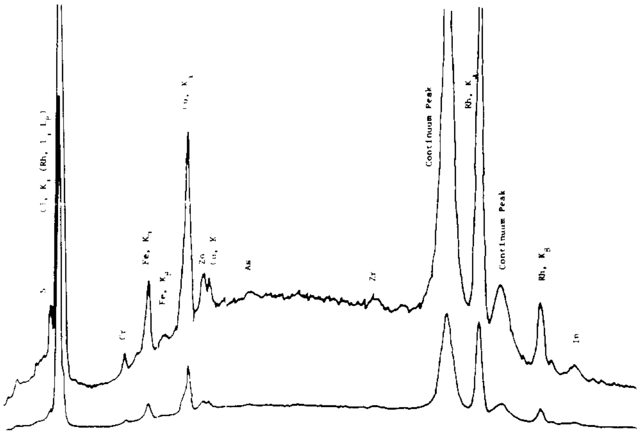


Figure 1. X-ray fluorescence spectrum of the Rh(I)–anthranilic acid polymer: 40.0 KeV, 0.05 Mamp under vacuum with a total count of 1000 s. No filter was used.

mained dark brown. This is not the first report of the darkening phenomenon—Bailar observed this change in a palladium-phosphine polymer.[13b]

Rhodium is not the only metal present in the beads. Figure 1 displays an X-ray fluorescence spectrum and reveals the presence of copper and other metals; the role, if any, of these is unknown presently.

In terms of a general concept of bonding, a model is being considered in which anthranilic acid serves as a bidentate (N and CO_2) ligand. It is possible that phenyl also serves as a ligand since in the homogeneous Rh(I)-*N*-phenylanthranilic acid complex phenyl is proposed to serve as a ligand.[8] In this model, the "tight ligand" is the nitrogen and the labile group(s) is (are) the carboxylate or/and phenyl. The advantage of an amine, compared to phosphine, is that oxidation is less likely.

Conclusion

Based on studies to this time it does appear that the catalyst described herein combines attractive features of both heterogeneous and homogeneous catalysts. No single homogeneous catalyst hydrogenates the variety of functional groups that this catalyst does. Hydrogenation rates[27] and catalyst stability compare favorably with any polymer-bound hydrogenation catalyst previously reported.

Acknowledgment. The author would like to thank Dr. Paul Cook of WKU for generous support in procuring patents and Dr. T. V. Rebagay of the Institute for Mining and Minerals Research for ESCA spectra.

Note Added in Proof. The hydrogenation of benzene using a phosphine anchored polymer was reported while this article was in press: F. Pinna, C. Candilera, G. Strukul, M. Bonivento, and M. Graziani, *J. Organomet. Chem.* **159,** 91 (1978).

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