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06-6; *trans*-IrCl(CO)(PPh₃)₂, 15318-31-7; *trans*-RhCl(CO)(PEt₃)₂, 15631-52-4; *trans*-RhCl(CO)(PPh₃)₂, 15318-33-9; Fe, 7439-89-6; Ir, 7439-88-5; Rh, 7440-16-6.

Supplementary Material Available: Listings of the posi-

tional and thermal parameters for the non-hydrogen atoms (Table A) and phenyl carbon atoms (Table B), calculated hydrogen atom parameters (Table C), and the structure factors (Table D) for 1 (29 pages). Ordering information is given on any current masthead page.

Dibenzo[*a,e*]cyclooctatetraene in a Proposed Test for Heterogeneity in Catalysts Formed from Soluble Platinum Group Metal Complexes

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The problem of distinguishing homogeneous from heterogeneous catalysis is discussed. A method based on dibenzo[*a,e*]cyclooctatetraene, a potent selective poison for homogeneous catalysts, is compared with filtration, nitrobenzene reduction, and Hg inhibition methods. RhCl(PPh₃)₃ (both free and polymer supported), RuCl₂(PPh₃)₃, [Rh(nbd)(PPh₃)₂]PF₆, and [Ir(cod)(PMePh₂)₂]PF₆/CH₂Cl₂ (cod = 1,5-cyclooctadiene) all show properties consistent with homogeneous catalysis, and Pd/C, colloidal Pd, and a system usually considered homogeneous, RhCl₃(py)₃/NaBH₄/dmf (py = pyridine), all show properties consistent with heterogeneous catalysis. The advantages and limitations of the method are discussed.

Over the past 20 years there has been considerable interest in catalysis of organic reactions¹ by metal complexes. Homogeneous catalysis can have important advantages over the well-known heterogeneous catalysts² such as Pd/C. An important question arises in these studies: how does one know that a catalyst really is homogeneous? Even if it has been prepared from a soluble metal complex, the metal itself may have been precipitated under the reaction conditions, to give either metal powder or a metal film or, especially in polar solvents, colloidal metal.³ Visual inspection of the catalytic mixture can be helpful. If sufficient precipitation occurs, a metal film or powder may be noticed, but colloidal preparations are often bright and clear. It might be thought that filtration or centrifugation would be helpful. Unfortunately colloidal preparations pass through even micropore filters and, in general, survive centrifugation.

If colloids were unlikely to form under the conditions of "homogeneous" catalysis, the risk of error would be small. However, when one looks at a typical synthesis of colloidal platinum metals, one can see how close the conditions⁴ (metal compound, ligand, reducing agent, polar solvent) often are to those typical in homogeneous catalysis.

Even if a colloid is present, the question still arises whether the catalytic activity observed is due to the homogeneous or heterogeneous component of the system. The inverse problem may also arise. A heterogeneous catalyst may dissolve under the reaction conditions and only the homogeneous component be active.

The question of homogeneity vs. heterogeneity is especially important when a reaction previously only known

on a metal surface is effected by a supposed homogeneous system. We have discussed one such case in detail: alkane activation.⁴

The hydrogenation system [Ir(cod)(Pc-Hx₃)(py)]PF₆/CH₂Cl₂ (cod = 1,5-cyclooctadiene; c-Hx = cyclohexyl; py = pyridine) has certain properties in which it resembles heterogeneous catalysts: it reduces even hindered substrates and it is stable to air; therefore, the possibility that colloidal iridium might be the active species had to be considered. More recent results showing that the catalyst has very high regio- and stereoselectivity support its homogeneity.⁵ The system also passed the light-scattering test which we are developing and which will be reported elsewhere.⁶ Finally, the iridium system does not reduce PhNO₂. As we have discussed previously, nitrobenzene hydrogenation is very rapid on platinum group metal surfaces and we have proposed the absence of PhNO₂ reduction as a criterion for the absence of platinum group metal surfaces in catalytic systems. There are, however, many systems that are claimed to be homogeneous and yet reduce PhNO₂; probably many of these are authentically homogeneous, but we felt that among them might be some heterogeneous systems and that the group deserved further study.

In this paper we describe a proposed test for homogeneity relying on dibenzo[*a,e*]cyclooctatetraene (dct), a potent selective poison for homogeneous catalysts. It might better be described as a suicide inhibitor, for as an olefin, it resembles a common class of substrate in catalysis, but although it binds to the catalyst, it resists further transformation. As we found in earlier work⁷ on dct it forms very strongly bound complexes with a variety of platinum group transition metals. In contrast to most

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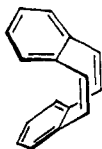


Figure 1. The rigid tub conformation of dibenzo[*a,e*]cyclooctatetrene (dct).

olefins, it can not be hydrogenated, presumably because of the rigidity of its tub conformation (Figure 1). $[\text{IrH}_2(\text{dct})(\text{PPh}_3)_2]\text{BF}_4$ (1), for example, is stable at least to 180 °C even in air.⁷

It occurred to us that perhaps dct would poison authentic homogeneous catalysts by binding to the metal to form catalytically inert complexes like 1. On the other hand, it might affect heterogeneous catalyst to a far lesser extent because binding to a surface would be expected to be weak in view of the tub conformation. In this way dct might provide a criterion of homogeneity for a catalyst. The results reported here show that these ideas may well be valid. Any test for homogeneity can only be accepted after extensive study. Each may prove to be applicable only to a limited group of catalysts. For example, the dct test might fail in a system, such as a metal porphyrin complex that cannot bind a diene, or with first-row metals where dct binding might be weaker. What is needed is an array of tests so that each can have its reliability and range of applicability determined by cross-checking. It is the purpose of this paper to provide preliminary evidence for the utility of the dct test.

Other criteria have been suggested. Maitlis⁸ uses a filtration method to see if catalytic activity resides in the filterable fraction of a catalytic system. This is not expected to be applicable to cases where a colloidal suspension has been formed, since colloids pass through even micropore filters. The test would not be expected to be applicable to systems in which only freshly precipitating metal or the colloidal precursor to this precipitating metal is active. It is also less convenient to use in cases where air sensitivity or extreme conditions of temperature or pressure make filtration difficult. Collman⁹ has used a polystyrene-based substrate into which only soluble species can enter. This would not be expected to be applicable to cases such as polystyrene-anchored $\text{RhCl}(\text{PPh}_3)_3$, in which one might want to know whether rhodium crystallites have been formed under a particular set of catalytic conditions. Problems might also arise in the case of a highly ionic catalyst, e.g., ethanolic metal salts, in which case the catalyst might not enter the pores of the substrate because of an incompatibility between the polar medium and the nonpolar substrate.

Whitesides¹⁰ has used the heterogeneous catalyst poison,¹¹ liquid Hg; this method may prove to be complementary to the present one. Others¹² have looked for changes in product distributions or catalytic rates as a catalyst goes over from homogeneous to heterogeneous operation. This can be valuable but does not apply to cases in which no such changeover is ever seen. Is the catalysis always homogeneous or always heterogeneous?

We have also used dynamic light scattering.⁶ This detects and characterizes colloidal particles but does not give

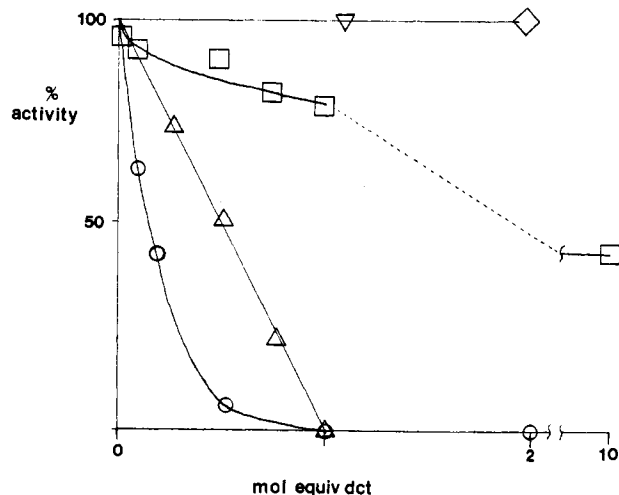


Figure 2. The effect of dct on the catalytic activities of various systems in 1-hexene hydrogenation. The data are taken from Table I and show the effect of varying amounts of dct on the following systems: $\text{RhCl}_3(\text{py})_3/\text{NaBH}_4/\text{dmf}$, \diamond ; Pd colloid, ∇ ; Pd/C/hexane, \square ; $[\text{Ir}(\text{cod})(\text{PMePh}_2)_2]\text{PF}_6$, \triangle ; $\text{RhCl}(\text{PPh}_3)_3$, \circ .

information as to whether any particulate is catalytically active or not.

In this paper we describe a test based on dct that appears to be applicable to all the cases mentioned above, and we compare it with some other criteria that have been suggested.

Results and Discussion

Dibenzo[*a,e*]cyclooctatetraene (dct) is a rigid tub-shaped molecule (Figure 1) that seems to bind strongly to metal complexes but not to metal surfaces. We find that a variety of catalytic reactions mediated by soluble metal complexes are completely inhibited by dct at a level of 1 dct/metal atom (Table I). The inhibition is often rapid (e.g., $[\text{Ir}(\text{cod})(\text{PMePh}_2)_2]\text{PF}_6/\text{CH}_2\text{Cl}_2$, 30 s; $\text{RhCl}(\text{PPh}_3)_3/\text{C}_6\text{H}_6$, 10 min; $\text{RuCl}(\text{PPh}_3)_3/\text{C}_6\text{H}_6\text{-EtOH}$, 30 min) but in some cases, especially where a coordinating solvent, such as MeOH or thf is used, the inhibition appears slowly. Of those cases we have examined, the extreme case is $[\text{Rh}(\text{nbd})(\text{PPh}_3)_2]\text{PF}_6/\text{thf}$ ¹³ (nbd = norbornadiene) in which the inhibition is only complete after 2 h of stirring in the absence of H_2 .

Our experimental protocol takes account of this (see Experimental Section). In each case we first generate the catalytic species in the way described for each system, then add dct and stir for 2 h in the absence of H_2 , and measure the catalytic activity of the mixture. Treatment of the solutions with dct in the presence of H_2 was less effective; we do not understand why. Although its rigidity makes it kinetically slow to bind in some cases, it is very tightly held, once bound. In no case was dct hydrogenated; this is very difficult to do even under extreme conditions with homogeneous or heterogeneous catalysts.

Figure 2 shows the effect of increasing amounts of dct on the inhibition of $[\text{Ir}(\text{cod})\text{L}_2]\text{PF}_6$ ($\text{L} = \text{PMePh}_2$). The linearity and the completeness of the inhibition at a 1:1 ratio of dct to Ir strikingly demonstrate the homogeneity of this catalyst.

The effect of $\text{RhCl}(\text{PPh}_3)_3$ ¹⁴ is different. Complete inhibition again occurs at a 1:1 ratio, but the curve of Figure

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Table I. Experimental Results with dct and Hg Inhibitors

catalyst ^a	inhibitor ^b	temp, °C	ratio ^c	rate ^d		ref
				mL min ⁻¹	% ^e	
RhCl(PPh ₃) ₃	dct	25	0.0	4.0	100	14
			0.1	2.5	63	
			0.2	1.7	43	
			0.5	0.25	20	
			1.0	0.0	6	
			2.0	0.0	0	
[Ir(cod)(PMePh ₂) ₂]PF ₆	Hg dct	0	<i>f</i>	4.0	100	19
			0.0	11.0	100	
			0.25	8.5	77	
			0.50	5.8	53	
			0.75	2.4	22	
			1.0	0.0	0	
Pd/C/hexane	Hg dct	0	<i>f</i>	11.0	100	
			0.0	10.9	100	
			0.01	10.3	95	
			0.1	10.1	93	
			0.5	9.8	90	
			0.75	8.9	82	
Pd/C/dmf	Hg dct	30	1.0	8.5	78	
			10.0	4.6	42	
			<i>f</i>	0.0	0	
			0.0	3.5	100	
			1.0	3.0	86	
			1.0	2.0	80	
Pd/C/EtOH-H ₂ O	dct	30	0.0	2.5	100	
			1.0	2.0	80	
Pd/colloid	dct	25	0.0	2.8	100	21
			2.0	2.8	100	
Rh/colloid	Hg dct	25	<i>f</i>	0.0	0	
			0.0	0.5	100	
[Rh(nbd)(PPh ₃) ₂]PF ₆	Hg dct	25	<i>f</i>	0.0	0	13
			0.0	3.3	100	
RuCl ₂ (PPh ₃) ₃	Hg dct	25	2.0	0.0	0	15
			0.0	3.0	100	
RuCl ₃ (py) ₃ /NaBH ₄	Hg dct	25	<i>f</i>	3.3	85	16
			0.0	1.0	100	
polymer-bound RhCl(PPh ₃) ₃	Hg dct	25	2.0	1.0	100 ^g	
			<i>f</i>	0.0	0	
	dct		0.0	14.0 ^h	100	
			2.0	0.0	0	
	Hg		<i>f</i>	13.0 ^h	93	

^a The catalyst precursors were treated as described in the experimental section to give the active systems. ^b More properly, potential inhibitor. ^c Molar ratio of inhibitor to catalyst, calculated as total metal content. ^d Of H₂ uptake. ^e Percentage of uninhibited rate. ^f Excess Hg: see text. ^g Similar results after 48 h of stirring with dct. ^h mL h⁻¹.

1 shows that the activity at intermediate ratios is lower than in the iridium case. This is because the deactivation product in the iridium case is *cis,trans*-[IrH₂(dct)L₂]PF₆ and in the rhodium case is [RhCl(dct)L] + 2L.⁷ Only in the Rh case is excess L displaced from the catalyst by dct. This partially inhibits the activity of the remaining rhodium not already poisoned by dct.

The case of polystyrene-bound RhCl(PPh₃)₃ is an interesting one. The catalyst is clearly heterogeneous in the sense that the solid phase appears to be the active catalyst. It is believed to be closely allied mechanistically with the homogeneous RhCl(PPh₃)₃ and should be poisoned by dct. This expectation was verified experimentally. This case not only provides an experimental distinction between heterogeneous catalysis and heterogenized homogeneous catalysis but also demonstrates the versatility of the dct test.

The catalyst formed from RuCl₂(PPh₃)₃¹⁵ is also inhibited at 1 mol equiv of dct and seems to be homogeneous, as is also suggested by its high selectivity for 1-alkenes.

Liquid mercury had little or no effect on any of the homogeneous catalysts that we studied (see Experimental Section and Table I). This is consistent with a homogeneous origin for the catalytic activity in each case. The two tests, dct and Hg, seem useful to complement each other, helping to confirm the validity of the results obtained.

Heterogeneous catalysts behave differently in their sensitivity to poisoning. They are not completely poisoned even by a large excess of dct, and at the level of 1 mol equiv of dct in no case did the activity fall below 78% of the rate observed without dct. Colloidal preparations seem to be much less sensitive than supported catalysts, no change in rate being observed for colloidal Rh and Pd at 2.0 mol equiv of dct. This is not a solvent effect, because dct has comparable poisoning power for Pd/C in hexane, dmf, and EtOH-H₂O. We are now comparing the catalytic properties of colloidal metals with those of classical supported heterogeneous catalysts to see if other and perhaps useful differences exist.

The fact that dct fails to inhibit true heterogeneous catalysts can probably be ascribed to its tub shape. To bind well it would presumably have to adopt the highly

unfavorable planar geometry.⁷ Ligands such as PPh₃ or Ph₂P(CH₂)₂PPh₂ would not be expected to be selective poisons because there is nothing to prevent them binding to a metal surface just as easily as to a metal complex.

Liquid mercury poisoned each of the heterogeneous catalysts (see Table I), consistent with a heterogeneous origin for the catalytic activity observed.

We next examined the case of which a proposed homogeneous catalyst that reduces PhNO₂: RhCl₃(py)₃/NaBH₄/dmf¹⁶ (py = pyridine; dmf = dimethylformamide). In this system 1 equiv of NaBH₄ is added to a dmf solution of RhCl₃(py)₃, and the mixture is subsequently treated with H₂ to generate the active catalyst. A darkening of the solution takes place, and the active mixture is formed. Not only does it reduce PhNO₂ but it also hydrogenolyzes alkyl halides, another reaction normally seen for heterogeneous but not homogeneous catalysts. There is a very slight turbidity to the solution, but the slight amount of precipitate present is not catalytically active. All the activity resides in the filtrate.

Addition of dct to the solution, following the usual procedure (see Experimental Section), led to a complete retention of activity consistent with heterogeneous catalysis by a colloid. This result prompted us to examine the system further. Using liquid mercury added to the solution, a complete inhibition of catalysis was observed. Once again this suggests heterogeneity.

Dynamic light scattering on the diluted catalyst (see Experimental Section) shows the presence of particles (ca. 2000-Å radius) in the solution, once again suggesting a heterogeneous but nonfilterable colloidal component. We cannot exclude the possibility that the observed colloid was formed on dilution, however.

Maitlis method, filtration of the solution through Celite, leads to an increase in catalytic activity of the filtrate. Possibly, free pyridine or BH₄⁻ are partially removed by this treatment. As would be expected if a colloid were present, catalytic activity is not removed by the filtration. The filtered precipitate has no catalytic activity.

We conclude that in the RhCl₃(py)₃/NaBH₄/dmf system, at least in our hands, the catalytic activity is probably due to the presence of a nonfilterable heterogeneous component, most likely a rhodium colloid. This colloid seems to form on treatment of the RhCl₃(py)₃/NaBH₄/dmf system with H₂; the role of the dmf may be to stabilize it. Both catalytic phenomena and the formation of colloids can be very sensitive to minor impurities in the system or the exact conditions of operation. It remains possible, therefore, that minor differences of this type have prevented us from exactly reproducing the reported system.¹⁶ The properties we observed are, however, very close to those found previously.¹⁶

A possible objection to these suggestions arises from studies^{16b} showing up to ca. 60% asymmetric induction in the reduction of methyl 3-phenylbut-2-enoate by RhCl₃(py)₃/NaBH₄/(+)-N-(1-phenylethyl)formamide. This degree of induction is often considered as being more consistent with homogeneous rather than heterogeneous catalysis. Izumi's¹⁷ elegant work on the modification of heterogeneous catalysts with chiral organic compounds such as tartaric acid has shown that substantial (60–90%) optical yields can be obtained in this way. Colloidal metals would be expected to be at least as sensitive to modifying reagents as are supported heterogeneous catalysts. This

objection therefore loses its force.

In contrast, we find that RhCl(PPh₃)₃ and [Ir(cod)(PMePh₂)₂]BF₄, RuCl₂(PPh₃)₃, [Rh(nbd)(PPh₃)₂]PF₆, and polystyrene-supported RhCl(PPh₃)₃ are entirely homogeneous by the Hg and by the dct tests.

Conclusion

It seems that dct and Hg may be useful complementary selective poisons for catalytic systems involving the platinum metals. They probe the system under the conditions of the reaction, without further manipulation. Dct may fail for non-platinum group metals; or for systems of mechanistic types we have not yet examined. The Hg criterion may fail, for example, when an untreated heterogeneous catalyst dissolves under the conditions of the reaction to give a soluble active species but fails to do so in the presence of Hg. We have also observed some color changes on stirring homogeneous catalysts with mercury. Small changes in catalytic activity were observed over the time scale of the experiments, e.g., for RuCl₂(PPh₃)₃, and some chemical changes may be taking place. Some metal complexes are known to react with metallic mercury to give unusual products.¹⁸

The dct and Hg tests have not yet given contrary indications; should this happen it would suggest that the tests had been extended beyond their ranges of validity and so help establish what these ranges are. If dct inhibits at a 1:1 ratio or if Hg fails to inhibit, homogeneity is strongly indicated. True homogeneous systems might fail the tests, but it is unlikely that true heterogeneous ones would pass them. Agreement between the two tests, however, provides an indication that the results are probably valid.

There is no reason to think that the dct nor Hg tests are limited to hydrogenation catalysts; we hope to extend our studies to other types in the future. We have not yet examined the method in its application to other than platinum group metal catalysts, because the risk of metal deposition is perhaps most high in this group and because metal-olefin binding is expected to be strongest to these metals. Further work is in hand on other possible suicide inhibitors.

Experimental Section

RhCl(PPh₃)₃, RuCl₂(PPh₃)₃,¹⁵ [Rh(nbd)(PPh₃)₂]PF₆,¹³ and [Ir(cod)(PMePh₂)₂]PF₆¹⁹ were obtained by literature methods. A constant pressure hydrogenation apparatus was used for the catalytic runs.²⁰ Dct was synthesized by the method of ref 7 using Li/Hg, or it can be obtained commercially (ICN Pharmaceuticals, K&K Division). Olefins were distilled from potassium, fractionally distilled, and stored under N₂. Benzene was distilled from K/Ph₂CO, CH₂Cl₂ from CaH₂, and EtOH from Mg. Hexanes were treated with concentrated H₂SO₄ and distilled from P₂O₅. Solvents and substrates were obtained from Aldrich Chemical Co. and distilled before use. Polystyrene-anchored RhCl(PPh₃)₃ was obtained from Strem Chemical Co.

Protocol for the dct Experiments. The catalytic system under study was generated from the precursor, H₂, and substrate was described below. H₂ absorption was followed for ca. 5 min. The required quantity of dct was added (see Table I), and the solution was degassed and then stirred under N₂ for 2 h. The activity of the catalyst was determined by adding H₂ and following the H₂ absorption curve. Comparison was made with the rate observed before treatment with dct.

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Protocol for the Hg Experiments. The catalytic system was generated as in the dct case. Mercury (1 mL, 13.5 g) was then added and the mixture stirred for 12 h. At the end of this time the activity of the catalyst was measured by adding the olefin and observing H₂ absorption as above. In the case of the Ir catalyst, which spontaneously deactivates easily,²⁰ we observed the rate directly after adding mercury.

RhCl(PPh₃)₃ Hydrogenations. RhCl(PPh₃)₃ (50 mg, 0.054 mmol) was dissolved in degassed benzene (20 mL) and 1-hexene (1 mL) added. H₂ was introduced to a total pressure of 1 atm and the H₂ absorption followed for 5 min at 25 °C. The required amount of dct was added and the solution degassed. The mixture was stirred for 2 h under N₂ and then degassed. H₂ was reintroduced and the rate of uptake observed.

Pd/C Hydrogenations. Pd/C (10%, 25 mg, 0.024 mmol) was added to a hexane (20 mL) solution of cyclohexene (0.8 mL). The mixture was treated as above, but H₂ uptake measurements were made at 0 °C. Measurements in EtOH-H₂O (1:1) and dmf were carried out in the same way, but at 30 °C.

[Ir(cod)(PMePh₂)₂]PF₆ Hydrogenations. The title complex (50 mg, 0.059 mmol) was dissolved in CH₂Cl₂ (10 mL), containing cyclohexene (0.8 mL, 8 mmol). H₂ uptake was followed at 0 °C as above.

RhCl₃(py)₃/NaBH₄/dmf Hydrogenations. RhCl₃(py)₃ (50 mg, 0.11 mmol) was dissolved in degassed dmf (20 mL). NaBH₄ (4.2 mg, 0.11 mmol) was added. The solution was degassed and stirred under H₂ at 25 °C for 10 min. Addition of the substrate, 1-hexene (1 mL, 8 mmol), led to H₂ uptake that was followed for 5 min at 25 °C. The degassed mixture was then stirred with dct for 2 h, and H₂ uptake measurements were made as above but at 25 °C.

Pd Colloid.²¹ Aqueous solutions of PdCl₂ (1%, 2 mL) and Na₂CO₃ (4%, 1 mL) were added to a polyvinyl alcohol (PVA) solution (1%, 50 mL). The mixture was made up to 100 mL with absolute ethanol. A 20-mL aliquot of the above mixture was degassed and stirred under H₂ for 5 min. To the mixture was added 1-hexene (1 mL, 8 mmol), and H₂ uptake was followed for 5 min at 25 °C. The degassed mixture was stirred with dct as above and H₂ uptake determined at 25 °C after 2 h.

Rh Colloid. An 0.5% Rh colloid, stabilized with PVA, was made as follows:²² to RhCl₃ (50 mg) in 1% PVA (50 mL, aqueous

solution) was added NaOH (1 N, 1 mL), and the mixture was neutralized with acetic acid. The preparation was then heated to 80 °C for 15 min. H₂ was then passed through the cooled mixture for 15 min to give a color change from yellow to black. The preparation was made up to 100 mL with EtOH, and the hydrogenation experiments were carried out as described above for Pd.

[Rh(nbd)(PPh₃)₂]PF₆ Hydrogenations. The title complex (50 mg, 0.058 mmol) in degassed THF (20 mL) was treated with H₂ for 15 min. H₂ uptake with 1-hexene as substrate was measured at 25 °C.

RuCl₂(PPh₃)₃ Hydrogenations. The title complex (50 mg, 0.052 mmol) was studied in a mixture of benzene (10 mL) and ethanol (10 mL). After 10 min of stirring under H₂, uptake was determined by using 1-hexene (1 mL, 8 mmol) as substrate at 25 °C.

Polystyrene-Bound RhCl(PPh₃)₃ Hydrogenation. Polystyrene-bound RhCl(PPh₃)₃ in the form of beads (2.2% Rh, 250 mg, 0.053 mmol) was studied in benzene (10 mL)-ethanol (10 mL) at 25 °C with 1-hexene (1 mL) as substrate.

Light-Scattering Studies. The equipment and methods used have been described.⁴ Light absorption by the RhCl₃(py)₃/NaBH₄/dmf system prevented measurements from being obtained directly, so the catalyst (5 mL) was diluted to 50 mL with water. A Stokes radius of ca. 2000 Å was obtained for the particulate observed.

Results. The results of the experiments are reported in Table I and some typical results shown in Figure 2.

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Registry No. RhCl(PoPh₃)₃, 14694-95-2; [Ir(cod)(PMePh₂)₂]PF₆, 38465-86-0; Pd, 7440-05-3; Rh, 7440-16-6; [Rh(nbd)(PPh₃)₂]PF₆, 32799-32-9; RuCl₂(PPh₃)₃, 15529-49-4; RuCl₃(py)₃, 16997-46-9; dct, 262-89-5; 1-hexene, 592-41-6; cyclohexene, 110-83-8.

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Methylchloropolysilanes and Derivatives Prepared from the Redistribution of Methylchlorodisilanes

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A new class of polyfunctional polysilanes has been prepared from the tetrabutylphosphonium chloride catalyzed Si-Si/Si-Cl bond redistribution of methylchlorodisilanes. These materials were shown to have a polycyclic structure with approximately seven rings per molecule when the reaction is carried to 250 °C. Derivatives of the parent polymethylchlorosilane polymer were prepared by modifying the residual silicon-chloride bonds. These reactions include alkylation, arylation, amination, reduction, and alcoholysis.

Introduction

Recently, there has been growing interest to develop polysilanes that can be shaped and thermally decomposed to yield ceramic fibers and other complex articles. The majority of the approaches to date utilize alkali-metal reductions to generate the polysilane backbone. For example, Yajima has prepared carbosilanes through thermolysis of polydimethylsilane.¹ West has reported a ce-

ramic-yielding polymer from phenylmethyl- and dimethylpolysilanes.^{2a,b} A series of copolymers were prepared from alkylmethyl- and dimethylsilane polymers by Wesson and Williams.³ Finally, Shin-Etsu Chemical researchers have coupled disilanes to generate ceramic precursors.⁴

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