Me$_2$Py)]$^-$, 2.299 (2);[19] [PtCl$_3$(caffeine)]$^-$, 2.294 (2); [PtCl$_3$-CO]$^-$, 2.289 (3).[20]   Thus the structural trans influence of caffeine is slightly less than that of Me$_2$SO or a chloro ligand, similar to that of other heterocyclic nitrogen donors and slightly greater than that of CO.

The triphenylmethylphosphonium cation is tetrahedral with the phenyl rings arranged as the blades of a propeller, as is usually found for this cation.[21–27] The phosphorus atom does not lie in any of the phenyl planes (Table VII). Smaller deviations of 0.013–0.136 Å have been reported before.[23–25]

Several workers have stated that the P–CH$_3$ bond is expected to be longer than the P–C$_6$H$_5$ bond because of the differing hybridization of the carbon atoms.[22,23,27,28] The P–CH$_3$ bond has been observed to be longer in several structures,[22,23,25] including the compound reported here, where the P–CH$_3$ bond (1.786 (6) Å) is insignificantly longer than the average of the P–C$_6$H$_5$ bonds (1.780 (10) Å). However, in all cases the differences in the P–CH$_3$ and P–C$_6$H$_5$ bond lengths are small enough to be accounted for by experimental error. We have averaged the P–CH$_3$ and P–C$_6$H$_5$ lengths found in all reported structures of the [P(C$_6$H$_5$)$_3$CH$_3$]$^+$ cation for which the standard deviations are less than 0.01 Å.[22–24,28]

The results averaged over six cations are as follows: P–CH$_3$, 1.785 (8) Å; P–C$_6$H$_5$, 1.784 (12) Å. There is, therefore, no detectable difference in the P–CH$_3$ and P–C$_6$H$_5$ distances in the [P(C$_6$H$_5$)$_3$CH$_3$]$^+$ cation. There is a difference in the P–C$_6$H$_5$ distance in structures where the C$_6$H$_5$ portion is refined as a rigid group (1.774 (8) Å, ref 22 and this work) and where the carbon atoms are refined independently (1.795 (4) Å[23,24,28]), but the difference is not significant.

Anticancer Activity

The salt K[PtCl$_3$(caffeine)] was examined for anticancer activity against the P388 lymphocytic leukemia by using a protocol previously described.[29] At a dose of 36 mg/kg in saline solution the compound produced a T/C of 150%, indicating substantial anticancer activity. However tests at the National Cancer Institute against L1210 lymphoid leukemia gave a best T/C of only 118%. These results establish that K[PtCl$_3$(caffeine)] has substantial anticancer activity against at least one type of cancer in mice. While more work is necessary to establish the most effective dose and to determine the scope of its activity, it seems that K[PtCl$_3$(caffeine)] represents a new class of antitumor compounds.

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Investigation of Unique Metal Complexes Produced with Polystyrene–2,2′-Bipyridine and Several Hydrogenation Catalysts Derived from This Copolymer

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The cleavage reactions between polystyrene-bound pyridine and 2,2′-bipyridine ligands, [P]-py and [P]-bpy, and the dimers [Rh(X)(CO)Cl]$_2$ (X = CO, (C$_6$H$_5$)$_3$P, or (tol)$_3$P) were studied. While the [P]-py cleavages produced products analogous to those found homogeneously, the reactions using [P]-bpy resulted in the formation of several metal complexes not found in solution. This is at least in part the result of the accessibility of the initially formed [P]-bpyRh complexes to subsequent reactions which cannot occur in the homogeneous case due to precipitation of the rhodium complex initially formed. These supported rhodium systems, as well as [P]-bpyPdCl$_2$ and [P]-bpyPtCl$_2$, were investigated as hydrogenation catalysts. In the case of the former two systems it was found that metal aggregates were formed. This was surprising in light of the general stability of bipyridine complexes. The [P]-bpyPtCl$_2$ system is an active catalyst for the hydrogenation of a number of substrates. Metal formation did not occur in this case.

Introduction

Much emphasis has been placed on demonstrating the usefulness of supporting metal complexes on functionalized polymers with regard to producing systems with unique chemical behavior. While this "heterogenization" is in itself advantageous in the case of catalytic systems, it has long been recognized that the support may be made to more directly influence chemical reactivity. This influence may be divided into active and passive categories. The substrate size selectivity exhibited by many polymer-supported catalysts[1] is an example

of an active polymer role. Site isolation of a complex, to inhibit metal dimer or cluster formation, is an example of a passive role by a support. Passive polymer influence is not limited to cases of effective site isolation. The precipitation of a solid product from a homogeneous solution provides a barrier to a more complete reaction (whether it be a thermodynamic or kinetic barrier). The dispersal of the product over a func-

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tionalized polymer will prevent crystalization, leaving it vulnerable to further reactivity. If subsequent reactions do occur, any direct analogy drawn between solution and polymer-bound products is of limited usefulness. However, in this case novel complexes may be formed which are unique to the heterogenized phase.

We report here our studies of the bridge-splitting reactions between polystyrene-bound pyridine, [P]-py, and polystyrene-bound 2,2'-bipyridine,[2] [P]-bpy, with the dimers [Rh(X)(CO)Cl]$_2$ (where X denotes CO, (C$_6$H$_5$)$_3$P, or (tol)$_3$P). The reactions with [P]-bpy provide a good example of the passive metal dispersal function the polymer may provide. In addition, the [P]-bpy polymer seems to play an active role in influencing the reaction products. The attachment of the 2,2'-bipyridine group to the polystyrene support is expected to lead to its binding via the C(6)[3] (adjacent to one nitrogen donor atom). This may result in a steric weakening of one of the [P]-bpy nitrogen bonds to rhodium and lead to the potential for monodentate coordination. Further support for the existence of such an effect exists from a study of the first stepwise formation constants for binding pyridine, 4-phenylpyridine, and 2-phenylpyridine to aquated copper(II).[4] As a result of both the passive and active influence of the polystyrene support in our systems, several unique metal complexes were prepared and characterized.

Also investigated were the activities of these [P]-bpy-supported rhodium complexes, as well as [P]-bpyMCl$_2$ complexes (M = Pt, Pd), in the catalytic hydrogenations of a number of substrates. Since coordination of metals to polymers functionalized with unidentate ligands many times results in significant metal leaching into solution, the bidentate [P]-bpy ligand seemed attractive. Card and Neckers have prepared a number of metal complexes with this support and reported them to be quite stable.[2] In addition, similar enthalpies of adduct formation[5] for the σ-donor properties of pyridine and tri-*p*-tolylphosphine ((tol)$_3$P) led us to suspect that bipyridine might function in a manner similar to phosphines in catalytic systems. Bipyridine is a slightly better σ donor and a poorer π acceptor than (tol)$_3$P. Both of these effects should enhance the tendency of the metal to undergo oxidative addition reactions. Finally, any tendency of the [P]-bpy ligand toward monodentate coordination due to steric interference from the polymer attachment would contribute to a greater degree of metal coordinative unsaturation and therefore to more facile substrate or H$_2$ coordination in the hydrogenation reaction.

Experimental Section

Cross-linked polystyrene gel resin (2%, 200–400 mesh) was purchased from Bio-Rad. The 5% (60–80 mesh) and 8% (80–150 mesh) cross-linked polystyrene gel resins, as well as the polystyrene–pyridine copolymer, [P]-py, were prepared by the suspension technique reported previously[6] (the [P]-py was prepared from 4-vinylpyridine directly). Polystyrene–2,2'-bipyridine samples were prepared as described by Neckers et al.[2] The resultant beads were Soxhlet extracted for 2 days and oven-dried. The rhodium precursors where prepared as reported in the literature.[7,8]

Infrared spectra were recorded on Perkin-Elmer Model 599B, and GLC spectra were obtained with use of a Varian Model 940 FID instrument using a 1 m, $^1/_{16}$ in. i.d. copper column packed with

Table I. Carbonyl Stretching Frequencies for Crystalline and Polymer-Supported Rhodium Complexes Studied

compound	solvent	bands, cm^{-1}
Rh(py)(CO)$_2$Cl	CHCl$_3$	2090, 2015
[P]-pyRh(CO)$_2$Cl	Nujol	2080, 2000
Rh(py)((tol)$_3$P)(CO)Cl		
[P]-pyRh((tol)$_3$P)(CO)Cl	Nujol	1960
[Rh(CO)$_2$Cl]$_2$	Nujol	2105, 2089, 2036
Rh(bpy)(CO)Cl	Nujol	1958
[P]-bpyRh(CO)Cl	Nujol	1990
([P]-bpy)$_m$Rh(CO)$_2$Cl^a	Nujol	2065, 1990

^{a} The subscript m denotes monodentate coordination of the [P]-bpy ligand.

Chromasorb P supported diethylene glycol adipate set at 50 °C. Components were identified by injecting authentic samples and comparing retention times.

[P]-bpyMCl$_2$ (M = Pt and Pd). A 1.0-g sample of polymer-bound bipyridine, [P]-bpy, was added to a filtered solution of 0.1 g of (C$_6$H$_5$CN)$_2$MCl$_2$[9] in acetone (30 mL) and the mixture refluxed for 12 h. After cooling, the beads were collected by suction, Soxhlet extracted with acetone, and air-dried. Elemental analysis for [P]-bpyPtCl$_2$: Pt, 0.93 Cl, 0.45. For [P]-bpyPdCl$_2$: Pd, 0.83; Cl, 0.92.

Polystyrene-Dispersed Palladium Metal. The polymer [P]-bpyPdCl$_2$ (500 mg) was added to a stirred solution of 1,4-dioxane (50 mL), 95% hydrazine (5 mL), and absolute ethanol (5 mL). After 12 h of stirring at room temperature, the black beads were collected by suction, washed with ethyl acetate–benzene (1:1) and ethanol, and air-dried.
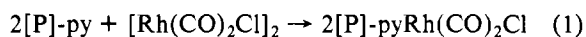
[P]-pyRh and [P]-bpyRh Species. The following general procedure was used to graft Rh(I) species onto [P]-bpy and [P]-py using [Rh(CO)$_2$Cl]$_2$, [Rh((tol)$_3$P)(CO)Cl]$_2$, and [Rh((C$_6$H$_5$)$_3$P)(CO)Cl]$_2$ as starting materials. The polymer (0.50 g) was added to 30 mL of toluene at room temperature. After the system was purged with bubbling argon for 30 min, the chloro-bridged rhodium dimer (30 mg) was added and the mixture stirred for 24 h under Ar. The brown beads were collected by suction, washed with toluene and absolute ethanol, Soxhlet extracted with toluene, and air-dried.

Hydrogenation Procedure. All catalytic runs were carried out in a 250-mL Parr pressure bottle equipped with a 200 psi Marsh pressure gauge and gas inlet–outlet tube for filling and purging. The bottle–copper tubing interface was sealed by a tightly clamped silicone rubber stopper. No pressure drop occurred from the sealed system in 24 h on pressurization to 120 psi at either room temperature or 120 °C. The apparatus was checked regularly for leaks to ensure there were no spurious pressure drops.

The following procedure is typical of that followed in the catalytic hydrogenations. The polymer sample (50 mg), substrate (5 mL), benzene solvent 30 mL, and a stir bar were loaded into the 250-mL Parr bottle, hooked to the pressurization apparatus, and purged by six repetitions of bottle pressurization to 100 psi H$_2$ and gas discharging. The bottle was then pressurized to 100 psi H$_2$ (at room temperature) and immersed in a preheated oil bath to begin the reaction. After 24 h the bottle was removed from the bath, cooled to room temperature, the final pressure recorded, and the filtrate analyzed for products.

Results and Discussion

I. Preparation and Characterization of Supported Rhodium Systems.
While in solution the cleavage reactions with both homogeneous 2,2'-bipyridine and pyridine[8] are straightforward, the reaction of [P]-bpy with these dimers proved to be somewhat more involved. The [P]-py cleavage resulted in products analogous to those formed in the homogeneous phase, as evidenced by their infrared spectra (reactions 1 and 2). The

$$2[P]\text{-py} + [Rh(CO)_2Cl]_2 \rightarrow 2[P]\text{-pyRh(CO)}_2Cl \quad (1)$$

$$2[P]\text{-py} + [Rh((tol)_3P)(CO)Cl]_2 \rightarrow$$
$$2[P]\text{-pyRh((tol)}_3P)(CO)Cl \quad (2)$$

infrared carbonyl absorption frequencies for all carbonyl-

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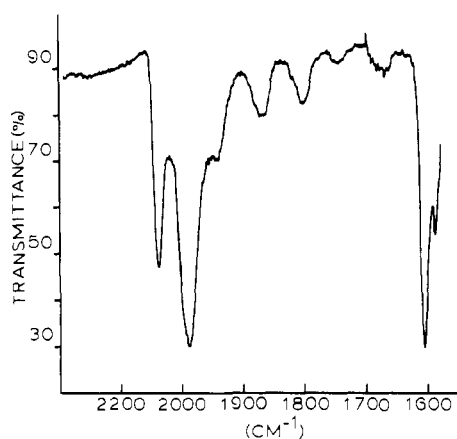(9) Karasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

Figure 1. Infrared spectrum of the polymer derived from the reaction of [P]-bpy with di-μ-chloro-tetracarbonyldirhodium (I). The shoulder at 1950 cm^{-1} and all absorbances downfield are due to the polystyrene support.
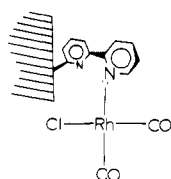

Figure 2.

containing species characterized in this study are listed in Table I. The pyridine and [P]-py cleavage products from reaction 1 exhibited two equal-intensity CO stretching bands.

The reaction between [P]-bpy and [Rh(CO)$_2$Cl]$_2$ was more complicated. The infrared spectrum in the carbonyl stretching region is displayed in Figure 1. This observation of two bands may be explained by either a dicarbonyl product such as a monodentate [P]-bpy-supported species (([P]-bpy)$_m$Rh-(CO)$_2$Cl) or two distinct CO-containing products. The homogeneous reaction produces only the deep purple solid Rh-(bpy)(CO)Cl (isolated in 95% yield) (reaction 3). Polymer

$$bpy + [Rh(CO)_2Cl]_2 \rightleftharpoons 2Rh(bpy)(CO)Cl + 2CO \quad (3)$$
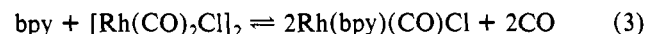
attachment via the 6-position of the bipyridine ligand may be expected to contribute to a weakening in the adjacent nitrogen coordination to rhodium via steric interference, and monodentate coordination of [P]-bpy could result as shown in the proposed structure of ([P]-bpy)$_m$Rh(CO)$_2$Cl (Figure 2). The infrared CO band positions in Figure 1 are similar to those for [P]-pyRh(CO)$_2$Cl. The much greater intensity of the 1990-cm^{-1} band in the [P]-bpy product is due to the contribution form bidentate [P]-bpyRh(CO)Cl (vide infra).

The homogeneous reaction between 2,2'-bipyridine and [Rh((tol)$_3$P)(CO)Cl]$_2$ proceeds stoichiometrically as shown in reaction 4. The Rh(bpy)(CO)Cl was isolated in 90% yield,

$$bpy + [Rh((tol)_3P)(CO)Cl]_2 \rightarrow$$
$$Rh(bpy)(CO)Cl + Rh((tol)_3P)_2(CO)Cl \quad (4)$$
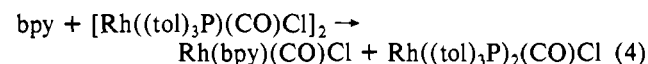
and the Rh((tol)$_3$P)$_2$(CO)Cl in solution was quantitatively detected with use of visible spectroscopy. The reaction between [P]-bpy and [Rh((tol)$_3$P)(CO)Cl]$_2$ was much slower, and its progress was monitored by infrared scans of bead samples in the CO region as a function of reaction time (Figure 3). During the course of this reaction the beads progressively changed from gold to dark brown. It is apparent from the strong band at 1990 cm^{-1} in Figure 3 that the predominant carbonyl-containing supported complex is a monocarbonyl, characterized as [P]-bpyRh(CO)Cl by analogy with the homogeneous reaction in eq 4. Rh((tol)$_3$P)$_2$(CO)Cl was detected in the final solutions by visible spectroscopy.
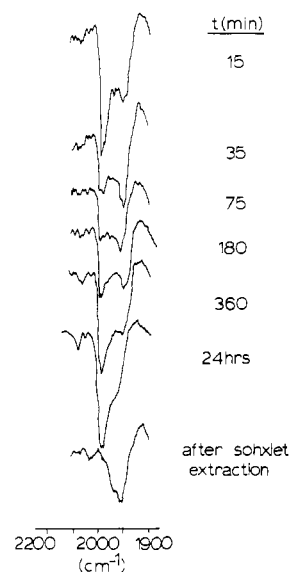

Figure 3. CO band intensity changes (at 1990 cm^{-1}) as function of reaction time and washing (final spectrum) for sample IIIb (Table II). The same results were found for samples IIIa and IIIc.

Table II. Composition of Various Supported Polymers Used in This Investigation (Substitution in Units of mmol/g of Polymer)

sample	bpy^a	Rh^b	P^c	Rh^d	P^d
Ia^e	0.59	0.37	0.05	0.34	0.07
Ib	0.59	0.28	0.26		
IIa^f	0.2			0.06	0.04
IIb	0.2	0.15	0.11	0.13	0.10
IIc	0.2		0.10	0.12	0.06
IId	0.2			0.03	0.02
IIe	0.2			0.03	0.01
IIf	0.2			0.06	0.04
IIg	0.2			0.10	0.06
IIIa^g	0.43		0.11	0.44	0.35
IIIb	0.43	0.15	0.04	0.18	0.10
IIIc	0.43	0.14	0.06	0.21	0.16

^{a} Determined from elemental analysis for N. ^{b} Determined from neutron activation analysis for Rh. ^{c} Determined for elemental analysis for P. ^{d} Calculated from visible spectra. ^{e} 2% cross-linked resins, 200–400 mesh. ^{f} 5% cross-linked resins, 60–80 mesh. ^{g} 8% cross-linked resins, 80–150 mesh. Sample IIIa was produced with twice the initial [Rh(CO)$_x$Cl]$_2$ concentration used for IIIb and IIIc.

A quantative analysis of the Rh((tol)$_3$P)$_2$(CO)Cl and [Rh((tol)$_3$P)(CO)Cl]$_2$ in the final solution and the rhodium and phosphorus on the final beads revealed that the [P]-bpy analogue of reaction 4 was by no means the exclusive process. These results are presented in Table II. The rhodium content on the beads was determined from the visible spectra of the final solutions by assuming that all rhodium not accounted for by the Rh((tol)$_3$P)$_2$(CO)Cl and [Rh((tol)$_3$P)(CO)Cl]$_2$ in solution was bound to the [P]-bpy beads. This assumption was supported by both the excellent fits in the simulation of the visible spectra and the good agreement between the supported rhodium contents calculated in this manner and those determined by neutron activation analyses on selected samples.

For all samples prepared the amount of rhodium bound to the beads was greater than could be explained by the polymer analogue of reaction 4. In fact for different samples reaction 4 could account for only 20–80% of the rhodium actually coordinated to the [P]-bpy support (determined from the Rh((tol)$_3$P)$_2$(CO)Cl found in the final solution). Therefore, a second reaction must be involved in which the net result is the coordination of both rhodium centers of the [Rh-((tol)$_3$P)(CO)Cl]$_2$ dimer to [P]-bpy groups. In addition, since
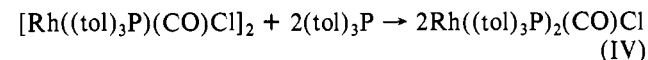
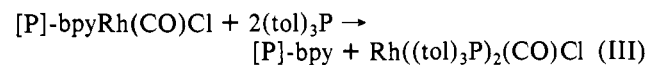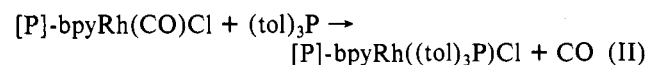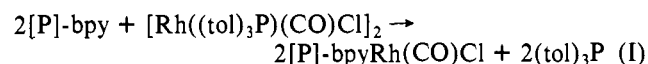free phosphine in solution will cleave the dimer to form Rh-((tol)$_3$P)$_2$(CO)Cl,[8] all phosphine not found in solution as Rh((tol)$_3$P)$_2$(CO)Cl and [Rh((tol)$_3$P)(CO)Cl]$_2$ must be bound to the polymer via coordination to rhodium. The values for the bead's predicted phosphorus contents are listed in Table II, as are those found by elemental analyses. This second process is represented in reaction 5. For sample Ia reaction

$$2[P]\text{-bpy} + [Rh((tol)_3P)(CO)Cl]_2 \rightarrow$$
$$2[P]\text{-bpyRh}((tol)_3P)Cl + 2CO \quad (5)$$
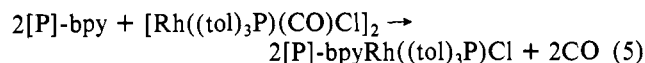
5 accounts for only 20% of the rhodium, while for sample IIIa it accounts for 80%.

Since reaction 5 represents a process unique to the polymer-supported bipyridine ligand, a closer examination was made. Two fundamental mechanisms are possible: (1) a direct or "concerted" formation with loss of CO or (2) and indirect process involving the intermediate formation of [P]-bpyRh-(CO)Cl. The infrared evidence in Figure 3 serves as strong evidence for the second mechanism. At 15 min of reaction a very strong CO band at 1990 cm^{-1} is observed, characteristic of [P]-bpyRh(CO)Cl. Samples scanned at 35 and 75 min exhibit progressively less intense bands. After this the 1990-cm^{-1} band grows in intensity, along with a weak band at 2065 cm^{-1}. As diagramed in Scheme I, this may be explained by the initial exclusive formation of [P-bpyRh(CO)Cl and subsequent competition for free (tol)$_3$P by [P]-bpyRh-(CO)Cl and [Rh((tol)$_3$P)(CO)Cl]$_2$. Since step I in the scheme produces only [P]-bpyRh(CO)Cl and free (tol)$_3$P, the immediate growth of the 1990-cm^{-1} band is expected. As the concentration of free phosphine builds up in the polymer matrix, steps II and III in the scheme, which both liberate CO from the polymer, would become increasingly competitive, resulting in a decrease in the 1990-cm^{-1} band intensity. Step IV consumes the free phosphine, thus reducing the potential for CO displacement in steps II and III. Further substantiation of the scheme comes from an examination of Table II. Sample Ia, produced from 2% cross-linked resin (200–400 mesh), possesses only 20% supported phosphine complex. Samples IIIa, IIIb, and IIIc are produced from 8% cross-linked resin (80–150 mesh) and possess from 55% to 80% phosphine complex. The lower cross-linking of sample Ia will result in larger pore sizes on swelling in toluene. This, in addition to the much smaller bead diameters of sample Ia, will result in faster diffusion rates for all solution species within the resin relative to those for samples IIIa, IIIb, and IIIc. The effect is greater access of free phosphine to [Rh((tol)$_3$P)(CO)Cl]$_2$ for sample Ia, and hence a decrease in the total amount of phosphine which may eventually coordinate to the polymer-bound rhodium.
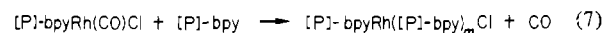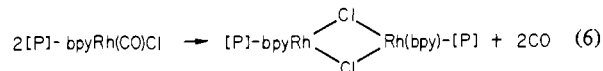
Scheme I

$$2[P]\text{-bpy} + [Rh((tol)_3P)(CO)Cl]_2 \rightarrow$$
$$2[P]\text{-bpyRh}(CO)Cl + 2(tol)_3P \quad (I)$$

$$[P]\text{-bpyRh}(CO)Cl + (tol)_3P \rightarrow$$
$$[P]\text{-bpyRh}((tol)_3P)Cl + CO \quad (II)$$

$$[P]\text{-bpyRh}(CO)Cl + 2(tol)_3P \rightarrow$$
$$[P]\text{-bpy} + Rh((tol)_3P)_2(CO)Cl \quad (III)$$

$$[Rh((tol)_3P)(CO)Cl]_2 + 2(tol)_3P \rightarrow 2Rh((tol)_3P)_2(CO)Cl \quad (IV)$$

Steps II and III in the scheme were substantiated by the reaction of sample Ia with excess phosphine. A small amount of Rh((tol)$_3$P)$_2$(CO)Cl and a polymer-supported rhodium complex with a 1:1 ratio of rhodium to phosphorus (sample Ib), characterized as [P]-bpyRh((tol)$_3$P)Cl, was produced. The homogeneous reaction between Rh(bpy)(CO)Cl and 2 equiv of phosphine produces Rh((tol)$_3$P)$_2$(CO)Cl and free

Table III. Results of the Catalytic Hydrogenation of Several Substrates with [P]-bpyPtCl$_2$

substrate	% yield	substrate	% yield
1-hexene	90	*trans*-2-hexene	5
cis- and *trans*-2-hexene	5	cyclohexene	5
1-heptyne	58 (alkane) 42 (alkene)	1,3-COD	very small
		1,5-COD	very small

2,2'-bipyridine stoichiometrically. The irreversibility of step II was demonstrated by carbonylating sample Ib in toluene at room temperature under 100 psi CO, resulting in only a very weak infrared band. In contrast, the carbonylation of sample IIg under identical conditions resulted in two medium strength bands at 2065 and 1990 cm^{-1}, which are assigned to ([P]-bpy)$_m$Rh(CO)$_2$Cl. This species is also unique to the [P]-bpy ligand. Indeed a small amount of this dicarbonyl complex is evident after 24 h of reaction between [P]-bpy and [Rh((tol)$_3$P)(CO)Cl]$_2$ (Figure 3). This could be produced from the CO liberated in step II of the scheme.

The lability of the CO ligand in [P]-bpyRh(CO)Cl is demonstrated by the complete loss of CO during Soxhlet extraction in THF (Figure 3). In the absence of free phosphine this may be explained by reactions 6 and 7 or reaction with

$$2[P]\text{-bpyRh(CO)Cl} \rightarrow [P]\text{-bpyRh}\underset{Cl}{\overset{Cl}{<>}}\text{Rh(bpy)-[P]} + 2CO \quad (6)$$

$$[P]\text{-bpyRh(CO)Cl} + [P]\text{-bpy} \rightarrow [P]\text{-bpyRh([P]-bpy)}_m\text{Cl} + CO \quad (7)$$

oxygen. The low values for phosphorus found by elemental analyses (Table II) are attributed to the unreliability of the analyses at these low concentrations. Throughout the remainder of this paper the final supported rhodium complex will be referred to as [P]-bpyRhXCl.

In the homogeneous reaction the insolubility of Rh(bpy)-(CO)Cl provides a driving force for the exclusive formation and isolation of this bipyridine product. In the polymer-supported system this stabilizing influence is not present, and subsequent reactions of [P]-bpyRh(CO)Cl occur. These findings emphasize two important statements about this area of chemistry. First, species can be prepared on the polymer whose solution counterpart does not exist. Second, it is not always safe to infer reactivity on a polymer support from analogous solution chemistry.

II. Catalytic Hydrogenations. (A) Hydrogenations with [P]-bpyPtCl$_2$. The results of the catalytic hydrogenations using [P]-bpyPtCl$_2$ are presented in Table III. It is evident that this supported complex possesses a high degree of selectivity toward the hydrogenation of terminal olefins. The size and chemical similarities of the substrates studied indicates this selectivity is not due to differences in their diffusion rates through the polymer. It is most likely a result of the differences in rates of formation of σ-alkyl–rhodium complex intermediates. For example the binding constants for the formation of primary σ-alkyls are ca. 50 times as great as those for the formation of corresponding secondary alkyls.[10]

An induction period of at least 5 h was observed prior to all catalytic runs (using 50 psi H$_2$, at 70 °C). This was the case for recycled catalyst samples as well as fresh samples. The ability to recycle these supported catalysts as well as the colorless filtrates indicates leaching is unimportant. The absence of catalysis of the nitrobenzene hydrogenation to aniline by the [P]-bpyPtCl$_2$ product, which is characteristic of sup-

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Table IV. Results of the Catalytic Hydrogenations of Several Substrates with [P]-bpyPdCl$_2$

substrate	% yield	substrate	% yield
1-hexene	70	1,3-COD	2 (alkane)
trans-2-hexene	35		98 (alkene)
cis- and *trans*-2-hexene	40	1-heptyne	61 (alkane)
			39 (alkene)
cyclohexene	60	methyl acrylate	not quantitated
1,5-COD	10 (alkane)		
	90 (alkene)	benzyl chloride	100
		nitrobenzene	not quantitated

ported platinum metal (on charcoal),[11] eliminates consideration of the metal as the active catalyst here.

Bailar and Brunner[12] have supported platinum(II) chloride on macroreticular polystyrene which was previously functionalized with pendant tertiary phosphine ligands. Their findings indicate that in order for the platinum polymer system to be catalytic reaction conditions of 150 °C and 550 psi of H$_2$ and the addition of tin(II) chloride were needed. The polystyrene–bipyridine support provides a system which is active under much milder conditions.

(B) Hydrogenations with [P]-bpyPdCl$_2$. The results of the hydrogenations catalyzed by [P]-bpyPdCl$_2$ are presented in Table IV. After one hydrogenation run the supported catalysts acquired a greenish coloration. The reduction of nitrobenzene to aniline indicates the formation of palladium metal under the conditions employed (70 °C, 50 psi H$_2$). A sample of polystyrene–bipyridine-dispersed palladium metal was prepared by reduction of [P]-bpyPdCl$_2$ with ethanolic hydrazine. Electron microscopy revealed metal aggregates ranging up to 200 Å in diameter, and the substrates 1-hexene, *p*-benzoquinone, and nitrobenzene were readily hydrogenated with this catalyst. The results in Table IV therefore must be considered to result from catalysis by a mixture of [P]-bpyPdCl$_2$ and palladium metal.

Both the catalyst precursor ([P]-bpyPdCl$_2$) and reaction conditions used here are different than those employed by Neckers et al.[2] Their milder hydrogenation conditions (25 °C, 1 atm H$_2$) would be expected to result in a reduced tendency to form metal crystallites. It is therefore not possible to draw any conclusions concerning metal formation in their system.

Neckers does propose that under his conditions [P]-bpyPd^0 is formed and is the active catalyst. This species may be monomeric or a metallic cluster. Bailar's study of ([P]-P-(C$_6$H$_5$)$_2$)$_2$PdCl$_2$-catalyzed hydrogenation[12] is consistent with Pd(II) as the active catalyst. As noted by Neckers it would appear that the bipyridine ligand promotes the reduction of palladium(II) to the zero oxidation state. This possibility is further borne out in the [P]-bpyRhXCl-catalyzed hydrogenations (vide infra).

(C) Hydrogenations with [P]-bpyRhXCl Systems. The poorer π-accepting capabilities of bpy compared to phosphine and the tendency of the [P]-bpy ligand to coordinate in a monodentate fashion should enhance the ability of [P]-bpyRhXCl to undergo oxidative addition reactions compared to an analogous phosphine-supported systems. Therefore the [P]-bpy-supported rhodium systems described earlier in this paper were investigated as 1-hexene hydrogenation catalysts. At 50 °C and under 100 psi H$_2$ with sample IIb an induction period of 5–6 h was observed before H$_2$ uptake and 1-hexene hydrogenation to hexane occurred. Subsequent recycled catalyst exhibited no induction period, in contrast to [P]-bpyPtCl$_2$ recycling, and the catalyst activity further increased.
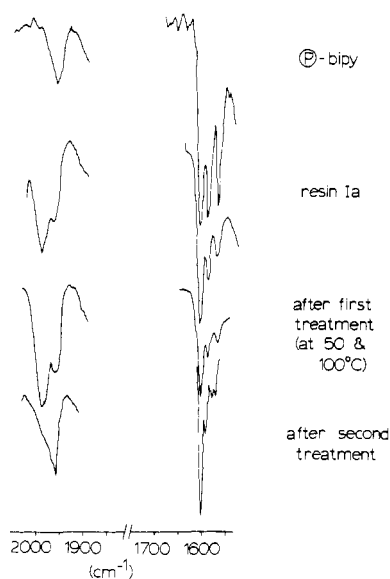

Figure 4. CO (at 1990 cm^{-1}) and 2,2'-bipyridine (at 1560 and 1580 cm^{-1}) band intensity changes as a function of treatment with H$_2$.

Cyclohexane and cyclohexene were detected in the filtrate after the second catalytic run. These products result from benzene hydrogenation and are characteristic of catalysis by rhodium metal. No benzene hydrogenation products were detected by gas–liquid chromatography after the first use of the supported catalyst, although complete conversion of 1-hexene to hexane was realized at this stage.

A photoelectron spectroscopic analysis of a recycled polymer sample capable of benzene hydrogenation detected binding energies of 314.5 and 310.0 eV for the Rh 3d$_{3/2}$ and 3d$_{5/2}$ electrons, respectively.[13] These do not correspond to either Rh metal (expected to produce bands of 311.8 and 307.1 eV) or Rh(I) species (producing bands at 312.7–313.2 and 308.1–308.4 eV) but do approach the values expected for Rh(III) species (at 314.4 and 309.7 eV for RhCl$_3$·3H$_2$O).[14] Freshly prepared samples of Rh metal on charcoal (from H$_2$ reduction of RhCl$_3$) have been found to possess large amounts of Rh$_2$O$_3$[15] which would account for the ESCA results. Electron transmission microscopy detected particles on the beads ranging from 20–40 Å in diameter. Therefore it appears that rhodium metal forms on the polymer as a result of H$_2$ reduction of the supported rhodium at 50 and 100 °C and that the 1-hexene hydrogenation may be explained by it.

Hydrogenation of 1-hexene catalyzed by [P]-bpyRh-((C$_6$H$_5$)$_3$P)Cl (sample Ib) at 100 psi H$_2$ and 100 °C also resulted in the formation of a small amount of cyclohexane and cyclohexene, in addition to hexane. Thus it appears this sample is reduced to rhodium metal as well.

An investigation of the infrared spectra of the Ia sample after increasing treatment with 100 psi H$_2$ at 50 and 100 °C reveals that both the CO IR band (at 1990 cm^{-1}) and the 2,2'-bipyridine bands (at 1560 and 1580 cm^{-1}) are present through several stages of H$_2$ treatment (Figure 4). After a second treatment with H$_2$ at 100 °C, the bpy bands decrease in intensity and the CO band disappears altogheter. However, a significant amount of cyclohexane was formed during the first reduction at 100 °C. The decrease in the 2,2'-bipyridine band intensities suggests the hydrogenation of this group to bipiperidine (loss of bpy from the hydrogenated polymer was

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ruled out by elemental analysis for N). This reduction is expected to cause increased metal center lability and hence metal aggregation.

Catalysis with the supported Wilkinson's catalyst, [P]-PPh$_2$Rh(PPh$_3$)$_2$Cl (2% cross-linked gel resin, 200–400 mesh, 0.03 mmol of Rh/g of beads) under conditions similar to those used for the [P]-bpyRh samples was investigated (80 psi H$_2$, 100 °C, 24-h reaction time). A small amount of cyclohexane was produced from the H$_2$ reduction of benzene solvent, again suggesting the formation of a small amount of rhodium metal. No detectable benzene hydrogenation products resulted from a hydrogenation of benzene with the homogeneous complex Rh((C$_6$H$_5$)$_3$P)$_3$Cl at 100 psi H$_2$ and 100 °C for 72 h.

We obtained turnovers in the 1-hexene hydrogenation with [P]-bpyRhXCl as great as 300 in first runs, without the attendant formation of detectable benzene hydrogenation products. This demonstrates an important point: the absence of aromatic hydrogenation products is not necessarily a valid criterion for ruling out catalysis by small metal particles. This is of course a result of the much greater reactivity of 1-hexene

than benzene toward hydrogenation.

These results also illustrate another point. With the exception of cases in which effective site isolation on a polymer has been achieved, it should be considered that for many polymer-supported transition-metal systems there is considerable potential for metal aggregation. The [P]-P(C$_6$H$_5$)$_2$Rh-((C$_6$H$_5$)$_3$P)$_2$Cl comparison to the homogeneous Rh((C$_6$-H$_5$)$_3$P)$_3$Cl system above is a good example.

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Reaction of (η^5-C$_5$H$_5$)$_3$UCl with Lithiated Phosphoylides. Preparation of Some Mono-, Bis-, and Tris(cyclopentadiene)uranium(IV) Phosphoylide Complexes

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The reaction between (η^5-C$_5$H$_5$)$_3$UCl and Li(CH$_2$)(CH$_2$)P(C$_6$H$_5$)$_2$ or Li(CH$_2$)(CH$_2$)P(CH$_3$)(C$_6$H$_5$) in 1:1 molar ratio produces (η^5-C$_5$H$_5$)$_3$UCHP(CH$_3$)(C$_6$H$_5$)$_2$ or (η^5-C$_5$H$_5$)$_3$UCHP(CH$_3$)$_2$(C$_6$H$_5$), respectively. When Li(CH$_2$)(CH$_2$)P(C$_6$H$_5$)$_2$ is allowed to react with (η^5-C$_5$H$_5$)$_3$UCl in 2:1 ratio or with (η^5-C$_5$H$_5$)$_3$UCHP(CH$_3$)(C$_6$H$_5$)$_2$ in 1:1 ratio the novel metallacycle (η^5-C$_5$H$_5$)$_2$U[CHP(C$_6$H$_5$)$_2$CH$_2$]$_2$U(η^5-C$_5$H$_5$)$_2$ can be isolated. Finally when the ratio of (η^5-C$_5$H$_5$)$_3$UCl to Li(η^5-C$_5$H$_5$) is 1:3, the respective complexes (η^5-C$_5$H$_5$)U[(CH$_2$)(CH$_2$)P(C$_6$H$_5$)$_2$]$_3$ and (η^5-C$_5$H$_5$)U[(CH$_2$)(CH$_2$)P(CH$_3$)(C$_6$H$_5$)]$_3$ are formed. These are the first phosphoylide complexes of an actinide. They are stable at room temperature under an inert atmosphere and demonstrate that organouranium complexes which are rich in metal–carbon σ bonds can be formed with phosphoylide ligands.

Complexes containing actinide–carbon σ bonds have attributed growing interest during the last few years,[1–3] and it is now well established that such bonds are often stable at and above room temperature. A good deal of recent study has focused on the preparation of compounds in which the actinide's coordination number is less than the most common value of 10.[4–6] Usually this has involved the use of bulky coligands, with the most notable examples being the bis(pentamethylcyclopentadienyl)uranium and -thorium complexes recently reported by Marks and co-workers.[6] Even though these investigations have demonstrated the existence of numerous compounds containing two actinide–carbon σ bonds, prior to this study, there was no thermally stable, neutral actinide complex with three or more such bonds.

Since phosphorus ylides are known to form very stable σ bonds with transition metals[7] and a few uncharged lanthanide ylide complexes are known,[8,9] we have begun an investigation of phosphorus ylides as ligands toward actinides. In this paper we report the reactions of some lithiated phosphoylides, Li-(CH$_2$)(CH$_2$)P(R)(C$_6$H$_5$), R = CH$_3$ and C$_6$H$_5$, with (η^5-C$_5$H$_5$)$_3$UCl and (η^5-C$_5$H$_5$)UCl$_3$·2THF.

Experimental Section

All manipulations were carried out under high-purity dinitrogen in a Vacuum Atmospheres glovebox equipped with an HE-493 Dri-Train, with use of standard Schlenk tube techniques or in a high-vacuum line. Reagents and solvents were of the highest commercially available purity and were dried and deoxygenated by appropriate means before use. Due to the extreme sensitivity of some of the compounds prepared in this study, care must be exercised to exclude oxygen, moisture, or protonic solvents.

Published procedures were used to prepare (η^5-C$_5$H$_5$)$_3$UCl,[10] (η^5-C$_5$H$_5$)UCl$_3$·2THF,[11] Li(CH$_2$)(CH$_2$)P(C$_6$H$_5$)$_2$,[9] Li(CH$_2$)(CH$_2$)-

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