manner analogous to **1**,[7] also reacts with acetone in pentane to give high yields of 2,4,4-trimethyl-2-pentene and an insoluble, ivory-colored precipitate whose infrared spectrum in Nujol is essentially identical with that of **2** (ν_{Nb-O} 880 cm^{-1}). Since obtaining large quantities of **3** is more difficult, however, **1** was used in further studies.

Table I lists some representative reactions of **1** with other common molecules containing the carbonyl function. Most were done on a 1-2 mmol scale with isolated **1** at 25° in the solvents shown. Alternatively **1** can be prepared in situ in pentane in quantitative yield from $Ta[CH_2C(CH_3)_3]_3Cl_2$ and 2 mol of $LiCH_2C(CH_3)_3$.[8] It can also be prepared directly from $TaCl_5$ and 5 mol of $(CH_3)_3CCH_2MgCl$ in diethyl ether but the reaction to give **1** is slow and the yield of olefin consequently suffers.[9]

Most notable of the Wittig-type reactions employing **1** are those which are not (or very rarely) successful with phosphorus ylides, IV-VI. **1** also reacts instantly with CO_2 to give at least a 50% yield (vs. theory) of di-*tert*-butylallene according to GLC/mass spectral analysis and ^1H NMR (τ 4.8 (1), τ 8.9 (9) in C_6D_6). In general, esters and amides appear to react more slowly than ketones and aldehydes, and molecules which are more substituted at the carbonyl carbon more slowly than those which have a more exposed carbonyl function (e.g., ethyl acetate reacts more slowly than ethyl formate). Molecules with bulky substituents (e.g., pivaldehyde) react too slowly under these conditions for practical purposes. Though relative rates of reaction and solvent effects have not been studied thoroughly, one could envision some degree of selectivity between isolated functional groups. It should also be noted in this context that **1** (in pentane) does not react readily with CH_3I, $C_6H_5CH_2Cl$, or ethylene oxide.

The overall reaction of the type shown in eq 1 formally consists of addition of the carbonyl function across the $Ta{=}CHCMe_3$ bond in a manner consistent with a $Ta(\delta+){=}C(\delta-)$ polarization. This is evidence that the neopentylidene α-carbon atom in **1**, like the methylene carbon atom in $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$,[1b] is nucleophilic. Note that carbene complexes in which C_{carb} is electrophilic react in the expected, opposite manner with polarized "unsaturated" bonds as in (for example) a phosphorus ylide.[10]

The mechanism of the reaction of **1** with the carbonyl function probably consists of at least two distinct steps. For example, when ethyl acetate is added to **1** in ether, the orange color changes hue slightly and heat is evolved. Shortly thereafter the color lightens steadily as **2** precipitates from the solution. Since **1** is electron deficient (14 valence electrons), and ketones and aldehydes are known to bond through the carbonyl oxygen atom to the metal in other electron-deficient Ta or Nb alkyls such as $Nb(CH_3)_2Cl_3$,[11] the first step in the reaction of **1** with a carbonyl function may simply be formation of a similar adduct. Subsequent "metathesis" then yields the olefin and oxygen strongly bound to Ta (initially probably $Ta{=}O$). Some support for this proposal comes from the observation that $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$, an 18-electron complex, only reluctantly reacts with acetone (80° in neat acetone) to give low yields of isobutylene. A betaine intermediate analogous to that invoked as an intermediate in the Wittig reaction[6] of course cannot be excluded by any of these data alone.

The findings reported here demonstrate that **1** is indeed a powerful, if somewhat esoteric, reagent for the preparation of *tert*-butyl substituted olefins, not only from aldehydes and ketones, but from esters and amides; several would probably prove difficult to prepare by standard techniques due to the steric demands of the *tert*-butyl substituent. They also demonstrate that analogies between early transition metals and main group elements can be significant and useful, and that some metal carbene complexes (at least $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$[1a,b] and possibly also **1**) can be described more accurately in terms of the ylide-type structure, $M(\delta+){=}C(\delta-)$.

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(2) "Alkylidene" complex is the preferred, more succinct description of what might also be called an "unstabilized carbene" complex. ("Stabilized carbene" complexes generally are those which contain a heteroatom such as O or N bound to the carbene carbon atom; see, for example, D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972), and references therein.) "Terminal" alkylidene complexes (i.e., $M{=}CHR$, R = alkyl or aryl) are so far unique to Nb and Ta though diphenylmethylene complexes of W[3a] and Mn,[3b] a benzocyclobutenylidene complex of Fe,[3c] and a diphenylcyclopropylidene complex of Cr[3d] are known.

(3) (a) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95**, 5833 (1973); (b) W. A. Herrman, *Chem. Ber.*, **108**, 486 (1975); (c) A. Sanders, L. Cohen, W. Giering, D. Kenedy, and C. V. Magatti, *J. Am. Chem. Soc.*, **95**, 5430 (1973); (d) K. Öfele, *Angew. Chem., Int. Ed. Engl.*, **7**, 950 (1968).

(4) (a) The oxyhalides, $Nb(O)Cl_3$ and $Ta(O)Cl_3$, are also polymers in the solid state ($\nu_{M-O} \approx 770$ cm^{-1})[4b,c] but monomers in the gas phase ($\nu_{M=O} \approx 1000$ cm^{-1})[4b,c] while $V(O)Cl_3$ ($\nu_{V=O}$ 1035 cm^{-1})[4b,c] and $V(O)[CH_2Si(CH_3)_3]_3$ ($\nu_{V=O}$ 990 cm^{-1})[4d] are monomers in the solid state. Therefore a polymeric Ta–O–Ta formulation for **2** (ν_{Ta-O} 870 cm^{-1}) is not unreasonable though a lower value for ν might have been expected based on the above data. (b) D. L. Kepert, "The Early Transition Metals", Academic Press, New York, N.Y., 1972; (c) R. A. Walton, *Prog. Inorg. Chem.*, **16**, 1 (1972); (d) W. Mowat, A. Shortland, G. Yaqupsky, N. J. Hill, M. Yaqupsky, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 533 (1972).

(5) Detailed mass spectral analysis courtesy of F. J. Kitson of the Central Research and Development Department.

(6) (a) G. Wittig, *J. Organomet. Chem.*, **100**, 279 (1975); (b) A. W. Johnson, "Ylid Chemistry", Academic Press, New York, N.Y., 1966.

(7) **3** is the product of the reaction between $Nb[CH_2C(CH_3)_3]_3Cl_2$ and 2 mol of $LiCH_2C(CH_3)_3$ in pentane at −78°. It is a red crystalline solid which is extremely soluble in pentane and (unlike **1**) does not sublime without decomposing. Its ^1H and ^{13}C NMR spectra are essentially identical with **1** and its identity thereby established. (Its thermal instability hampered meaningful elemental analyses.)

(8) $Ta[CH_2C(CH_3)_3]_3Cl_2$ is best prepared by stirring 1.5 mol of $Zn[CH_2C(CH_3)_3]_2$ and $TaCl_5$ in pentane at 25 °C for 12 h (cf. S. Moorhouse and G. Wilkinson, *J. Organomet. Chem.*, **52**, C5 (1973); *J. Chem. Soc., Dalton Trans.*, 2187 (1974); W. Mowat and G. Wilkinson, *ibid.*, 1120 (1973)). $Zn[CH_2C(CH_3)_3]_2$ was prepared by the standard Grignard method (bp 82°, 27 mm).

(9) An ether solution of $(CH_3)_3CCH_2MgCl$ (50 mmol) was added to $TaCl_5$ (3.58 g, 10 mmol) in 100 ml of ether at −78 °C under N_2. The mixture was heated to reflux for 16 h (**1** is stable under these conditions). Addition of 3 mmol of benzaldehyde followed by hydrolysis with 1 N HCl gave an ether layer which contained a 30% yield (vs. Ta) of *cis*- and *trans-tert*-butylstyrene (by quantitative GLC). The major product was neopentylphenyl carbinol (ca. 2 mol per Ta). The yield of the olefin decreased to ca. 5% when the reflux step was omitted.

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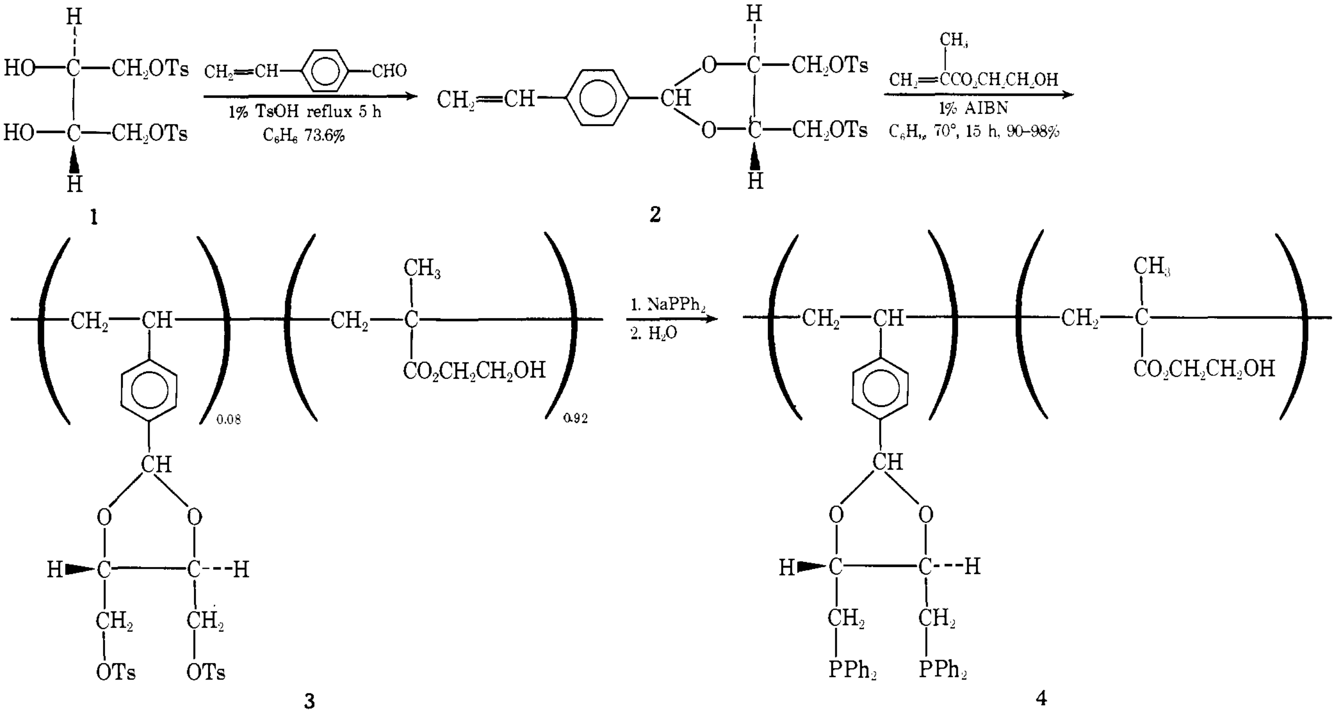
Transition Metal Catalyzed Asymmetric Organic Syntheses via Polymer Bound Chiral Ligands. Synthesis of *R* Amino Acids and Hydratropic Acid by Hydrogenation

Sir:

Although there are a number of methods for the synthesis of optically active organic compounds, there are several obvious advantages in obtaining a chiral product from a prochiral substrate via an optically active catalyst or enzyme. The reactions, via a homogeneous catalyst that owes its chirality to asymmetric phosphine ligands on the metal, have proven to be

Scheme I



valuable in asymmetric syntheses. The hydrogenation of prochiral acylamidoacrylic acids, in the presence of homogeneous chiral catalysts can be carried out to afford amino acids in high optical yields.[1-4]

One practical limit to performing homogeneously catalyzed reactions in the liquid phase is the difficulty of separating the product from the catalyst or removing the product continuously. To overcome this difficulty, homogeneous catalysts have been attached to a variety of supports, including cross-linked polymers. In this way the catalyst acquires the property of insolubility while maintaining the reactivity exhibited in solution. Thus, there is a new state of aggregation combining the properties of a polymer solid with those in solution. The only synthetic polymer support for a catalyst containing polymer-bound phosphine ligands coordinated to the transition metal is cross-linked polystyrene. In some cases, higher rates,[5-8] greater selectivity for nonpolar hydrocarbons (vs, polar ones)[7,9,10] and greater stereoselectivity[9,11,12] have been reported in more polar solvents, Although cross-linked polystyrene swells in nonpolar solvents it collapses in polar solvents, preventing penetration of the substrate. Acylamidoacrylic acids are hydrogenated to amino acid derivatives in high enantiomeric excess in the presence of a homogeneous rhodium catalyst containing the ligand 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphine)butane [(DIOP) Rh(S)Cl]. This same catalyst bound to polystyrene beads will not hydrogenate the acylamidoacrylic acids in a nonpolar solvent since the substrates are not soluble.[13] In polar solutions of the substrates, the bead pores collapse preventing entry of the acylamidoacrylic acid to the catalyst site.

In this communication, we wish to report the asymmetric hydrogenation of olefins using a Rh^{I}-DIOP catalyst supported on a polymer which swells in polar solvents, The reaction of (−)-1,4-ditosylthreitol[13] (**1**) with 4-vinylbenzaldehyde[14] afforded a new styryl monomer, 2-*p*-styryl-4,5-bis(tosyloxymethyl)-1,4-dioxolane (**2**) (mp 84-86° C, $[\alpha]^{25}D$ −30.9° (C2.7, benzene)), which was copolymerized at 70° with hydroxyethyl methacrylate (HEMA). The copolymerization was effected with azobisisobutyronitrile (AIBN), using the reactivity ratios[15] for *p*-methylstyrene and HEMA to incorporate 8 mol % of the styryl monomer **2** (charge: 31 mmol of **2**, 74.78 mmol of HEMA, and 0.1 g of AIBN in 60 ml of benzene). Since hydroxyethyl methacrylate contains ethylene dimethacrylate, a cross-linked copolymer was obtained.[16] This polymer (**3**) was treated with enough sodium diphenylphosphide[1b] in a dioxane-tetrahydrofuran mixture to react with all the hydroxyl functions in the HEMA portion plus the DIOP-tosalate groups to afford the cross-linked, hydrophilic, DIOP-bearing polymer (**4**). This polymer swells in alcohol and other polar solvents, but is insoluble as a result of cross-linking. The swelled gelatinous polymer can be easily filtered from ethanol and methanol.

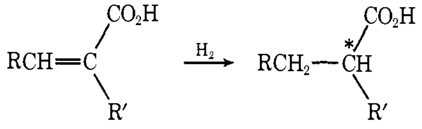
The rhodium complex was attached to the polymer **4** by a simple ligand exchange reaction similar to that used in the preparation of the homogeneous Rh^{I}-DIOP catalyst.[1b]

A typical hydrogenation procedure is as follows; To a 500-ml pressure bottle equipped with a magnetic stirrer under a nitrogen atmosphere, 25 mg (0.064 mmol) of $[RhCl(C_2H_4)_2]_2$, 5 ml of benzene, 15 ml of ethanol, and 1.6 g (0.51 mequiv of phosphorus) of phosphinated polymer **4** was added. The mixture was stirred at room temperature for 48 h under nitrogen to give the light yellow polymer-supported rhodium catalyst (**5**).

The hydrogenation (olefin/Rh = 50) was carried out with hydrogen at 1-2.5 atm at room temperature. As observed with other, similar systems[2i] the optical yield did not change within this pressure range.

The results of asymmetric hydrogenation of olefins catalyzed by polymer-supported complex **5** together with those obtained using the homogeneous Rh^{I}-DIOP complex are shown in Table I. The high optical yields obtained using the polymer-supported catalyst **5** are quite comparable to those obtained with the homogeneous catalyst.[1] The same absolute configuration of the products was also observed. The rates of hydrogenation with polymer-supported catalyst were slower than those with homogeneous catalysts possibly as a result of a slow diffusion of substrate into the polymer.[9,11,17] Although prochiral substrate **6b** was hydrogenated somewhat more slowly than **6a**, a better optical yield was obtained in the hydrogenation of **6b**. The insoluble catalyst could be reused by simple filtration under nitrogen with no loss of optical purity in the products. If, however, the catalyst is exposed to air enantio-

Table I. Asymmetric Hydrogenation of Olefins by Polymer-Supported Rh–DIOP Catalyst[a]



6 7

	R	R′
a	H	$NHCOCH_3$
b	Ph	$NHCOCH_3$
c	H	Ph

Substrate	Time (h)	Conversion[b] (%)	Optical yield[c] (%)	Configuration
a	5	100	52–60[d] (73)[e]	*R*
b	12	100	86 (81)	*R*
c	12	100	58–62[d] (63)	*S*

[a] Phosphinated polymer 4 = 1.6 g (0.51 mequiv of P); $[RhCl(C_2H_4)_2]_2$ = 25 mg (P/Rh = 4); substrate = 6.4 mmol (olefin/Rh = 50); solvent = benzene (5 ml) and ethanol (25 ml). Benzene was not used in recycle runs; reaction temperature = 25°; P_{H_2} = 1–2.5 atm (abs). [b] Conversion was measured by ^1H NMR. [c] Optical yields are calculated with respect to the following values of the optically pure compounds: *N*-acetyl-(*R*)-alanine, $[\alpha]$D +66.5° (*C* 2, H_2O) (S. M. Birbaum, L. Levintow, R. B. Kingsley, and J. P. Greenstein, *J. Biol. Chem.*, 194, 455 (1952)); L-*N*-acetyl-(*S*)-phenylalanine, $[\alpha]^{26}$D + 46.0° (*C* 1, EtOH) (T. P. Dang, J. C. Poulin, and H. B. Kagan, *J. Organomet. Chem.*, 91, 105 (1975); (*S*)-hydratropic acid, $[\alpha]^{25}$ +76.3° (*C* 1.6, $CHCl_3$) (S. P. Bakshi and E. E. Truner, *J. Chem. Soc.*, 171 (1961)). [d] Variations in optical yield were observed between batches; however, the optical yield varied <1%—upon repetitive use of the catalyst when oxygen was strictly excluded. [e] The results obtained using homogeneous Rh^I–DIOP catalyst are shown in parentheses.

selectivity is slowly lost.

Further work on the application of polymer-supported catalyst **5** and its analogues to hydrosilylation and hydroformylation is in progress.

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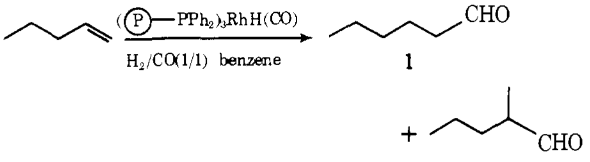
Unusual Selectivities in Hydroformylations Catalyzed by Polymer-Attached $(PPh_3)_3RhH(CO)$

Sir:

Recent studies[1-6] have shown that the use of homogeneous catalysts, attached to polymers, can exhibit several advantages when compared to normal homogeneous application. For example, increased substrate size selectivity,[1,2] increased activity,[3,4] easier catalyst recovery and recycle,[1-6] and protection of catalyst sites from water[6,7] have been demonstrated in various systems. We now present the results of a series of 1-pentene hydroformylations in benzene (eq 1), catalyzed by polymer-attached (Ⓟ—$PPh_2)_3RhH(CO)$,[8] which demonstrate (a) an unusually high linear/branched product selectivity,[9] (b) an unusual temperature dependence of this selectivity, and (c) an unusually high dependence of product selectivity upon pressure. The isomerization of 1-pentene to 2-pentene and production of pentane were not observed under the conditions studied.



1

2

(1)

The normal/branched (i.e., **1**/**2**) selectivity was 12.1 at 100° (16.1 at 120°) and 100 psi using highly phosphinated resin-A (40% of the phenyl rings contain $-PPh_2$ groups, % P = 7.01, P/Rh = 19), while the corresponding homogeneous application of the catalyst[10] (at 100°, 100 psi, P/Rh = 19) only produced a **1**/**2** ratio of 3.3. Similarly, at 140° and 400 psi, the selectivity was 6.1 for resin-A vs. 2.4 for homogeneous runs.[10] Resin-B (32% of the phenyl rings contain $-PPh_2$, % P = 6.16, P/Rh = 15.5) exhibited a selectivity of 4.9 at 800 psi and 70 °C vs. a value of 2.9 for corresponding homogeneous runs.[10] In general, polymer-attached catalysts were notably more selective than their homogeneous counterparts at high phosphine loadings and high P/Rh ratios. At low phosphine loadings and lower P/Rh ratios, the polymer-attached catalysts' selectivity resembled that of the corresponding homogeneous runs (see Figure 1, resin-C, and Table I). The selectivity decreased slightly in homogeneous runs as the temperature was increased (Figure 1). Wilkinson[11] previously observed this phenomena. In sharp contrast to homogeneous systems, selectivity *increased* slightly between 50 and 100 °C and then remained almost constant to 150 °C when resin-A was employed (400 psi). At 100 psi, resin-A exhibited a maximum selectivity of 16.1 at 120 °C. The selectivity, using resin-B at 800 psi, *increases* sharply