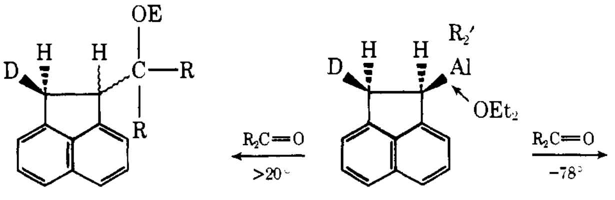
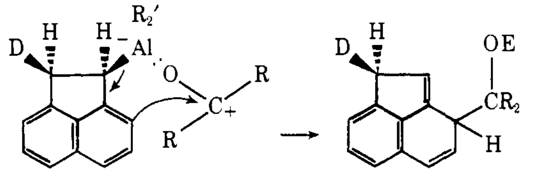
to undergo either protolysis (eq 2) or alkylation (eq 1) at C_1, can be attributed to the greater ease with which the naphthalene ring in **8** can be attacked by a ketone complex (**11**) having carbenium ion character (pathway a, eq 3).



9a, E = $R_2'Al$
b, E = H (after H_3O^+)

8



(4)

11

10a, E = $R_2'Al$
b, E = H (after H_3O^+)

Noteworthy is the observation that **8** reacts with these ketones at higher temperature (20-80°) to yield 1-acenaphthenylcarbinols (**9**), the thermodynamically controlled products, but the transformation of the kinetically controlled products, **10a**, into **9a** seems to involve dissociation into $R_2'Al{:}O{=}CR_2^+$ and $C_{12}H_8D^-$, for the configuration at C_1 in **9a** was shown to have been lost.

The foregoing results demonstrate that direct insertion of ketones into certain carbon-aluminum bonds does not involve synchronous breaking of C-Al bonds and making of C-C bonds, as suggested by the transition states depicted in **1** and **2**. Rather, the loss in configuration for such alkylations is more consistent with the formation of acyclic, carbenium ion intermediates (**6** and **11**), which can decompose stereospecifically with proton transfer (**6** in eq 2) or which can collapse nonstereospecifically to the insertion products (**5** and **9**) or to the allylic rearrangement products (**10a**).

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(10) New compounds gave elemental analyses and spectra in agreement with the assigned structures.

(11) Compound **7** has previously been characterized; cf. ref 9.

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(14) For example the structure of **9b** (R_2CO = 9-fluorenone), mp 172-174°, was established by its ^2H-decoupled NMR spectrum in benzene-d_6 at 60° (δ, TMS): 1.68 (s, OH), 2.30 (d, H_2 cis to fluorenyl group, J_{trans} = 4.0 Hz, 2.77 (br d, H_2 trans to fluorenyl group, J_{cis} = 8.5 Hz), 4.36 (br d, H_1), and 6.25-7.75 (m, aromatic H). The resonance signals at 2.30 and 2.77 ppm each integrated to an intensity of 0.5 proton.

(15) Structure **10b** (R_2CO = acetone) is based upon its NMR spectrum in CCl_4: 1.3 (s, CH_3), 1.9 (s, CH_3 (diastereotopic groups), 2.72 (s, OH), 3.21 (s, C_1H), 3.50 (s, C_3H), 5.70 (d of d, C_4–H, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 4.3 Hz, 6.15 (d, C_2–H, $J_{1,2}$ = 2.4 Hz), 6.44 (d of d, C_5–H, $J_{4,5}$ = 10.0 Hz, $J_{3,5}$ = 2.0 Hz), 6.75-7.5 (m, aromatic). This compound could be dehydrated, with a prototropic shift, to yield 3-isopropenylacenaphthene: mp 50-50.5°; NMR (CCl_4) 2.23 (s, CH_3), 3.25 (s, CH_2CH_2), 5.13 (br d of d, $=CH_2$), and 7.15-7.5 (m, aromatic).

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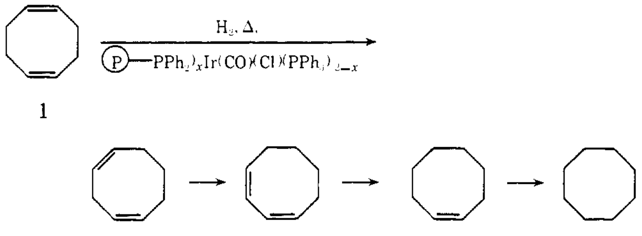
Unusual Rate Effects in the Hydrogenation of 1,5-Cyclooctadiene Catalyzed by Polymer-Anchored $Ir(CO)(Cl)(PPh_3)_2$

Sir:

Increased attention has recently been given to anchoring homogeneous transition metal catalysts to polymers.[1,2] Heterogenized catalysts can have advantages over their homogeneous counterparts such as (1) ease of separation from products,[1-5] (2) enhanced size[3] and positional[6] selectivity, (3) ability to carry out sequential catalytic reactions,[7,8] and (4) the potential isolation of reactive catalytic species which would normally further react.[9] However, the need for reagents to diffuse into cross-linked resins can retard reaction rates.[3,4,10] We now report example catalytic hydrogenations of 1,5-cyclooctadiene (1,5-COD), using resin-anchored $Ir(CO)(Cl)(PPh_3)_2$, which are faster than those catalyzed homogeneously at equivalent P/Ir ratios.[11] Furthermore, the internal mobility of resin-anchored phosphine ligands results in some unusual rate effects on changing temperature and varying the ligand concentration.

1,5-COD, **1**, was selectively hydrogenated over $Ir(CO)(Cl)(PPh_3)_2$ and its styrene-divinylbenzene-anchored analog. Successive isomerization to 1,4-COD, **2**, and 1,3-COD, **3**, occurs followed by hydrogenation to cyclooctene, **4**, and, finally, cyclooctane, **5**.



1

2 3 4 5

A series of diphenylphosphinated resins was prepared,[12] where the per cent P was varied: 1.25% (corresponds to 12% of the rings phosphinated), 1.91 (18), 2.02 (19), 4.02 (38), and 10.28 (96). Each of these resins was treated with $Ir(CO)(Cl)(PPh_3)_2$ to give a series of resin-anchored catalysts where P/Ir ratios of 3, 4, 7, 11, 12, and 22 were achieved. Thus, hydrogenation rates could be studied as a function of the P/Ir ratio over a range of total phosphine levels.

The rates of homogeneously and heterogeneously catalyzed reactions were compared using the same solvent volume and equal amounts of catalyst at equal P/Ir ratios.[13]

When compared at equal P/Ir ratios, the rate of hydrogenation was significantly faster using the anchored catalyst whenever the P/Ir ratio was <5. This occurred even at a high total per cent P on the polymer (where the dissociation equilibria[14-17] Ⓟ-PPh$_2$)$_2$Ir(CO)(olefin)Cl $\rightleftharpoons$ Ⓟ-PPh$_2$ + Ⓟ-PPh$_2$)Ir(CO)(olefin)(Cl) would be repressed). The magnitude of this anchored/homogeneous rate ratio is quite large at low P/Ir ratios as can be seen by comparing reactions 1 with 2 and 3 with 4 in Table I. All these reactions were carried out in benzene at 170° and 150 psi of H_2. Both the anchored and homogeneous complexes were recycled without loss of activity to demonstrate that the homogeneous catalyst did not have an anomolously short lifetime relative to that of the anchored catalyst.[18]

Table I. Comparative 1,5-COD Hydrogenation Rates, Catalyzed by Resin-Anchored or Homogeneous $Ir(CO)(Cl)(PPh_3)_2$ in Benzene at 170° and 150 psi H_2[a,b]

Reaction no.	Mode	P/Ir	Total % P on polymer	Time, hr	Conversion % 4	% 5
1	Homogeneous	3	—	33	37	3
2	Anchored	3	4.02	0.25	57	4
3	Homogeneous	4	—	48	44	3
4	Anchored	4	10.28	0.25	69	5
5	Homogeneous	6	—	72	68	11
6	Anchored	7	4.02	93	5	0
7	Anchored	7	1.25	0.20	68	6
8	Homogeneous	14	—	72	50	1
9	Anchored	12	2.53	94	19	2
10	Anchored	12	4.02	96	6	0
11	Homogeneous	22	—	72	15	0
12	Anchored	22	4.02	93	18	2

[a] All reactions employed 0.064 mmol of Ir, 27.8 mmol of 1,5-COD in 15 ml of benzene. [b] BioRad SX-1 styrene–divinylbenzene (1% divinylbenzene) (200–400 mesh) resin was employed in each reaction. These are swellable microporous resins in contrast to macroporous (macrorecticular) rigid resins.

The anchored/homogeneous rate ratio drops as the P/Ir ratio increases. For example, at P/Ir = 7, the hydrogenation rate, using the anchored catalyst, was slower at 4.02% P (38% of rings phosphinated) but faster at 1.25% P (12% of rings phosphinated) than the corresponding homogeneous rates. Increasing P/Ir to 12 or 20–22, it was found the homogeneous hydrogenation (and 1,5 → 1,4 and 1,4 → 1,3-COD isomerization) rates were greater. This behavior suggests that anchored phosphine moieties are not sufficiently mobile (i.e., on the time scale of key steps in the mechanism) to intercept anchored coordinatively unsaturated Ir intermediates at a rate equivalent to dissolved PPh_3 when P/Ir < 5. This is true even when the anchored phosphine concentration is high (i.e., 4.02 or 10.28%).

An unusual effect of temperature on the activity of the catalyst anchored to SX-1 resins was noted.[19] The ratio of the activity[20] of the anchored catalyst at 170° vs. 80° (a_r = activity at 170°/activity 80°) was measured at several net conversions between 10 and 68% and over a range of total per cent P between 1.91 and 10.28%. This ratio varied from 0.8 to 5. The value of a_r (170° vs. 80°) for the homogeneous catalyst, measured over the same P/Ir ratios, was always larger and was not observed to fall lower than 8-10. Assuming the same mechanism[14] operates over this temperature range, these observations can be tentatively explained in terms of the mobility of anchored -PPh$_2$ groups. This mobility should increase significantly as the temperature is raised from 80 to 170°. Thus, excess anchored -PPh$_2$ can more efficiently repress the dissociation equilibrium at higher temperatures, thereby retarding the rate. If the net activation energy of the isomerization-hydrogenation sequence is fairly low, this increased Ⓟ-PPh$_2$ mobility could retard the rate more than the temperature rise would increase it.

The hydrogenation rate (using the anchored system) decreased as the total per cent P on the polymer was increased, whenever P/Ir > 5, holding the P/Ir ratio constant (i.e., at 7, 11, 12, 22). This is in accord with greater chance of anchored -PPh$_2$ encountering a coordinatively unsaturated metal site as the total P density increases. In the range P/Ir = 3-4, the rates are very sensitive to changes in total per cent P and P/Ir. The role of diffusion was also briefly examined, in independent experiments, by comparing the rates using 1 and 2% divinylbenzene (DVB) resins where P/Ir = both 4 and 12 and total per cent P = 2.0. The rates of isomerization and hydrogenation at 170°, using 1 and 2% DVB, were almost identical. Since the bead size and both P/Ir and per cent P were the same, this shows that diffusion was not limiting at 170°.

The effects of P/Ir and percent P on rates and product selectivity are currently being studied for Ru, Rh, and Ir catalyzed processes.

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(11) The rate using dissolved $(PPh_3)_2Ir(CO)Cl$, without added PPh_3, was almost identical with that of the anchored system where P/Ir = 3.
(12) Styrene–divinylbenzene resins (commercial) were brominated under Freidel–Crafts conditions and then treated with Li^+ or $Na^+PPh_2^-$ as described previously.[4,7,8] BioRad Laboratories SX-1 and SX-2 resins (200–400 mesh) were employed.
(13) Excess PPh_3 was added to $Ir(CO)(Cl)(PPh_3)_2$, employed homogeneously, to achieve ratios >2.
(14) James and coworkers[15] proposed the predissociation equilibria $Ir(CO)(Cl)(PPh_3)_2 \rightleftharpoons Ir(CO)(Cl)(PPh_3) + PPh_3$ accounted for the rate inhibition by PPh_3. More recently Burnett[15] and Strohmeier[16] provided evidence favoring the dississociative equilibrium of the five-coordinate complex $Ir(CO)(Cl)(olefin)(PPh_3)_2$ to $Ir(CO)(Cl)(olefin)(PPh_3)$ to account for the effect of PPh_3 on rate. The four-coordinate species then adds H_2 oxidatively in what was thought to be the rate determining step. In all cases an inverse rate dependence on PPh_3 was found.
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(19) This effect has not yet been studied for the full range of anchored P/Ir ratios or SX-2 resins.
(20) The term activity is used in place of rate since it is difficult to define the value of concentration of catalyst or concentration of phosphine within the polymer matrix. Also the actual concentration of reagents inside the beads may not be the same as in solution. Thus, the ratio of the reaction times it took the reduction to proceed to each specific per cent completion (i.e., 10, 20, 30%, . . .), at 170° vs. at 80°, was used as a definition of activity.

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