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THROUGH-SPACE MOLECULAR INTERACTIONS BETWEEN ACYCLIC POLYETHERS AND RHODIUM(I), WITH PROMOTION OF OXIDATIVE ADDITION

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Summary

The representative oxidative addition reaction of chlorotris(triphenylphosphine)-rhodium(I) with propionyl chloride at 25–35°C is promoted 5–10 fold by linear polyethers at about 10% of the stoichiometric amount of either reactant. Through space molecular interactions occur. The electron density at rhodium(I) is altered by each linear array $\text{-(}CH_2CH_2O\text{)-}_n$, and this is revealed in the perturbation by Rh compounds of resonances at 3.85–3.50 ppm in ^1H NMR spectra of the polyethers. These spectral changes are partially reversed upon addition of deuterium oxide, which successfully competes with the Rh compounds for the ethereal binding sites.

Introduction

Rhodium(I) is an important catalytic center for carbonylation, decarbonylation and hydroformylation; hydrogenation and dehydrogenation; and isomerization, oligomerization and polymerization of alkenes and alkynes [1]. A critical step in each of these homogeneous-phase processes is an oxidative addition [2] to rhodium(I). Studies of chemistry in the homogeneous phase can lead to an improved understanding of heterogeneous systems, where there is a defined need [3] for data on molecular interactions of metallic ions with carbon, hydrogen and oxygen atoms.

Evidence is presented herein for promotion of oxidative addition to rhodium(I) by catalytic amounts of polyethers in anhydrous media [4]. Molecular interactions of polyethers and Rh centers are correlated with specific reaction events by using proton nuclear magnetic resonance (^1H NMR) spectroscopy. Other reports exist [5] where the interaction of oxygen atoms of ethers and alcohols with Rh compounds is utilized to (a) prepare isolable solvates, (b) provide differential bulk-solvent effects on the course of oxidative additions to rhodium(I), (c) promote phase-transfer and micellar-catalyzed reaction sequences in partially aqueous media, (d) transfer hydrogen from the ether or alcohol (as a reactant) to an organic acceptor molecule and (e)

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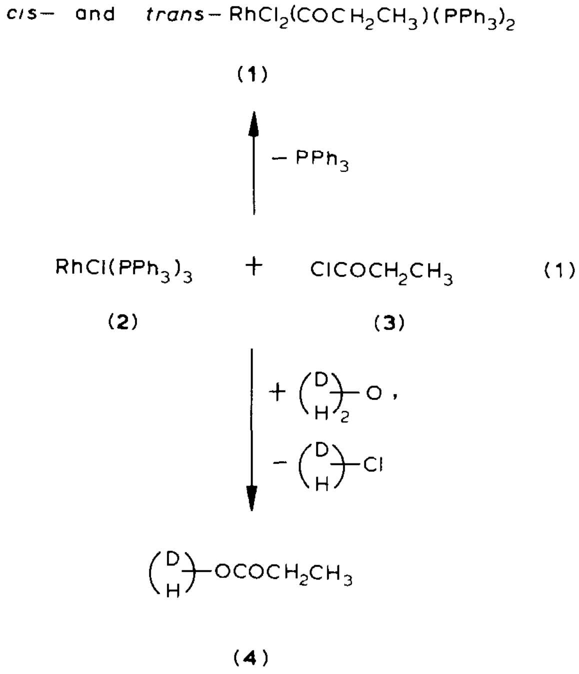
effect [6–10] asymmetric hydrogenation of alkenes. These results all reveal molecular interactions of oxygen-containing compounds with rhodium(I).

Polyethers constitute a special group of ethers. Molecules with more than five or six contiguous ethyleneoxy units exhibit special, ordered conformations [11]. These long $-CH_2CH_2O-$ arrays bind tightly to alkali metal ions [12,13] and, also, confer solubilizing tendencies to some surfactants [14].

Results and discussion

Representative oxidative addition to rhodium(I)

Acylrhodium(III) compounds [$HRh^{III}(COR)L_n$] are key intermediates in hydroformylation processes [15], and they directly arise from oxidative addition of an aldehyde, RCHO, to rhodium(I). Specialized situations [16,17] have yielded stable, isolable hydridoacylrhodium(III) compounds. Similar, but more stable, products [$ClRh^{III}(COR)L_n$; e.g. **1** in eq. 1] are obtained [17] from acyl halides and rhodium(I) reagents, and a study of these products can relate to the chemistry of hydroformylation, decarbonylation via the Tsuji Reaction [19,20] or oxidative additions, in general, with rhodium(I).



Reaction 1 in chloroform (or deuteriochloroform) is free of competitive binding of solvent [18] to **1**, **2** or polyethylene oxides [9]. Progress in reaction 1 can be monitored gas chromatographically (for propionic acid, **4**, a derivative of acyl chloride **3**; cf. Table 1) and spectroscopically for *cis*- and *trans*-**1** (cf. Tables 2 and 3). Quantification of propionic acid (at δ 2.37 ppm (quartet, $-CH_2-$) [21]) reveals that no acid formation occurs prior to introduction of water or deuterium oxide. No hydrolysis or back reaction (to give **4**) of product **1** follows the addition of H_2O or D_2O.

The rate for reaction of **2** and **3** is moderate at room temperature, and the reaction is essentially complete after 15 min. Significantly longer times or higher

TABLE 1

UPTAKE OF ClCOEt BY $RhCl(PPh_3)_3$ [a]

Additive (conc.)	Reaction temperature (°C)	Reaction time (min)	Reaction of ClCOEt (%)
none	33.7 ± 1.6	1.20	8.9
		3.12	47.7
		5.17	84.2
		15.13	87.8
$MeO(CH_2CH_2O)_{10}C_{16}H_{33}$ (**5**) (0.0137 *M*)	29.8 ± 0.4	0.67	72.7
		1.52	86.8
		2.17	88.4
		10.08	87.6
$Ph_2P(CH_2CH_2O)_{10}C_{16}H_{33}$ (**6**) (0.0133 *M*)	29.20 ± 0.02	0.62	85.3
		2.13	87.5
		5.10	89.9
		15.12	85.5

[a] $[RhCl(PPh_3)_3]/[ClCOEt] = 0.141\ M/0.121\text{-}0.123\ M$.

TABLE 2

CHARACTERISTIC NMR SIGNALS FOR $RhCl_2(COEt)(PPh_3)_2$ (**1**) AT 30.0°C

Isomer	^1H NMR values [a]		$^{31}P\{^1H\}$ NMR values [b]
	$-CH_2-$	$-CH_3$	
cis-$RhCl_2(COEt)(PPh_3)_2$, *cis*-**1**	δ 4.02 (quartet, J(H–H) 7.1 Hz)	δ1.17 (t)	δ30.2 (d, J(Rh–P) 168 Hz)
trans-$RhCl_2(COEt)(PPh_3)_2$, *trans*-**1**	δ2.96 (quartet, J(H–H) 7.2 Hz)	δ 0.78 (t)	δ 22.7 (d, J(Rh–P) 113 Hz)

[a] Literature values, ref. 18. [b] Downfield of externally measured 85% H_3PO_4.

TABLE 3

TEMPERATURE DEPENDENCE OF *cis:trans* ISOMER COMPOSITION FOR $RhCl_2(COEt)(PPh_3)_2$ (**1**) [a]

Temperature (°C)	[*cis*-$RhCl_2(COEt)(PPh_3)_2$]/[*trans*-$RhCl_2(COEt)(PPh_3)_2$] [b]
−55	100/0
−30	80/20
0	50/50
+15	40/60
+30	20/80
+30 (after 1 d at room temperature)	15/85 [c]

[a] From $[RhCl(PPh_3)_3]/[ClCOEt] = 0.144\ M/0.126\ M$ after >1.67 min at ~23°C and followed by quenching at liquid nitrogen temperature. [b] Based on relative intensities of ^1H NMR bands for $-CH_3$ (cf. Table 2); to nearest ±5% and following equilibration over ~1/2 h at a given temperature. [c] Based on relative intensities of ^1H NMR bands for $-COCH_2-$ (cf. Table 2).

temperatures [19] are unnecessary for a complete reaction. A 16% conversion of **3** to **1** is found graphically (cf. Table 1), after 1.67 min at 33.7 ± 1.6°C. The same reaction (with $[RhCl(PPh_3)_3]/[ClCOEt] = 0.144\ M/0.126\ M$) was quenched at liquid nitrogen temperature after > 1.67 min at ~ 23°C to show an incomplete conversion (32% based on an alternative measurement at −55°C, of the ^1H NMR band intensity for $-COCH_2-$). The pathway to *cis*- and *trans*-**1** is believed [22] to involve an associative oxidative addition, to form **1** with subsequent elimination of PPh_3 (^{31}P NMR: δ −5.5 to −6.0 ppm). *cis*-Isomer **1** is the kinetically-determined product and *trans*-isomer **1** is the thermodynamically-determined one (cf. Table 3).

The presence of free, unreacted EtCOCl, **3**, in the quenched reaction solution (reaction for > 1.67 min at room temperature, followed by chilling to ≤ −55°C) indicates that the oxidative addition reaction of **3** and $RhCl(PPh_3)_3$ (**2**) is not diffusion-controlled. Therefore, added polyethers may affect the rate of this reaction.

Polyether effects

Added linear polyethers accelerate the rate of the reaction $\mathbf{2} + \mathbf{3} \rightarrow \mathbf{1}$ (eq. 1) [4]. Purified (cf. Table 4) polyethers $CH_3O(CH_2CH_2O)_{10}(CH_2)_{15}CH_3$ (**5**) and $Ph_2P(CH_2CH_2O)_{10}(CH_2)_{15}CH_3$ (**6**) have been used at concentrations ($0.0135 \pm 0.0002\ M$) of 9.6 to 11.2% of the molarity of the reactants **2** and **3**. These organometallic reactions were performed in a glovebag under dry, deoxygenated nitrogen in an oil bath, which was maintained at constant temperature using externally heated and circulated fluid. Close reproducibility of reaction temperatures between runs was not achieved. Investigations with the polyether-containing systems were at 4–5°C below the temperature for the additive-free system; however, the reaction was faster in the presence of either polyether **5** or **6** (cf. Table 1). After a reaction time of three min, the reaction was less than 50% complete with no polyether present; but with either of the polyethers present, the reaction was 85–90% complete at this time. Graphical displays of data in Table 1 illustrate that (a) an induction period exists for oxidative addition of **3** to **2** and that (b) rate enhancement by polyether **6** is somewhat greater than by polyether **5**. Approximate rate constants, which are based on the assumption that reaction between **2** and **3** is simple and bimolecular, are $0.084\ M^{-1}s^{-1}$, $0.49\ M^{-1}s^{-1}$, and $0.78\ M^{-1}s^{-1}$ for the systems with no added polyether, with added **5**, and with **6**, respectively. These parameters can be compared to a value of $0.316\ M^{-1}s^{-1}$ [23] for hydrogenation of cyclohexene in benzene with H_2 and the catalyst $RhCl(PPh_3)_3$ at 25°C.

TABLE 4

ELEMENTAL ANALYSES OF POLYETHERS 5 AND 6

Compound	Composition	Analysis (Found (calcd.) (%))		
		C	H	P
5 [a]	$C_{37}H_{76}O_{11}$	63.82 (63.76)	10.89 (10.99)	–
5·$3H_2O$ [b]	$C_{37}H_{82}O_{14}$	59.43 (59.17)	11.18 (11.01)	–
6 [b]	$C_{48}H_{83}O_{10}P$	67.91 (67.73)	9.84 (9.83)	4.03 (3.64)

[a] Elemental analysis by Galbraith Laboratories, Inc. (Knoxville, TN). [b] Elemental analysis by Baron Consulting Co. (Orange, CT).

The polyether effect requires a significantly lower amount of additive ($\times 10^{-2}$ to $\times 10^{-3}$ of the moles of solvent) and produces a somewhat larger rate effect than has been reported [24–26] for solvent effects on some rhodium(I)-catalyzed reactions. The positive polyether rate effect is attributed to associative ether–rhodium(I) interactions [5] (cf. the section below on ^{1}H NMR). These molecular interactions increase electron density at rhodium(I) and enhance [2] the reactivity of rhodium(I) toward oxidative addition. (A *para*-methoxy substituent on arylphosphine ligands of rhodium(I) participates, instead, in through-bond electron donation to rhodium(I) but shows a similar (eight-fold [27]) rate enhancement for oxidative addition (of methyl iodide) to the rhodium.) Phosphine exchange is not essential to the observed enhancements. A low level of phosphine **6** (vs. phosphine **2**) was employed; phosphine exchange is a relatively slow displacement [22]; and rate enhancement in the propionyl chloride system (eq. 1) even is provided by the phosphine-free polyether **5** (cf. Table 6).

Added polyethers (**5** or **6**) hasten the build-up of product **1** (Table 2). Also, there is preliminary semiquantitative ^{1}H NMR spectral evidence that reaction mixtures which contain polyether **5** consistently exhibit 10–35% more of the *trans*-isomer than is found for analogous polyether-free samples at the same reaction interval (over 5–60 min). In difference with systems containing no polyether or those with added **5**, mixtures which include polyether **6** show some short-term (at reaction times to 45 min) stabilization for *cis*-**1**.

^1H NMR of $-CH_2OCH_2-$ regions; molecular interaction of $-CH_2OCH_2-$ units and rhodium ions

Proton NMR signals at 7.90–6.75, 4.2–3.95 and 3.25–2.80 ppm are characteristic of rhodium compounds **1** and **2**. Signals at 3.85–3.50 ppm are unique to the $-CH_2OCH_2-$ groups of added polyethers **5** or **6** in the reaction shown in eq. 1. Resonances in the region 3.85–3.50 ppm are perturbed by Rh cations, and this observation is substantiated by isolated literature reports. For example, upon incorporation of ethanol into the rhodium compound $[RhH_2(PPh_3)_2(EtOH)_2]^+(ClO_4)^-$, small upfield shifts occur [28] for δ (CH_2) and δ (CH_3) of the ethanol.

Evidence for interaction of rhodium ions with the oxygen of an ether is presented in Tables 5–7. Addition of rhodium compound **2** to polyethers **5** or **6** leads to changes in minor ^{1}H NMR resonances in the region 3.85–3.50 ppm (Table 5). Both

TABLE 5

^{1}H NMR BANDS AT 3.85–3.50 ppm, FOR **5**[a] AND **6**[b] ±**2** AT 30–33°C

Polyether	δ for polyether (only)[c]		δ for polyether + **2**[c]	
	Major band	Minor band(s)	Major band	Minor band(s)
5	3.651–3.62	3.71–3.697	3.643–3.62	3.683–3.678, 3.607–3.57 (2°)
6	3.645–3.63	3.711–3.710, 3.528 (2°), 3.506 (2°)	3.63	3.83–3.81 (2°), 3.60

[a] **5**/**2** = 0.058 *M*/0.143 *M* at 30.0±0.2°C and 0.071 *M*/0.142 *M* at 32–33°C. [b] **6**/**2** = 0.0073 *M*/0.187 *M* at 32–33°C. [c] In ppm.

TABLE 6

TEMPERATURE EFFECT ON ^1H NMR SIGNALS OF **5** + **2** [a]

Temperature, in °C (±0.2°C)	δ, major band	δ, minor band(s)
−30.0	3.670	–
0.0	3.651	3 683
+30.0	3.643–3.62	3.683–3 678, 3.607–3.57 (2°)

[a] 0.058 *M* **5** with 0 143 *M* **2**.

the number of minor resonances and the Δδ between each major resonance and its attendant minor resonances are changed. These minor resonances are of particular interest, and their change upon temperature increase (from −30.0 to +30.0°C) is shown in Table 6 (for a mixture of **5** and **2**). Mixed rhodium compounds also interact with **5** and **6**. This is illustrated in the appearance of several new minor resonances upon contact of these species (Table 7 and also, for **5** and **6** individually, Table 5). These minor resonances at 3.85–3.50 ppm show significant increases in intensity (relative to the intensity of the major resonances in this region) upon contact with **1** and **2**. By contrast, the minor resonances are diminished or totally lost, if deuterium oxide is added to reaction mixtures of **1** and **2** which also contain **5** or **6**. Water competes with rhodium ions for binding of oxygen sites of the polyethers, and the strong tendency of the polyethers to complex with water is further established by isolation of the complex **5** · $3H_2O$ (cf. Table 4 for an elemental analysis).

Conclusions

The multiple oxygen atoms in each molecule of a polyether provide a high local concentration of ether units for molecular interactions with rhodium(I). These through-space molecular interactions increase the electron density at rhodium(I) loci. Consequently, the rate of oxidative addition to rhodium(I) is enhanced. For these favorable associations, anhydrous reaction media are a prerequisite. Water success-

TABLE 7

COMPOSITE OF ^1H NMR BANDS AT 3.85–3.50 ppm, FOR **5** AND **6** WITH RHODIUM COMPOUNDS **1** AND **2**

Band intensity	δ values (ppm)	
	For polyether **5** [a]	For polyether **6** [b]
major	3.64–61	3.63–3.58
minors	3.85–3.79,	3.80–3.78,
	3.76–3.72,	3.75–3 74,
	3.69–3 67,	3.69,
	–	3.65–3.64,
	3.61–3.56	3.57–3.53

[a] 0.07 *M* **5** and 0.14 *M* Rh compounds at 32–33°C. [b] 0.007 *M* **6** and 0.19 *M* Rh compounds at 32–33°C

fully competes with Rh ions for polyether oxygen atoms; water destroys beneficial interactions between ethers and rhodium(I).

Experimental

GLC was performed on a Hewlett–Packard 5730A chromatograph equipped with a 5880A Series terminal, a thermal-conductivity detector (carrier gas He, temperature 70°C), and glass injection port liners (which were loaded with silica gel). The single column (6′ × 1/8″ OD, Ni) contained supported SE-30 (5%). NMR spectra were recorded on a Hitachi–Perkin–Elmer R-20A instrument (^{1}H NMR (60 MHz; 32–33°C probe temperature)) or a JEOL FX-90Q instrument (^{1}H NMR (89.55 MHz), ^{31}P{^{1}H}NMR (36.23 MHz), ^{13}C{^{1}H} NMR (22.49 MHz) at 30.0 ± 0.2°C, unless otherwise specified) in $CDCl_3$ with $SiMe_4$ as an internal standard. A literature preparation [29] for $RhCl(PPh_3)_3$ was followed. All open rhodium-containing solutions were manipulated in a glovebag under dried, deoxygenated nitrogen. Liquid compounds were dried and deoxygenated.

Kinetic studies. Solutions were stirred (at one rate) and equilibrated in the constant temperature bath (over ≥ 10 min) prior to addition of each reaction component. Dried and deoxygenated compounds **5** and **6** were added as solutions (in $CDCl_3$) and propionyl chloride was distilled prior to each (duplicate) set of runs. Timed aliquots of reacted liquors were quenched with metered H_2O (combined with a known volume of the solubilizer t-BuOH) and, then, stored at 0–5°C prior to their GLC analyses. A series of $EtCO_2H$-containing knowns was prepared daily for the determination of GLC standardization curves.

*Formation of **1**; polyether effect.* A polyether-free (control) run contained 0.141 *M* **2** and 0.124 *M* **3** in $CDCl_3$. Concentrations in this and in the polyether-containing runs were compared semi-quantitatively via repeated scanning of ^{1}H NMR spectra (60 MHz; 32–33°C probe temperature) over the interval of 7–60 min. After 60 min, D_2O (in stoichiometric excess of **3**) was added.

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