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Kinetics and Mechanism of the Hydrogenolysis of a Ruthenium(II) Acyl Complex

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N,N′-Dimethylacetamide (DMA) and toluene solutions of the acyl complex dicarbonylchloronorbornenoylbis(triphenylphosphine)ruthenium(II), $RuCl(COC_7H_9)(CO)_2(PPh_3)_2$ (**1**), react with 1 mol equiv of H_2 to give $RuHCl(CO)_2(PPh_3)_2$ (**2**) and the unsaturated aldehyde product 2-norbornene-5-carboxaldehyde, C_7H_9CHO (**3**). A subsequent, relatively slow hydrogenation of C_7H_9CHO by a further 1 mol of H_2 to give the saturated aldehyde norbornane-2-carboxaldehyde, $C_7H_{11}CHO$ (**4**), is catalyzed by **2**. A detailed kinetic study on the hydrogenolysis of **1** in DMA at 65 °C reveals a first-order rate dependence on total Ru concentration, an inverse dependence on added PPh_3 ligand concentration, and a first- to zero-order dependence on H_2 pressure. A mechanism involving PPh_3 dissociation as the first step followed by hydrogenolysis of the resulting intermediate accounts for these observations. Values of k_1 and k_{-1}/k_2 in DMA have been evaluated at 65 °C ($k_1 = 4.5 \times 10^{-5}\ s^{-1}$, $k_{-1}/k_2 = 1.6$) and the activation parameters for the k_1 step determined ($\Delta H^\ddagger = 69 \pm 7$ kJ mol^{-1}, $\Delta S^\ddagger = -126 \pm 13$ J K^{-1} mol^{-1}); k_1 and k_{-1} are the rate constants for the dissociation and reassociation of PPh_3, and k_2 is the rate constant for the hydrogenolysis step. The activation parameters for the corresponding k_1 step in toluene solution are very different; $\Delta H^\ddagger = 128 \pm 13$ kJ mol^{-1}, $\Delta S^\ddagger = +62 \pm 6$ J K^{-1} mol^{-1}. Association of DMA in the transition state is proposed to account for the differences. Rough estimates of the rate of the hydrogenolysis step, and a Ru–P solution bond dissociation energy (assuming the kinetic intermediate in toluene is five-coordinate), are presented, as well as a discussion on the nature of the hydrogenolysis step.

Introduction

Homogeneous hydroformylation of alkenes mediated by transition-metal complexes has been the subject of extensive research.[1] Hydrogenolysis of a transition-metal acyl complex to afford the product aldehyde and the metal hydride complex—often the catalyst precursor—is the final step in both stoichiometric and catalytic hydroformylation of alkenes. Generation of aldehyde from, for example, a cobalt acyl can be accomplished also by using a cobalt hydride, but under hydroformylation conditions hydrogenolysis by H_2 seems to prevail.[2-4] The kinetics and mechanisms of earlier steps in hydroformylation, such as formation of metal alkyls[5] and subsequent CO migratory insertion to give corresponding acyl intermediates,[6,7] have been studied in much detail. In contrast, there are very few reports of kinetic studies on the final, product-forming, H_2-hydrogenolysis step, the general instability of acyl complexes constituting a major hurdle. Acyl complexes, especially those containing group VIII metals, are kinetically unstable and may undergo facile carbonyl migratory deinsertion,[8] as well as reductive-elimination reactions.[7] The work of Markő, Ungvàry, and co-workers[4] and the earlier report in 1971 by Thomas[9] concern hydrogenolysis of cobalt acyl complexes and are probably the only such kinetic studies described so far. No kinetic studies on H_2-hydrogenolysis of ruthenium acyl complexes have been reported.

Earlier work from this laboratory has reported on the synthesis and characterization of the stable six-coordinate ruthenium acyl complex $RuCl(COC_7H_9)(CO)_2(PPh_3)_2$ (**1**).[10] This complex appeared to be an excellent candidate for conducting a detailed investigation into the hydrogenolysis reaction, and described here are the results of this investigation in *N,N′*-dimethylacetamide (DMA)[11] and toluene solutions.

Experimental Section

All synthetic reactions were carried out with use of standard Schlenk techniques. All solvents were dried over appropriate drying agents, distilled under N_2, and degassed prior to use. The gases argon (HP), nitrogen (USP), and carbon monoxide (CP) were used without further purification. Hydrogen (USP) was passed through an Engelhard Deoxo catalytic hydrogen purifier to remove traces of oxygen. Reagent grade triphenylphosphine (Strem) was used as supplied. Norbornadiene (Eastman) was purified by passing through a column of activated alumina prior to use. 5-Norbornene-2-carboxaldehyde (Aldrich) was purified by vacuum distillation at 58–60 °C and stored under argon.

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[2] The nondetection of $CoH(CO)_4$ by IR spectroscopy under hydroformylation conditions, in the $Co_2(CO)_8$-catalyzed system, has been considered consistent with this,[3] while the more recent work of Markő, Ungvàry, and co-workers reveals more substantial evidence.[4]

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[10] (a) Dekleva, T. D. Ph.D. Dissertation, The University of British Columbia, Vancouver, BC, Canada, 1983. (b) Dekleva, T. D.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1350.

[11] Joshi, A. M. M.Sc. Dissertation, The University of British Columbia, Vancouver, BC, Canada, 1986.

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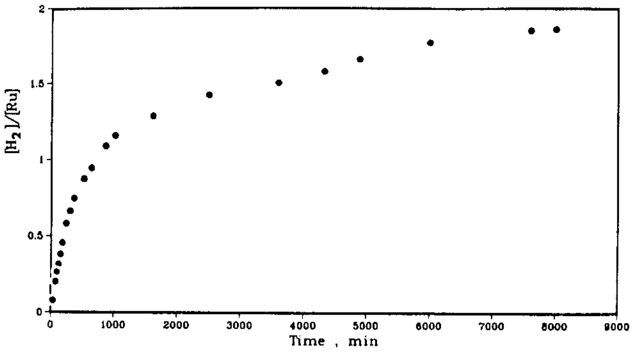


Figure 1. Uptake of H_2 by a DMA solution of $RuCl(COC_7H_9)(CO)_2(PPh_3)_2$ (1) at 4.56×10^{-3} M (65 °C under 760 Torr of H_2).

Norbornane-2-carboxaldehyde was prepared by hydrogenation of a methanol solution of the norbornene precursor under H_2 pressure (4 atm) with Pd/C as catalyst; methanol was pumped off and the product purified by distillation.

The norbornadiene complex $RuHCl(C_7H_8)(PPh_3)_2$ was prepared by a published procedure;[12] the norbornenoyl complex $RuCl(COC_7H_9)(CO)_2(PPh_3)_2$ (1) was synthesized by carbonylation of a benzene solution of $RuHCl(C_7H_8)(PPh_3)_2$ and fully characterized spectroscopically, as reported earlier.[10] Anal. Calcd for 1, $C_{46}H_{39}O_3ClP_2Ru$: C, 65.91; H, 4.66; Cl, 4.24. Found: C, 65.75; H, 4.61; Cl, 4.11. IR (Nujol, cm^{-1}): ν_{CO} 2024 s, 1940 vs, 1910 sh; $\nu_{C=O}$ 1610 w. $^{31}P\{^1H\}$ NMR (ppm): 30.4 (s, DMA, C_6D_6 lock). The white hydrido carbonyl complex $RuHCl(CO)_2(PPh_3)_2$ (2) was prepared by carbonylation of $RuHCl(PPh_3)_3{\cdot}C_6H_6$ in DMA solvent.[13] Anal. Calcd for 2, $C_{38}H_{31}O_2ClP_2Ru$: C, 63.55; H, 4.32. Found: C, 63.15; H, 4.35. IR (Nujol, cm^{-1}): ν_{CO} 2043, 2035, 1993, 1982 (all s). ^1H NMR ($CDCl_3$ ppm): δ(Ru-H) -4.50 (t, ^2J(P-H) = 19.4 Hz). $^{31}P\{^1H\}$ NMR (ppm): 39.5 (s, DMA, C_6D_6 lock). Of a number of possible geometrical isomers of 2, only one has been isolated in pure form (a white solid) and assigned the cis-cis-trans structure shown in eq 1.[13,14]

Infrared spectra were recorded on a Nicolet 5DX FT-IR spectrophotometer as Nujol mulls between CsI plates. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker WP80 (80 MHz for ^1H, 32.44 MHz for ^{31}P) and Varian XL-300 (300 MHz for ^1H, 121.42 MHz for ^{31}P) FT-NMR spectrometers. All ^{31}P NMR shifts are reported relative to 85% H_3PO_4, with downfield shifts taken as positive. Gas chromatographic anlayses were performed on a Carle AGC311 (constant temperature) gas chromatograph equipped with thermal conductivity and flame ionization detectors, using an OV101 (3 m, packed) column and helium as the carrier gas.

Gas-uptake measurements for stoichiometric or kinetic studies, and hydrogen solubility measurements,[15,16] in DMA and toluene solvents were performed on a conventional constant-pressure, constant-temperature gas-uptake apparatus. The hydrogen gas uptakes by solutions of 1 were measured at total ruthenium complex concentrations, $[Ru]_T$, ranging from 2.5×10^{-3} to 8.0×10^{-3} M at different H_2 pressures (190–760 Torr), and at various temperatures (45–70 °C), with only one parameter being changed at a time. The general procedure employed for gas-uptake measurements has been described elsewhere.[17]

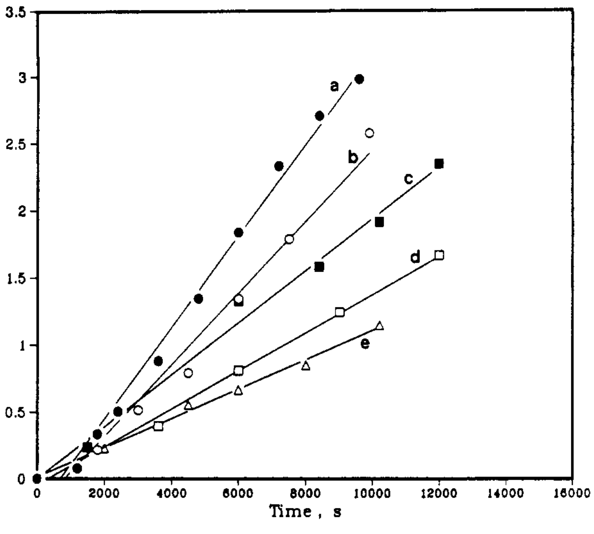
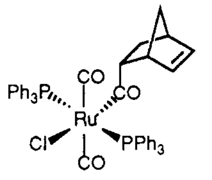


Figure 2. H_2-uptake plots for the hydrogenolysis of 1 in DMA at 65 °C at various $[Ru]_T$ (10^{-3} M): (a) 7.58; (b) 6.03; (c) 4.81; (d) 3.88; (e) 2.50.

Results

The DMA solutions of 1 absorbed about 1 mol equiv of hydrogen over ~20 h at 65 °C, under 1 atm of H_2 (Figure 1). An extremely slow absorption of H_2 was then noted beyond the first 1 mol equiv of H_2 uptake, until finally ~1.9 equiv of H_2 per Ru was consumed in 130 h (Figure 1). These observations are explained (see below) by (i) hydrogenolysis of 1 by the first 1 mol of H_2 leading to the hydridoruthenium product 2 and the corresponding aldehyde 3 (eq 1)

$$\underset{1}{RuCl(COC_7H_9)(CO)_2(PPh_3)_2} + H_2 \rightarrow \underset{2}{RuHCl(CO)_2(PPh_3)_2} + \underset{3}{C_7H_9CHO} \quad (1)$$



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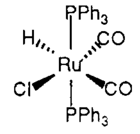

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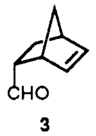
followed by (ii) a relatively slow hydrogenation of the unsaturated aldehyde 3 to the saturated aldehyde 4 by a second 1 mol of H_2 (eq 2).

$$\underset{3}{C_7H_9CHO} + H_2 \rightarrow \underset{4}{C_7H_{11}CHO} \quad (2)$$



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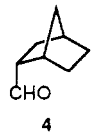

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The hydrogenolysis of 1 in DMA was also monitored by ^{31}P NMR spectroscopy (C_6D_6 lock). The singlet for 2 appeared at 39.5 ppm and grew in intensity as the hydrogenolysis reaction proceeded; after ~1 mol equiv of H_2 uptake, the ^{31}P NMR signal due to 1 (30.4 ppm) had disappeared. Removal of solvent from the reactant solution at this stage yielded a pale yellow solid. This was identified as 2 by comparison of the various spectroscopic

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[12] Hallman, P. S.; McGarvey, B. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3143.

[13] (a) James, B. R.; Markham, L. D. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 373. (b) James, B. R.; Markham, L. D.; Hui, B. C.; Rempel, G. L. *J. Chem. Soc., Dalton Trans.* **1973**, 2247.

[14] Examination of the $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 25 °C) of 2 shows the substituted, ortho, and meta carbon resonances of the phenyl groups of PPh_3 as apparent 1:2:1 triplets, with $|J(CP) + J(CP')|$ values of 46.6, 13.3, and 9.5 Hz, respectively,[10a] indicative of mutually trans PPh_3 ligands; see: Mann, B. E.; Shaw, B. L.; Stainbank, R. E. *J. Chem. Soc., Chem. Commun.* **1972**, 151.

[15] H_2 solubility data at various temperatures, expressed as Henry's law constant $K = [H_2]/(H_2 \text{ pressure})$ (10^6 M $Torr^{-1}$): in DMA, 2.32 (30 °C), 2.70 (50 °C), 2.82 (60 °C), and 2.86 (65 °C); in toluene,[16] 3.32 (46 °C), 3.39 (50 °C), and 3.48 (55 °C).

[16] *Solubility Data Series (IUPAC)*; Young, C. L., Ed.; Pergamon Press: New York, 1981; Vol. 5/6 (Hydrogen and Deuterium), p 169.

[17] (a) James, B. R.; Rempel, G. L. *Discuss. Faraday Soc.* **1968**, *46*, 48. (b) *Can. J. Chem.* **1966**, *44*, 233. (c) James, B. R.; Mahajan, D. *Isr. J. Chem.* **1977**, *15*, 214.

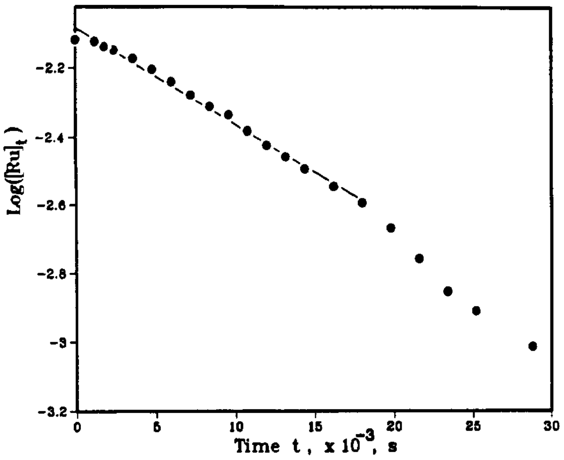

Figure 3. H_2-uptake plot analyzed for a first-order dependence on Ru, assuming the 1:1 H_2:Ru stoichiometry of reaction 1 ([1] = 7.58 × 10^{-3} M, at 65 °C in DMA at 760 Torr of H_2). k_{obs} from the slope of the line is 4.62 × 10^{-5} s^{-1}; the value from the initial rate measurement is 4.45 × 10^{-5} s^{-1}.

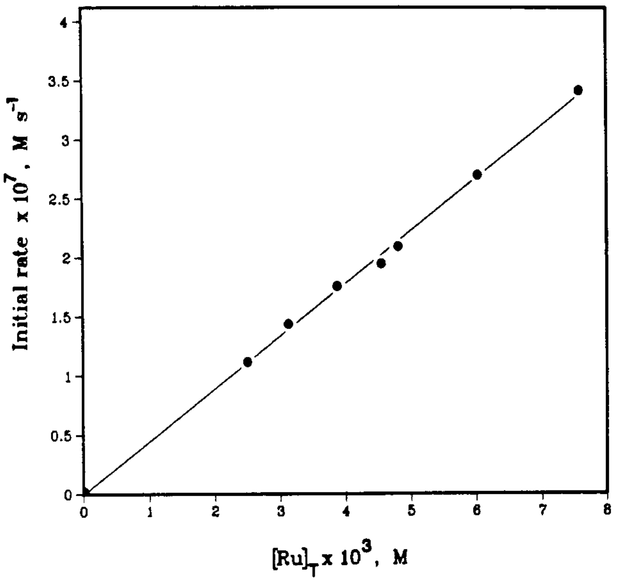

Figure 4. Dependence of the initial rate of hydrogenolysis of 1 on $[Ru]_T$ in DMA at 65 °C and 760 Torr of H_2.

data ($^{31}P\{^1H\}$ and ^1H NMR shifts, carbonyl bands in IR spectra) with those observed for an authentic sample of 2, which is a white solid, however. The yellow color of the solid is presumed to be due to the presence of small amounts of an intense yellow photoisomerization product of 2, as evidenced by a weak, characteristic IR absorption band at ~1885 cm^{-1}.[18] The inorganic product of the hydrogenolysis of 1 in toluene was also identified as 2.

The unsaturated aldehyde product 3 formed during the hydrogenolysis and its subsequent hydrogenation product 4 were detected and identified by comparison with 5-norbornene-2-carboxaldehyde and norbornane-2-carboxaldehyde, respectively, with use of gas chromatography[19] and IR spectroscopy. Trace amounts of the saturated aldehyde 4 could be detected by GC after approximately 0.9 mol equiv of H_2 uptake.

The rates of hydrogen uptake by 1 (Figure 2) remained close to linear over a longer range (up to ~0.3–0.4 mol equiv) than expected for pseudo-first-order behavior, presumably because of an additional contribution from the concurrent hydrogenation of 3 according to eq 2. Kinetic data, as readily measured initial rates, for the hydrogenolysis of 1 in DMA at 65 °C are summarized in Table I. For an in-depth kinetic study, DMA was chosen as the solvent over toluene because of the convenient lower vapor pressure of the former (10–35 Torr)[20] compared to that of

Table I. Kinetic Data for Hydrogenolysis of $RuCl(COC_7H_9)(CO)_2(PPh_3)_2$

$10^3[Ru]_T$, M	P_{H_2}, Torr	$10^3[H_2]$, M	init rate × 10^7, M s^{-1}
	In DMA at 65 °C		
2.50	760	2.17	1.11
3.13	760	2.17	1.42
3.88	760	2.17	1.75
4.56	760	2.17	1.95
4.81	760	2.17	2.09
6.03	760	2.17	2.69
7.58	760	2.17	3.40
4.56	660[a]	1.89	1.96
4.56	660	1.89	1.93
4.56	570	1.63	1.99
4.56	380	1.09	1.91
4.56	190	0.54	2.01
4.56	760	2.17	1.22[b]
4.56	570	1.63	1.09[b]
4.56	300	0.86	0.73[b]
4.56	760	2.17	0.73[c]
4.56	760	2.17	0.53[d]
4.56	760	2.17	0.46[e]
4.56	760	2.17	0.00[f]
	In Toluene at 46 °C		
2.84	690	3.02	0.406
3.02	690	3.02	0.417
4.21	690	3.02	0.639
2.84	690	3.02	~0.002[g]
2.50	350[h]	1.53	0.393

[a] CO added at 100 Torr; total pressure 760 Torr. [b–f] In the presence of added $[PPh_3]$; *b–f* = 0.97 × 10^{-3} 2.42 × 10^{-3} 3.87 × 10^{-3} 4.83 × 10^{-3} and 4.56 × 10^{-3} M, respectively. [g] At added $[PPh_3]$ = 2.0 × 10^{-2} M. [h] Argon added at 440 Torr; total pressure 790 Torr.

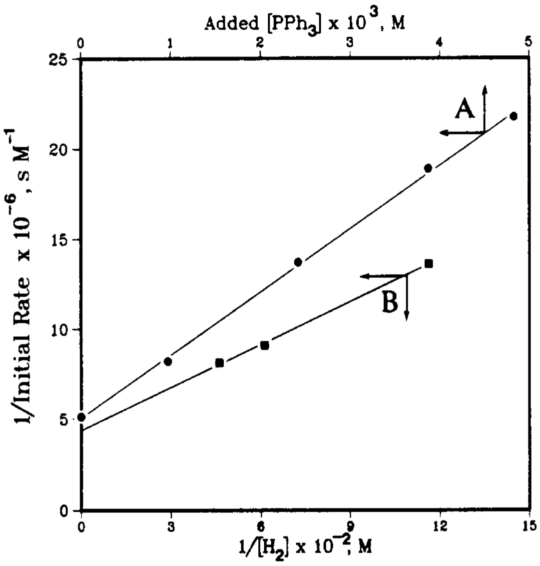

Figure 5. (A) Dependence of (initial rate)$^{-1}$ on added $[PPh_3]$ at $[Ru]_T$ = 4.56 × 10^{-3} M (760 Torr of H_2, in DMA at 65 °C; see Table I (footnotes *b–f*) and eq 8). (B) Dependence of (initial rate)$^{-1}$ on $[H_2]^{-1}$ at $[Ru]_T$ = 4.56 × 10^{-3} M and added $[PPh_3]$ = 9.7 × 10^{-4} M (in DMA at 65 °C; see Table I (footnote *b*) and eq 8).

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(18) Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1977**, *16*, 744.

(19) Retention times of 14.8 and 13.0 min for 3 and 4, respectively, at 100 °C (OV 101 3-m packed column, FID, carrier gas helium at 30 mL/min).

(20) *N,N'*-Dimethylacetamide *General Information Bulletin*; Industrial and Biochemicals Department, E. I. du Pont de Nemours and Co.: Wilmington, DE, 1962.

Table II. Dependence of k_{obs} on Temperature[a]

solvent	temp, K	$10^5 k_{obs}$, s^{-1}	solvent	temp, K	$10^5 k_{obs}$, s^{-1}
DMA	323	1.40	toluene	319	1.49
	328	2.31		323	2.60
	333	2.97		328	5.92
	338	4.45			
	343	7.05			

[a] Errors in k_{obs} are estimated at 5–10%.

toluene (100–300 Torr)[21] over the temperature range employed (45–70 °C). The individual rate plots could be analyzed reasonably well for a first-order dependence on [Ru] (Figure 3), while the plot of initial rates against $[Ru]_T$ is linear (Figure 4) with the pseudo-first-order rate constant k_{obs} being obtained from the slope.

The influence of added PPh_3 was investigated at $[Ru]_T = 4.56 \times 10^{-3}$ M, under 760 Torr of hydrogen pressure. The rate of hydrogenolysis decreased with added phosphine, and at an ~10-fold excess of PPh_3 no hydrogen uptake was observed over 24 h (Table I); a plot of 1/rate vs added $[PPh_3]$ is linear (Figure 5A).

The effect of varying the H_2 pressure (P_{H_2}) was also studied at $[Ru]_T = 4.56 \times 10^{-3}$ M without and with added PPh_3 (Table I). In the absence of added phosphine, a zero-order dependence on H_2 pressure was observed from 760 to 190 Torr, while at the added PPh_3 concentration of 9.7×10^{-4} M, decreases in the rate of hydrogenolysis were observed on decreasing the H_2 pressures from 760 to 300 Torr (Table I); for these latter data, a plot of 1/rate vs $1/[H_2]$ is linear (Figure 5B). For a reaction carried out under a mixture of H_2 and CO ($P_{H_2} = 660$ Torr, $P_{CO} = 100$ Torr), the initial rate was essentially the same as that measured under just 660 Torr of H_2 (Table I).

An initial rate of $\sim 3.5 \times 10^{-8}$ M s^{-1} was measured for the "initial" consumption of the second 1 mol of H_2 at 65 °C and 760 Torr of H_2 pressure ($[Ru]_T = 4.56 \times 10^{-3}$ M) in the range 0.95–1.20 mol equiv of H_2 uptake. A DMA solution of **3**, in the presence of a stoichiometric amount of **2**, slowly absorbed H_2 at 65 °C, with an initial rate of the same order of magnitude ($\sim 10^{-8}$ M s^{-1}) as that observed for the "start" of the second mole of H_2 uptake by solutions of **1** at corresponding Ru concentrations. The hydrogenation of **3** was also found to be catalyzed by **2** at 65 °C in DMA; with $[\mathbf{2}] = 4.00 \times 10^{-3}$ M and $[\mathbf{3}] = 0.17$ M ($[\mathbf{3}]/[\mathbf{2}] = 42$), an initial linear rate of 1.35×10^{-6} M s^{-1} was observed.

The initial rates for hydrogenolysis of **1** were also measured in toluene, in the temperature range 45–55 °C ($[Ru]_T = (2.5\text{–}4.5) \times 10^{-3}$ M, $P_{H_2} = 690$ Torr); at three temperatures the plots of initial rates vs $[Ru]_T$ were linear, with the pseudo-first-order rate constant being obtained from the slope. The rate data in toluene at 46 °C are listed in Table I. The hydrogenolysis of **1** in toluene (as in DMA) is inhibited by added phosphine, and at a 7-fold excess of PPh_3 (Table I) little hydrogen uptake was observed over 24 h at 46 °C. A single H_2-uptake experiment under 350 Torr of H_2 pressure, in the absence of added PPh_3 (Table I), reveals a zero-order dependence on H_2 pressure for the hydrogenolysis rate in toluene (at least for $P_{H_2} = 350\text{–}690$ Torr).

Analysis of the Kinetic Data. For reaction 1 in DMA, to explain the first-order dependence on $[Ru]_T$, the inverse dependence on added $[PPh_3]$, and the first- to zero-order dependence on H_2 pressure, the mechanism shown by eqs 3–5 is proposed, where k_1, k_{-1}, and k_2 are the rate constants of the individual steps and K' (which has to be large, see below) represents the equilibrium constant for reaction 5.

$$\underset{\mathbf{1}}{RuCl(COC_7H_9)(CO)_2(PPh_3)_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{1a}}{[RuCl(COC_7H_9)(CO)_2(PPh_3)]} + PPh_3 \quad (3)$$

$$[RuCl(COC_7H_9)(CO)_2(PPh_3)] + H_2 \xrightarrow{k_2} [RuHCl(CO)_2(PPh_3)] + C_7H_9CHO \quad (4)$$

$$[RuHCl(CO)_2(PPh_3)] + PPh_3 \overset{K'}{\rightleftharpoons} \underset{\mathbf{2}}{RuHCl(CO)_2(PPh_3)_2} \quad (5)$$

Application of the steady-state treatment to the intermediate $[RuCl(COC_7H_9)(CO)_2(PPh_3)]$ gives the rate law

$$\text{rate} = -\frac{d[Ru]}{dt} = \frac{d[H_2]}{dt} = \frac{k_1 k_2 [Ru][H_2]}{k_{-1}[PPh_3] + k_2[H_2]} \quad (6)$$

At constant $[H_2]$ and constant $[PPh_3]$, the rate equation (eq 6) reduces to

$$\text{rate} = k_{obs}[Ru]$$

where

$$k_{obs} = \frac{k_1 k_2 [H_2]}{k_{-1}[PPh_3] + k_2[H_2]} \quad (7)$$

The ruthenium dependence, measured in the absence of added PPh_3, is first order as is evident particularly from the straight-line plot shown in Figure 4; this requires that the $k_{-1}[PPh_3]$ term remain effectively constant and/or negligible. The independence of the reaction rate on $[H_2]$, under the conditions at which the Ru dependence was measured, requires that $k_2[H_2] \gg k_{-1}[PPh_3]$, and this, coupled with what must be a large value for K' (since the product is $RuHCl(CO)_2(PPh_3)_2$ and $[PPh_3]$ cannot increase markedly during any single run), leads to the simple first-order dependence on metal concentration ($k_{obs} = 4.45 \times 10^{-5}$ s^{-1} at 65 °C, from Figure 4).

For initial rates, eq 6 applies, with [Ru] = initial total amount ($[Ru]_T$), and the equation can be rearranged to give

$$\frac{1}{\text{initial rate}} = \frac{k_{-1}[PPh_3]}{k_1 k_2 [Ru]_T [H_2]} + \frac{1}{k_1 [Ru]_T} \quad (8)$$

At constant $[Ru]_T$ and $[H_2]$, therefore, the plot of 1/rate vs added $[PPh_3]$ should be linear; the rate constant k_1 and the relative magnitudes of k_{-1} and k_2 can be obtained from the intercept and the slope, respectively. Values of $k_1 = 4.5 \times 10^{-5}$ s^{-1} and $k_{-1}/k_2 = 1.6$ are obtained from such a plot (Figure 5A) for the conditions shown at 65 °C.

Under the conditions where $k_{-1}[PPh_3] \ll k_2[H_2]$, in the absence of added PPh_3, eq 6 reduces to

$$\text{initial rate} = k_1 [Ru]_T \quad (9)$$

which is independent of $[H_2]$, as found experimentally (see Table I). However, the rate dependence on $[H_2]$ should eventually go from zero to first order as the hydrogen concentration is lowered, when $k_{-1}[PPh_3]$ becomes comparable to $k_2[H_2]$. Further, the rate should become strictly first order in $[H_2]$, if and when $k_{-1}[PPh_3] \gg k_2[H_2]$. The $k_{-1}[PPh_3] \gg k_2[H_2]$ condition was achieved by addition of PPh_3, although such an addition also resulted in an overall lowering of the rates due to the inverse dependence on $[PPh_3]$. The effect of $[H_2]$ on the rate, at an added $[PPh_3]$ of 9.7×10^{-4} M (Table I), is apparently not large enough to obtain a strictly first-order H_2 dependence; nevertheless, the decrease in the rate with the lowering of

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[21] *Handbook of Chemistry and Physics*, 56th ed. Weast, R. C., Ed.; CRC Press: Cleveland, OH, 1975; p D-198.

H_2 pressure reveals the required zero- to first-order transition. According to eq 8, the plot of 1/rate against $1/[H_2]$, at constant $[Ru]_T$ and $[PPh_3]$, is expected to yield a straight line; for the conditions shown, such a plot is linear (Figure 5B) and values of $k_1 = 5.0 \times 10^{-5}$ s^{-1} and $k_{-1}/k_2 = 1.9$ at 65 °C are calculated from the intercept and the slope, respectively, of the limited data. The agreement with the values obtained from the phosphine-dependence data (Figure 5A) is good, and the internal consistency strongly supports the suggested mechanism.

The dependence of k_{obs} on temperature in DMA was studied in the range 50–70 °C, under conditions where (at least at 65 °C) k_{obs} approximates closely to k_1; the data are summarized in Table II. The plot of ln (k_{obs}/T) vs $1/T$ yields a good straight line, from which values of $\Delta H^{\ddagger} = 69 \pm 7$ kJ mol^{-1} and $\Delta S^{\ddagger} = -126 \pm 13$ J K^{-1} mol^{-1} are calculated.

The kinetic data obtained for reaction 1 in toluene are limited, first order in Ru, zero order in H_2 in the absence of added PPh_3, and an inverse dependence on added PPh_3, but are sufficient to indicate that the same mechanism of eqs 3–5 pertains. The k_{obs} values listed in Table II are again presumed to be k_1 values, and the limited Eyring plot is linear, yielding values of $\Delta H^{\ddagger} = 128 \pm 12$ kJ mol^{-1} and $\Delta S^{\ddagger} = 62 \pm 6$ J K^{-1} mol^{-1} for the activation parameters in toluene.

Discussion

The approximately 2 mol equiv of H_2 uptake by solutions of **1** is explained by the hydrogenolysis of **1** (eq 1) and the subsequent hydrogenation of the unsaturated aldehyde product **3** to the saturated aldehyde **4** (eq 2). The inorganic product of the hydrogenolysis reaction is identified as **2**.

Independent measurements of H_2 uptake by DMA solutions of **3** in the presence of **2**, at 65 °C, show that the hydrogenation to **4** is catalytic in **2**; with $[\mathbf{2}] = 4.00 \times 10^{-3}$ M, initial rates of 3.8×10^{-8} and 1.35×10^{-6} M s^{-1} are obtained for $[\mathbf{3}]/[\mathbf{2}] = 1$ and 42, respectively. If the catalytic system were first order in the aldehyde substrate concentration, then the expected initial catalytic rate would be $\sim 1.6 \times 10^{-6}$ M s^{-1} $(3.8 \times 10^{-8} \times 42)$, under the conditions mentioned above. This is close to the experimentally noted 1.35×10^{-6} M s^{-1} value and strongly indicates that the catalytic rate is first order in [**3**]. These data are also consistent with the rate of consumption of the second 1 mol equiv of H_2 ($\sim 3.5 \times 10^{-8}$ M s^{-1}; $[Ru]_T = 4.56 \times 10^{-3}$ M), measured during the H_2 uptake by **1**.

The hydrogenation of **3**, which is ~7 times slower than the hydrogenolysis reaction in DMA, causes little interference in measurement of the initial rates of the latter. However, the rate data analysis for a first-order ruthenium dependence, within a single run, clearly shows a deviation from the straight-line log [Ru] vs time plot (Figure 3) toward a rate higher than expected beyond about 0.7 mol of H_2 uptake. The additional contribution to the rate of H_2 uptake is attributed to the concurrent hydrogenation of **3**.

The relatively slow rate of hydrogenation of **3**, catalyzed by **2**, is consistent with previous findings. In earlier studies from this laboratory,[13b] **2** was found to be quite inefficient as an olefin hydrogenation catalyst, under temperature and H_2-pressure conditions similar to those used during the present work. The $RuCl_2(CO)_2(PPh_3)_2$-catalyzed selective hydrogenations of diene and triene substrates to monoenes, reported by Fahey,[22] are considered to involve **2** as the catalytically active species. Much more severe conditions were employed (130–150 °C, $P_{H_2} = 15$–20 atm), and the rates were slowest for the hydrogenation of internal alkenes. The catalytic activity of ruthenium complexes is commonly found to decrease with the introduction of π-acceptor carbonyl groups.[23]

The presence of a vacant coordination site on the metal is usually essential for H_2 activation to take place. The six-coordinate Ru–acyl complex **1** is pictured as becoming coordinatively unsaturated through loss of PPh_3, although coordination of DMA to **1a** prior to H_2 activation cannot be ruled out and, indeed, solvation in the transition state en route to **1a** is indicated (see below). The possibility of CO dissociation from **1** is ruled out because (a) the rate of hydrogenolysis remains unaffected by the presence of external CO and (b) the ruthenium product is still a dicarbonyl. Indeed, the kinetic data argue unambiguously for loss of coordinated phosphine ligand in a slow (k_1) step (eq 3). In some isomerization reactions of *trans,trans,-trans*-$RuCl_2(CO)_2(PR_3)_2$ complexes, of geometry similar to that of **1**, the key step is the initial dissociation of a CO rather than a phosphine ligand.[24]

The k_1 value of 4.5×10^{-5} s^{-1} at 65 °C obtained from the dependence of hydrogenolysis rate on added $[PPh_3)$ is, within experimental error, the same as the k_{obs} value of 4.45×10^{-5} s^{-1} obtained from the $[Ru]_T$ dependence measured in the absence of added phosphine. Under the latter conditions, clearly $k_{-1}[PPh_3] \ll k_2[H_2]$ (eq 6), with the rate being independent of H_2 from 190 to 760 Torr ((0.54–2.17) $\times 10^{-3}$ M). The steady-state concentration of PPh_3 must remain extremely low, and indeed the failure to detect any free PPh_3 by ^{31}P NMR spectroscopy in solutions of **1** means that the equilibrium constant K_1 for the dissociation of PPh_3 (eq 3) is immeasurably small. In any case, the hydrogenolysis of **1** does not result in a buildup of free PPh_3 as the reaction proceeds; the equilibrium constant K' for reaction 5 must presumably be very large, and the originally dissociated PPh_3 quickly coordinates to the $[RuHCl(CO)_2(PPh_3)]$ species to form **2**. This requirement is consistent with earlier observations on the K' equilibrium[13b,18,22b] and ^{31}P NMR data for solutions of **2**.

The k_{-1}/k_2 ratio of 1.6, obtained from the inverse dependence of hydrogenolysis rate on added $[PPh_3]$ (Figure 5A), means that the rates of the phosphine association to, and hydrogenolysis of, $[RuCl(COC_7H_9)(CO)_2(PPh_3)]$ (eqs 3 and 4) become comparable at relatively low added $[PPh_3]$. Consequently, in the presence of added PPh_3, the H_2 dependence is expected to go from zero to first order. Such a shift in H_2 dependence is evident from the data of Table I, even at the relatively small added $[PPh_3]$ of 9.7×10^{-4} M ($[PPh_3]/[Ru]_T = 0.21$), and as $[H_2]$ is of the same order of magnitude as $[PPh_3]$, this immediately implies qualitatively that the k_{-1}/k_2 ratio is close to unity. Also, the k_1 value of 5.0×10^{-5} s^{-1} and the k_{-1}/k_2 ratio of 1.9 obtained from the H_2-dependence data (Figure 5B) are in acceptable agreement with those determined experimentally from the inverse PPh_3 dependence. That equilibrium 3 is immeasurably small in $\sim 10^{-3}$ M solutions of **1** requires that $K_1 < 10^{-5}$ M, and use of the determined k_1 value gives estimates of $k_{-1} > 5$ M^{-1} s^{-1} and therefore $k_2 > 3$ M^{-1} s^{-1} (at 65 °C).

The measured $\Delta H^{\ddagger}$ value of 69 ± 7 kJ mol^{-1} for the hydrogenolysis reaction in DMA refers to the k_1 step and is thus the enthalpy of activation for phosphine dissociation from **1** in DMA solvent. *If* the activated complex

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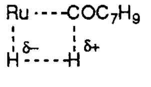
resembles closely a five-coordinate intermediate, then 69 kJ mol^{-1} could approximate to the bond dissociation energy of the Ru–P bond. However, the $\Delta S^{\ddagger}$ value strongly suggests that solvation in the transition state is important, and solvation energies are likely contributing to the overall activation enthalpy value. The large negative $\Delta S^{\ddagger}$ value (−126 J K^{-1} mol^{-1}) obtained for a rate-determining apparent ligand dissociation step must result from differences in solvation of the ground-state reactant and the activated state; the degree of solvation in the latter must be greater. For a transition state close to complete dissociation of phosphine, solvation of the five-coordinate intermediate and free phosphine could lead to an overall negative entropy of activation. In the much less polar and weakly coordinating toluene solvent, the k_1 values are quite similar to those measured in DMA (at least over the temperature range studied) but the activation parameters are remarkably different. The activation enthalpy is almost doubled (128 kJ), but this is now offset by a moderately favorable activation entropy (+62 J K^{-1}). A ligand dissociation step for a reaction in toluene invariably shows a positive $\Delta S^{\ddagger}$ value, reflecting a "loosening" of the bound ligand with presumed little difference in solvation of the ground and transition states.[25] Ignoring any involvement of toluene in the transition state, the 128-kJ value would represent a maximum estimate for the solution Ru–P bond dissociation energy within **1**; the trans-disposed PPh_3 ligands would lead to a relatively weak Ru–P bond. Dissociation of a phosphine from the complexes *trans*-$RuCl_2(CO)(PR_3)_3$ has been shown to be the key step in their isomerization to the cis form. The measured activation parameters for this step for the R_3 = Ph_2Me, $PhMe_2$, and Me_3 systems in various chlorine-containing solvents are respectively as follows: $\Delta H^{\ddagger}$ (±2) = 119, 130, and 130 kJ mol^{-1}; $\Delta S^{\ddagger}$ (±8) = 58, 63, and 33 J K^{-1} mol^{-1}. The values are remarkably similar to our values in toluene. In our system, one of the mutually trans phosphines must be lost; in the $RuCl_2(CO)(PPh_3)_3$ system, where positive $\Delta V^{\ddagger}$ values confirm the dissociative nature of the reaction, the phosphine lost was considered to be the one trans to CO.[24]

The mechanism of eqs 3 and 4, a dissociative step followed by hydrogenolysis of the coordinatively unsaturated intermediate, is exactly analogous to those described for reactions of $CH_3COCo(CO)_2[P(OMe_3)]_3$ and $EtOCOCo(CO)_4$ with H_2, these complexes dissociating a phosphite[9] and CO ligand,[4] respectively, prior to hydrogenolysis. In the cobalt systems, however, the corresponding k_1 values, in hydrocarbon solvents such as *n*-octane, are almost 1000 times greater at 25 °C than the extrapolated k_1 value in our ruthenium system; this is perhaps a contributing factor to the relatively low hydroformylation activity of ruthenium–carbonyl–phosphine complexes compared to those of analogous cobalt complexes.[1]

Hydrogenolysis reactions (cf. eq 4) are known to proceed often via oxidative addition of H_2, followed by fast reductive elimination of the products,[26,27] and a seven-coordinate Ru^{IV}–$(H)_2$ transition state and even a Ru^{II}–$(\eta^2$-$H_2)$[28] transition state are both plausible (k_2 step). That PPh_3 reacts preferentially, compared to H_2, with the intermediate **1a** (k_{-1}/k_2 = 1.6) shows that electronic effects dominate steric considerations in determining these relative reactivities (see below also); the same conclusion has been reached for the cobalt acyls,[4] where, for example, the coordinatively unsaturated species $EtOCOCo(CO)_3$ shows a kinetic preference for PPh_3 over H_2 with $k_{-1}/k_2 \approx 100$ at 25 °C in 1-octanol.[4c] This kinetic preference perhaps offers indirect support for the oxidative-addition pathway for hydrogenolysis with its requisite electronic promotion energy (Ru(II) → Ru(IV); Co(I) → Co(III)). Interestingly, the data for the single experiment with added PPh_3 in toluene (Table I, footnote *g*) can be used to show that in this solvent k_{-1}/k_2 must be about 30; this implies that k_{-1} is larger and/or k_2 is smaller in toluene than in DMA, where k_{-1}/k_2 = 1.6. *If* the difference were reflected entirely in k_2 values, a 30-fold increase in the hydrogenolysis step in DMA could be taken as favoring heterolytic activation of H_2 and a four centered transition state as shown in **5**;



5

oxidative addition of H_2 is also favored in more polar media, but differences are much smaller, e.g. a factor of 3 between DMF and toluene for H_2 addition to Vaska's compound.[29] However, k_{-1} is anticipated to be larger in toluene than in DMA because of binding/solvation by DMA in the intermediate **1a** (see above), and thus, the relative k_{-1}/k_2 values could still be consistent with an oxidative-addition/reductive-elimination sequence for reaction 4.

Of importance, Grundy and Jenkins[30] have synthesized the five-coordinate, monomeric $RuCl(COEt)(CO)(PPh_3)_2$ complex (**6**) and demonstrated that its chemistry is consistent with the availability of a vacant coordination site; reactivity toward H_2 was not reported. Because of the close analogy of the complex to our kinetic intermediate **1a** (eqs 3 and 4), we synthesized the propionyl complex by the reported procedure[30] but found it to be completely unreactive toward 1 atm of H_2 in DMA at ~50 °C. This surprised us, and we have no ready explanation for the nonreactivity; the propionyl complex and our proposed intermediate **1a** differ only in the nature of the acyl and the presence of a PPh_3 ligand versus a CO ligand. Differences in the reactivity of **1a** and **6** with H_2 must result from electronic factors: the extra CO ligand, a strong π-acceptor, in **1a** would tend to reduce oxidative-addition-type reactivity, while the perhaps more electronegative R substituent in **1a** within the RCO groups might favor (relative to **6**) reactivity via the transition state shown in **5**.

Preliminary experiments show that solutions of **1** react slowly with excess HCl (added as DMA·HCl[31]), according to eq 10 ($t_{1/2} \approx$ 1 day at 20 °C). Complex **7** is readily

$$\underset{\mathbf{1}}{RuCl(COC_7H_9)(CO)_2(PPh_3)_2} \xrightarrow{HCl} \underset{\mathbf{7}}{RuCl_2(CO)_2(PPh_3)_2} + C_7H_9CHO \quad (10)$$

identified by IR and NMR spectroscopy as the cis,cis,trans isomer;[13,22,24] thus, the reaction is directly analogous to

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reaction 1, and a related mechanism may apply. The reactivity of 1 with HCl (as with H_2) is in marked contrast to the reaction of $RuCl(COEt)(CO)(PPh_3)_2$ with HCl, which gives the hydroxycarbene complex $RuCl_2(CO)(C(OH)Et)(PPh_3)_2$;[30] i.e., protonation occurs at the acyl oxygen rather than carbon as seen with 1. Again, differences in electronegativity of the alkyl and alkenyl groups might account for the reactivity differences. Notably, en route to formation of 7 in reaction 10, a Ru intermediate with a ^{31}P singlet at 33.0 ppm was observed, this converting to the 17.0 ppm singlet characteristic of 7; however, we have been unable to detect any associated proton of a carbene hydroxide.[30]

Conclusions

The kinetics of the solution hydrogenolysis of the six-coordinate Ru(II) acyl complex $RuCl(COR)(CO)_2(PPh_3)_2$, where R = norbornenyl, to give $RuHCl(CO)_2(PPh_3)_2$ and RCHO reveal that the process occurs via dissociation of a PPh_3 ligand, followed by reaction of the resulting five-coordinate intermediate with H_2; the same pathways pertain to some cobalt acyl systems, studied previously because of their importance in hydroformylation. Activation parameters measured for the Ru system in DMA and toluene are very different; the former reflect a strongly solvated transition state, while the latter are consistent with little involvement of toluene in the transition state and then imply an upper value of 128 kJ mol^{-1} for the solution Ru–P bond dissociation energy (for mutually trans-disposed phosphines). Relative reactivities of the kinetic intermediates toward H_2 and PPh_3, and comparison with the behavior of a related Ru(II)–propionyl complex, reveal the importance of electronic effects in the hydrogenolysis step, although it is difficult to distinguish between an oxidative-addition/reductive-elmination ($+H_2$, $-RCHO$) pathway and a concerted four-center transition-state (heterolytic H_2 activation) pathway. The reaction of the norbornenoyl complex with HCl, to give $RuCl_2(CO)_2(PPh_3)_2$ and RCHO, contrasts with that of the propionyl species, which gives a hydroxycarbene derivative.

An incidental finding is that $RuHCl(CO)_2(PPh_3)_2$ catalyzes the H_2-hydrogenation of the norbornene aldehyde to the norbornane aldehyde, albeit slowly at 1 atm of H_2.

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New (Diarylgermyl)lithiums

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The new (diarylgermyl)lithiums R_2GeHLi (2; R = phenyl, mesityl) were prepared in good yields by hydrogermolysis reactions of *tert*-butyllithium in THF. The stability of compounds 2 depends on the nature of the R group and the solvent. For R = Ph, in the presence of an amine (Et_3N or Et_2NMe), the same reaction leads to the formation of the polygermanes $H(GePh_2)_nH$ (n = 2–4). The characterization of compounds 2 by IR and ^1H and ^{13}C NMR spectroscopy and their complexation with a crown ether are also reported. They are characterized by deuterolysis and alkylation reactions (with MeI and Me_2SO_4). Their germylation reactions with $>$Ge–Cl reagents constitute a convenient way for synthesizing organohydropolygermanes. Compounds 2 also react with acyl chlorides to give new germyl ketones, $R_2HGeCOR'$, and the unexpectedly stable β-germyl diketone $Ph_2Ge(COMes)_2$. They add easily to the carbonyl group of aromatic ketones or aldehydes, leading to the corresponding germylated alcohols.

Introduction

The organogermyl alkali-metal compounds R_3GeM (M = Li, Na, K) are very useful in organometallic synthesis, for example for the germylation of organic halides, metal halides, carbonyl compounds, etc.[1-4]

Among them, however, there are only a few reports regarding organogermyl alkali-metal compounds.[3-5] In the case of the lithium series, the only known (organogermyl)lithiums have been postulated in the reaction of organodihydrogermanes with RLi compounds (R = Me, Bu, Ph);[6] however, in these reactions the authors have always observed competition between metalation and alkylation reactions.[3]

In this paper, we report a modification of the hydrogermolysis procedure that allows a more specific synthesis of (diarylgermyl)lithium compounds stabilized by solvent and steric effects.

Results and Discussion

Preparation of R_2GeHLi. Recently, we have reported the synthesis in good yields of stable R_2GeHLi in THF solution from the reaction of R_2GeH_2 with t-BuLi:[7]

$$\underset{1}{R_2GeH_2} + t\text{-BuLi} \xrightarrow[-\text{BuH}]{\text{THF},\ T\ °\text{C}} \underset{2}{R_2GeHLi} \qquad (1)$$

2a, R = Ph (−40 °C, 95%);
2b, R = Mes (−20 °C, 84%)

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