Efficient and Selective Catalytic Dehydrogenation of Alkanes using Rhodium(I) Arsine Complexes

Joseph A. Miller* and Linda K. Knox

Exxon Chemical Company, Basic Chemicals Technology, P.O. Box 4900, Baytown, Texas 77522-4900, USA

Arsine complexes of rhodium(I) efficiently catalyze the transfer dehydrogenation of alkanes under an atmosphere of hydrogen, while at the same time producing decreased levels of 'direct hydrogenated' sacrificial olefin relative to that derived from similar phosphine-based catalysts.

While a variety of transition metal-based systems which activate alkane C–H bonds have been described during the past decade, few have actually demonstrated the capacity to functionalize these substrates in an efficient, catalytic manner.[1] Recently, Goldman and co-workers demonstrated that rhodium phosphine complexes can effectively catalyse the transfer dehydrogenation of alkanes under mild reaction conditions, provided that the process is carried out in the presence of hydrogen.[2] Unfortunately, the presence of hydrogen also leads to competing 'direct' (*i.e.*, non-transfer type) hydrogenation of the sacrificial olefin, thus mandating the need for an excess of this substrate. We now report that arsine complexes of rhodium, which are known to be relatively sluggish homogeneous hydrogenation catalysts,[3] function very efficiently as transfer dehydrogenation catalysts under these conditions and produce considerably less 'direct hydrogenated' sacrificial olefin than do similar phosphine-based rhodium compounds. Moreover, these rhodium arsine catalysts are highly active in systems employing simple alk-1-enes as sacrifical hydrogen acceptors [eqn. (1)].

$$R^1CH_2CH_2R^2 + R^3CH{=}CH_2 \xrightarrow[H_2]{\text{Rh–As cat.}} R^1CH{=}CHR^2 + R^3CH_2CH_3 \quad (1)$$

As an example, heating a solution of cyclooctane (10.0 ml), ethylene (200 mmol), and $[RhCl(AsPh_3)_2]_2$ **1**† (0.035 mmol) at 60 °C for 4 h under 500 psi H_2 produced a 20.4% yield of cyclooctene by GC analysis (turnover number, TON, = 216 moles cyclooctene per mole Rh added).‡ Continued reaction in the presence of a fresh charge of ethylene (200 mmol) increased the yield even further, providing 27.6% of cyclooctene after four more hours. Even at this considerable level of conversion only a very small amount of diene byproduct (cycloocta-1,3-diene; 0.39% yield) was observed by GC. By contrast, a similar phosphine complex, $RhCl(PPh_3)_3$, did not produce any detectable cyclooctene under identical reaction conditions. In this regard, it is interesting that the rate of cyclooctane dehydrogenation promoted by **1** was not markedly affected by the presence of added $AsPh_3$. Lowering the amount of **1** (0.0035 mmol) in the same reaction resulted in significantly increased catalyst efficiency, delivering a cyclooctene yield of 13.1% after 4 h (TON = 1,385). Propylene also functions effectively as the hydrogen acceptor olefin, as substitution of it for the ethylene in the above reactions affords cyclooctene yields/catalyst TONs of 16.2%/171 and 4.66%/493, respectively, for runs utilizing 0.035 and 0.0035 mmol of **1** as catalyst. The carbonyl complex $Rh(CO)Cl(AsMe_3)_2$ **2**[5] is also highly effective for promoting transfer dehydrogenation reactions under hydrogen atmosphere, although slightly increased temperatures from those employed above for catalyst **1** are required to realize high conversion rates. For example, reaction of **2** (0.05 mmol) with a mixture of cyclooctane (10.0 ml) and ethylene (200 mmol) under H_2 pressure (500 psi) at 100 °C gave a yield of cyclooctene after 4 h of 19.3% (TON = 287). By comparison, similar reaction of $Rh(CO)Cl(PMe_3)_2$[2a,b] with cyclooctane–ethylene provided only 1.77% (TON = 26.4) of cyclooctene during the same time period. As with catalyst **1**, decreasing the concentration of the carbonyl containing rhodium catalyst **2** (0.005 mmol) in the otherwise identical reaction led to a greatly elevated catalyst efficiency, producing a 16.6% yield of cyclooctene (TON = 2,460). The triphenylarsine-based carbonyl complex $Rh(CO)Cl(AsPh_3)_2$,[6] is also an effective transfer dehydrogenation catalyst, although slightly lower catalyst efficiency is realized from its use as compared with **2**.

Substrates other than cyclooctane also undergo transfer dehydrogenation in the presence of rhodium arsine complexes, but at sharply decreased rates. For comparison, the dehydrogenation of cyclooctane, cycloheptane, or *n*-heptane (74.3 mmol of substrate) promoted by **1** (0.035 mmol catalyst; 200 mmol ethylene, 500 psi H_2; 60 °C; 4 h) yielded the corresponding olefin products in TONs of 216, 30.6 and 3.8§, respectively.

As a consequence of their relatively poor olefin hydrogenation activity, Rh–As complexes provide significantly lower ratios of hydrogenation to dehydrogenation in these transfer dehydrogenation reactions compared to similar phosphine-based rhodium catalysts. To illustrate this finding, heating a mixture of cyclooctane (10.0 ml) and hept-1-ene (25 mmol) under 1000 psi H_2 at 100 °C in the presence of **2** (0.01 mmol) afforded 36.2 turnovers for cyclooctene formation and 344 turnovers for heptane formation after 4 h. Thus, the ratio of hydrogenated product (heptane) to dehydrogenated product (cyclooctene) was found to be 9.5 : 1. On the other hand, when the identical reaction was promoted by $Rh(CO)Cl(PMe_3)_2$ the amounts of hydrogenation (1972 turnovers for heptane) and dehydrogenation (3.4 turnovers for cyclooctene) products formed correspond to a ratio of 580 : 1. Substantial improvements in this type of selectivity are also observed for catalyst **1** in comparison with $RhCl\{P(C_6H_{11})_3\}(PMe_3)_2$.[2b]

In an effort to facilitate catalyst separation and recovery, we synthesized a heterogeneous arsine-based rhodium catalyst by covalently grafting **1** onto polystyrene beads. Thus, chloromethylated polystyrene beads¶ were placed in THF and arsinated ($\geqslant$ 85% substitution of chloride) by reaction with Ph_2AsLi[7] at 25 °C. The arsinated resin was then treated with a solution of **1** in THF at room temperature to yield the polystyrene-bound rhodium arsine complex **3** (*ca.* 20% of polymer-bound As groups complexed to Rh). Like its soluble progenitor, this heterogeneous catalyst also proved to be effective for promoting the transfer dehydrogenation of alkanes. As an illustration, a mixture of **3** (1.2 g), cyclooctane (10.0 ml), and ethylene (200 mmol) was heated at 60 °C in the presence of H_2 (500 psi) for 4 h. The clear, colourless solution was decanted from the catalyst beads and shown by GC analysis to contain a 6.52% yield of cyclooctene. The recovered catalyst was then recycled through five additional reactions without an appreciable decrease in cyclooctene yield or Rh content in the residual catalyst. It is worth noting that this is the first report describing the successful 'heterogenation' of a soluble transition-metal complex which retains its ability to activate C–H bonds.

We thank Drs L. W. Dennis and R. I. Botto (Exxon Research and Engineering Company) for obtaining the ^{13}C NMR spectra and microanalytical data, respectively, used in assigning the reformulated structure to catalyst **1**.

Received, 15th March 1994; Com. 4/01545B

Footnotes

[†] On the basis of ^{13}C NMR data, microanalyses, and molecular weight measurements, we have reformulated the reported complex, $RhCl(AsPh_3)_3$,[3a,4] as $[RhCl(AsPh_3)_2]_2$.

[‡] All reactions described were carried out in a 100 ml Parr 'Micro Reactor' autoclave, which was equipped with a glass liner and stirred magnetically with a Teflon-coated stir bar. No metal reactor parts were in contact with the reaction solution.

[§] A mixture of *n*-heptenes was obtained.

[¶] 'Merrifield's peptide resin', Kodak Laboratory Chemicals; 1% divinylbenzene copolymer beads; 200–400 mesh.

References

1 R. H. Crabtree, *Chem. Rev.*, 1985, **85**, 245; W. D. Jones and F. J. Feher, *Acc. Chem. Res.*, 1989, **22**, 91; *Activation and Functionalization of Alkanes*, ed. C. L. Hill, Wiley, New York, 1989; M. Tanaka and T. Sakakura, in *Homogeneous Transition Metal Catalyzed Reactions*, ed. W. R. Moser and D. W. Slocum, American Chemical Society, Washington, DC, 1992, vol. 230, pp. 181.

2 (*a*) J. A. Maguire and A. S. Goldman, *J. Am. Chem. Soc.*, 1991, **113**, 6706; (*b*) J. A. Maguire, A. Petrillo and A. S. Goldman, *J. Am. Chem. Soc.*, 1992, **114**, 9492; (*c*) K.-C. Shih and A. S. Goldman, *Organometallics*, 1993, **12**, 3390.

3 (*a*) J. T. Mague and G. Wilkinson, *J. Chem. Soc. A*, 1966, 1736; (*b*) C. O'Connor and G. Wilkinson, *Tetrahedron Lett.*, 1969, 1375; (*c*) A. S. Hussey and Y. Takeuchi, *J. Org. Chem.*, 1970, **35**, 643.

4 H. C. Volger and K. Vrieze, *J. Organomet. Chem.*, 1967, **9**, 527.

5 J. T. Mague, M. O. Nutt and E. H. Gause, *J. Chem. Soc., Dalton Trans.*, 1973, 2578.

6 J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 214.

7 A. Tzschach and W. Deylig, *Chem. Ber.*, 1965, **98**, 977.