



Review

Homogeneous metal catalysis for conversion between aromatic and saturated compounds



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Abbreviations: acac, acetylacetonate; ASE, aromatic stabilization energy; BARf, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate; BINAP, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl; BIPHEP, 2,2'-bis(diphenylphosphino)-1,1'-biphenyl; bipy, 2,2'-bipyridine; cod, 1,5-cyclooctadiene; coe, cyclooctene; Cp*, 1,2,3,4,5-pentamethylcyclopentadienyl; DCE, 1,2-dichloroethane; DIOP, 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane; DMAD, dimethyl acetylenedicarboxylate; dppe, 1,2-bis(diphenylphosphino)ethane; Et-FerrocTANE, 1,1'-bis(2,4-diethylphosphotano)ferrocene; MorPhos, (3,5-dioxa-4-phospha-cyclohepta[2,1-a:3,4-a']dinaphthalen-4-yl)morpholine; MP²-SEGPPOS, 5,5'-bis(2,5-dimethyl-1*H*-phosphol-1-yl)-4,4'-bibenzo[*d*][1,3]dioxole; PhTRAP, 2,2''-bis[(diphenylphosphino)ethyl]-1,1''-biferrocene; PipPhos, (3,5-dioxa-4-phospha-cyclohepta[2,1-a:3,4-a']dinaphthalen-4-yl)piperidine; RSE, resonance stabilization energy; SEGPPOS, 5,5'-bis(diphenylphosphinyl)-4,4'-bibenzo[*d*][1,3]dioxole; SynPhos, [(5,6),(5',6')-bis(ethylenedioxy)biphenyl-2,2'-diyl]bis(diphenylphosphine); TBAI, tetra-(*n*-butyl)ammonium iodide; TBE, *tert*-butylethylene; TFE, 2,2,2-trifluoroethanol; TfOH, triflic acid; THQ, 1,2,3,4-tetrahydroquinoline; TOF, turnover frequency; TON, turnover number; Tp, tris(pyrazolyl)borate; triphos, 1,1,1-tris(diphenylphosphinomethyl)ethane; TsDPEN, *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine; C₃*-TunePhos, (6,8-dimethyl-7,8-dihydro-6*H*-dibenzo[*f,h*][1,5]dioxonine-1,13-diyl)bis(diphenylphosphine).

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ABSTRACT

In the past few decades, homogeneous catalysis of arene and heteroarene reduction has grown into a mature research field. In particular, hydrogenation of heteroaromatic systems facilitates rapid access to many classes of fine chemicals and pharmaceutically relevant compounds. In this review, we discuss the advancements made in the field of homogeneous metal-catalyzed arene and heteroarene hydrogenation from its early beginnings to the present day. We also review homogeneous catalysts for the reverse dehydrogenation of cyclic saturated species back to their aromatic counterparts, as well as single-catalyst systems capable of performing reversible hydrogenation-dehydrogenation reactions.

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1. Introduction

1.1. Scope

The main contents of this review comprise studies of homogeneous metal catalysts for the reduction of arenes and heteroarenes to cycloalkanes and saturated heterocycles, respectively. The extent of literature surveyed ranges from the early entries of the 1970s to the present day. A separate section also details catalysts developed for achieving the reverse transformation, *i.e.* dehydrogenation of cycloalkanes and saturated heterocycles back to their aromatic counterparts. A fifth, final section highlights single-catalyst systems designed to effect reversible hydrogenation-dehydrogenation of various *N*-heterocycles.

Homogeneous catalysis of enantioselective heteroaromatic¹ hydrogenation has already been extensively reviewed by Zhou [1–3] and others [4–6], and thus will only be treated sparingly herein. Examples of molecular catalysts affixed to solid supports are not included in this review, as significant uncertainty exists regarding the nature of the active species in these systems [7]. Soluble metal nanoclusters active in arene hydrogenation [8] are also excluded.

1.2. Homogeneous versus heterogeneous catalysis

1.2.1. Distinctions

Categorization of metal-based catalysts as either homogeneous or heterogeneous has classically been based on the apparent solubility or insolubility of the species in question. In 1985, however, Schwartz [9] proposed adoption of a more relevant criterion: the nature of the material's catalytically active sites. Specifically, this classification scheme identifies homogeneous and heterogeneous catalysts as those operating *via* active sites of identical or diverse composition, respectively, irrespective of their solubility profiles. By such an evaluation, soluble metal colloids and nanoclusters for example would still be considered heterogeneous, while insoluble zeolites would nonetheless be designated as homogeneous [10].

A more precise set of definitions notwithstanding, unambiguous determination of a catalyst's homogeneous or heterogeneous

nature remains a particularly challenging experimental task to this day. Many of the early methods devised to probe this property, including the oft-used mercury poisoning test, have been demonstrated potentially ineffective when applied individually². In an effort to overcome these deficiencies, Finke [10] assembled a suite of analytical techniques designed for effective general use when rigorously applied *in toto*. Specifically, these consist of TEM characterization of all isolated metal-containing species, kinetic studies, *quantitative* catalyst poisoning experiments, and other mechanistic experiments as required to rationalize all the observed reaction phenomena.

Following this protocol, Finke has elucidated the true nature of a number of purportedly homogeneous arene hydrogenation catalysts [11–13]. Among those investigated, [Cp*RhCl₂]₂ (originally reported by Maitlis [14]) presented a particularly complex case [13]. For although Finke found benzene hydrogenation to actually proceed *via* a heterogeneous active species³, cyclohexene hydrogenation did in fact appear to operate through a homogeneous species (Scheme 1). Finke attributed the differing behavior to the reaction conditions: under the more strongly reducing conditions required for benzene hydrogenation, discrete precatalysts such as [Cp*RhCl₂]₂ are more likely to degenerate into heterogeneous metal(0) colloids and nanoclusters⁴.

Such a thorough examination as in the above studies has not been performed for many of the catalytic systems featured in this review. We have chosen, however, to err on the side of inclusivity. Readers are also encouraged to refer to Dyson's 2003 review [7] for more in-depth treatment of the debate concerning those arene hydrogenation catalysts whose homogeneous or heterogeneous nature remains in question.

1.2.2. Advantages and disadvantages

The greater robustness of heterogeneous catalysts *vis-à-vis* their homogeneous counterparts often renders use of the former more practical under the frequently forcing conditions required

² For further details on the strengths and weaknesses of these tests, see Ref. [167].

³ This species was later identified as subnanometer Rh₄ clusters of the general form Rh₄(Cp*)_aCl_bH_c ($\bar{a} = 2.4$, $\bar{b} = 4$). For further details, see Refs. [168,169].

⁴ Páez has reported a similar dependence on reaction conditions for the tungsten-based hydrogenation catalyst W(CO)₃(CH₃CN)(TPPMS)₂ (TPPMS = sodium (3-sulfonatophenyl)diphenylphosphine). Specifically, the catalyst exhibits heterogeneous behavior at pH <6, but homogeneous reactivity at pH >6. For further details, see Ref. [170].

¹ To the best of our knowledge, only three examples of this transformation have been reported for an all-carbon aromatic unit. The substrates in each case have consisted of fused bicycles only; see Section 3.5 for details.

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