Editor choice paper

Selective hydrogenation of the C=O bond of ketones using Ni(0) complexes with a chelating bisphosphine

Areli Flores-Gaspar [a], Paulina Pinedo-González [a], Marco G. Crestani [a], Miguel Muñoz-Hernández [b], David Morales-Morales [c], Brian A. Warsop [d], William D. Jones [d], Juventino J. García [a,*]

[a] *Facultad de Química, Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico*
[b] *Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Cuernavaca, Morelos 62210, Mexico*
[c] *Instituto de Química, Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico*
[d] *Department of Chemistry, University of Rochester, Rochester, NY, 14627, USA*

ARTICLE INFO

ABSTRACT

The nickel complexes [(dippe)Ni(η^2-O,C-benzophenone)] (**2**), [(dippe)Ni(η^2-O,C-4-methylbenzophenone)] (**3**), [(dippe)Ni(η^2-O,C-acetophenone)] (**4**), [(dippe)Ni(η^2-O,C-acetone)] (**5**), [(dippe)Ni(η^2-O,C-fluorenone)] (**6**), [(dippe)Ni(η^2-O,C-di(2-pyridyl) ketone)] (**7a**) [(dippe)Ni(κ^2-N,N-di(2-pyridyl) ketone)] (**7b**), [(dippe)Ni(κ^2-O,O-2,2'-pyridil)] (**8**), [(dippe)Ni(κ^2-O,O-benzil)] (**9a**), and [((dippe)Ni)$_2$(η^2-O,C-benzil)] (**9b**) were prepared by the reaction of [(dippe)Ni(μ-H)]$_2$ (**1**) with the corresponding ketone or 1,2-diketone at room temperature. The structures of compounds **2**, **6**, **9a** and **9b** were confirmed by X-ray crystallography. The selective hydrogenation of the two types of substrates was undertaken using H$_2$, giving high conversions to the corresponding reduction products, either alcohols or alkanes. Tunable reaction conditions to promote the partial or total hydrogenation (hydrogenolysis) of the substrates are described.

1. Introduction

A variety of organic substrates containing the CO group are important in synthesis since they can be transformed into many other different functional groups [1]. Partial and total reduction of the carbonyl group serve as important examples of these transformations as they give the corresponding alcohols or alkanes, but preparative methods that may drive these reactions selectively have been seldom optimized in the past. In the first case, the partial reduction has been observed to take place only when an excess of a conventional reducing agent such as LiAlH$_4$, NaBH$_4$, Al(OPr^i)$_3$, or EtSiH are used and the reaction is followed by a hydrolysis [2]. In the second case, Raney-nickel [3] as well as Wolff-Kishner and Clemmensen reductions [4] are typically used, although the tolerance to other functional groups in the target molecules is an issue that remains challenging.

Industrially, large-scale processes that involve the catalytic hydrogenation of numerous organic functions are operated worldwide [5]. The metal catalysts and the processes in which they participate can be classified depending on the hydrogen source that is used. A first set of reactions can be described as *direct hydrogena-tions* if molecular hydrogen is used as the reducing agent, whereas a second set can be described as *transfer hydrogenations* whenever an organic compound is used as the hydrogen source. A seminal contribution to the latter set was made by Noyori and co-workers who developed a homogeneous asymmetric transfer hydrogenation system employing complexes of the type [RuCl$_2$(P–P)(1,2-diamine)], where (P–P) is a chiral bisphosphine [6]. Currently, ruthenium is still the most widely used metal for this reaction [7], but similar reactivities have also been observed with other compounds using iridium [8] and rhodium [9]. Shvo's ruthenium catalyst has been used in a broad range of hydrogen transfer reductions, including carbonyl reductions [10]. Recently, Baratta et al. reported the use of osmium complexes with the formula, [OsCl$_2$P$_2$(Pyme)] (P = phosphine, Pyme = 1-(pyridin-2-yl)methanamine)), as active catalysts for the reduction of ketones in basic alcohol media [11], and an effective iron-based catalyst was reported by Casey for the selective hydrogenation of aldehydes and ketones under mild conditions [12]. The use of nickel in homogeneous hydrogenation of ketones is relatively scarce; however, heterogeneous examples are rather common, but not always well understood [13]. With the aim of developing inexpensive and efficient catalysts, we herein disclose the use of bisphosphine-nickel(0) complexes which are active catalysts for the homogeneous hydrogenation of mono- and diketones, giving their corresponding alcohols or alkanes in high conversions and tunable conditions.

* Corresponding author. Tel.: +52 55 56223514; fax: +52 55 56162010.
E-mail address: juvent@servidor.unam.mx (J.J. García).
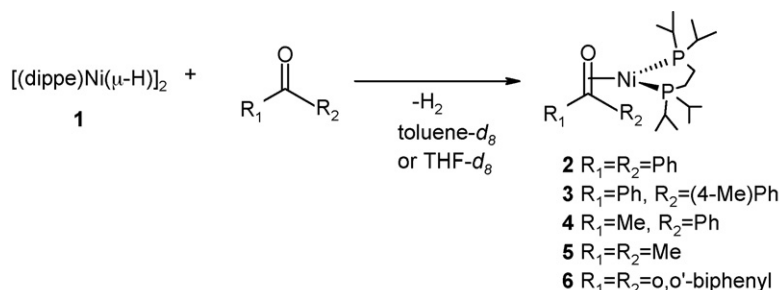
Scheme 1. Formation of [(dippe)Ni(η^2-*C,O*-ketone)] complexes **2–6**.
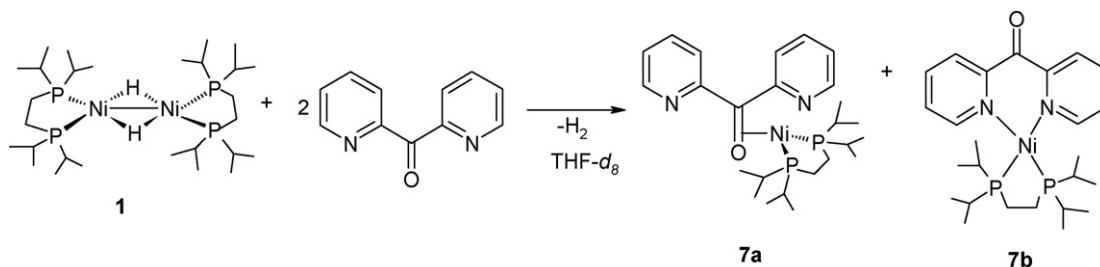
Scheme 2. Formation of [(dippe)Ni(η^2-*C,O*-di-2-pyridyl ketone)] (**7a**) and [(dippe)Ni(κ^2-*N,N*-di-2-pyridyl ketone)] (**7b**).

2. Results and discussion

2.1. Reactivity of [(dippe)Ni(μ-H)]$_2$ **1** with monoketones

As has been reported previously, the nickel(I) dimer **1** can be used to cleave the C–C [14], C–S [15], and C–CN [16] bonds of a variety of substrates, following reductive elimination of H$_2$ and *in situ* generation of the reactive nickel(0) moiety, [(dippe)Ni^0]. **1** has been found to react with monoketones at room temperature in toluene-d_8 and THF-d_8 solutions, allowing the formation of stable η^2-*C,O* complexes with formula [(dippe)Ni(η^2-*C,O*-ketone)] (**2–6**). Scheme 1 summarizes the reactions that take place.

Complexes **2–6** typically display two doublets in the range 60–72 ppm with P–P coupling constants in the range of 66–77 Hz in their ^{31}P{^{1}H} NMR spectra. The presence of the doublets is characteristic of two non-equivalent phosphorus atoms coordinated to a metal center, the magnitude of the coupling constants being indicative of $^2J_{P-P}$ through a Ni(0) center, i.e. [(P–P)Ni(η^2-*C,O*-ketone)]. The ^{13}C{^{1}H} NMR spectra of the same complexes exhibited a doublet of doublets in the range δ 82–87 for the carbon in the coordinated C=O bond, which appeared shifted to *high-field* when compared with the corresponding carbonyl signal in the free ketones (observed as a singlet in the region of δ 195–206). The changes in chemical shifts and multiplicities are consistent with coordination of the carbonyl moiety to nickel(0). It is worth noting that a different reaction outcome was observed in the reaction of **1** with di(2-pyridyl) ketone, which yielded two different products, the expected [(dippe)Ni(η^2-*O,C*-di(2-pyridyl) ketone)] (70%) **7a**, and the unexpected [(dippe)Ni(κ^2-*N,N*-di(2-pyridyl) ketone)] (30%) **7b**. The latter compound corresponds to a bis-*N,N* chelate complex whose structure is illustrated in Scheme 2. In the ^{31}P{^{1}H} NMR spectrum compound **7a** displayed two doublets at δ 63.9 and 72.4 with $^2J_{P-P}$ = 57.6 Hz.[16] **7b** exhibited a broad singlet centered at δ 116.7 arising from the equivalence in the phosphorus atoms coordinated to the nickel(0) center.

X-ray quality crystals for complex **2** were grown from a concentrated solution in benzene at room temperature. The ORTEP representation of this compound is presented in Fig. 1 and the complete crystallographic and structure refinement data are summarized in Table 1. The geometry around the Ni center corresponds to square planar and shows a considerable lengthening of the η^2-coordinated carbonyl group (1.343(2) Å) *vs.* that of the free ligand (1.223 Å) [17]. The NiCO plane is nearly coplanar with the NiP$_2$ plane (4.2°). The almost equidistant Ni–P1 and Ni–P2 bond lengths suggest that the Ni(dippe) fragment is symmetrically bonded. Similarly, an X-ray structure of fluorenone adduct **6** shows a lengthened C–O bond to 1.326(5) Å, compared with 1.222 Å in the free ketone (Fig. 2) [18], and the angle between the NiP$_2$ and NiCO planes is 3.0°. A closely related structure has been reported by Hillhouse and coworkers [19].
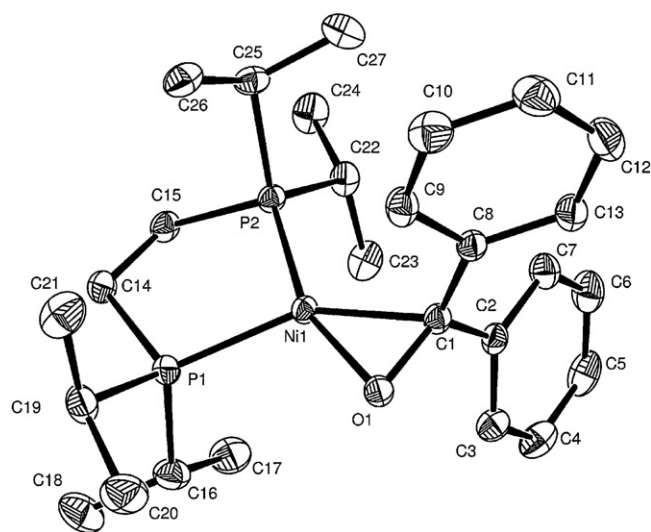

Fig. 1. ORTEP representation of **2** showing thermal ellipsoids at the 30% probability level. Selected bond distances (Å): O1–C1 (1.343(2)), Ni1–O1 (1.8549(11)), Ni1–C1 (1.9734(16)), Ni1–P1 (2.1722(5)), Ni1–P2 (2.1461(5)). Selected bond angles (deg): O1–Ni1–C1 (40.94(6)), O1–Ni1–P1 (109.42(4)), C1–Ni–P1 (150.15(5)), O1–Ni–P2 (159.21(4)), C1–Ni–P2 (118.28(5)), P1–Ni–P2 (91.267(18)).