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Iron-catalyzed alkylation of nitriles with alcohols

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Abstract: A general, efficient iron-catalyzed α -alkylation of nitriles with primary alcohols via a hydrogen-borrowing pathway has been developed, allowing a wide variety of alkylated nitriles to be readily accessible. Detailed mechanistic studies suggest that the reaction proceeds via an olefin intermediate with the turnover rate limited by the hydrogenation of the olefin with an iron hydride. Apart from participating in the alkylation, the nitrile is found to play an important role in promoting the formation of and stabilizing the active catalytic species.

Nitriles are versatile building blocks in organic synthesis. They can be easily transformed into a plethora of compounds, e.g. amides, carboxylic acids, ketones and oxazolines (Scheme 1).^[1] Moreover, there are many drugs and natural products containing cyano groups.^[2] Amongst the methods for the synthesis of nitrile compounds, the α -alkylation of alkylnitriles with alcohols via a hydrogen borrowing or hydrogen auto transfer strategy^[3] provides an environmentally benign route, with water as the only by-product. Transition metal complexes, including Ru,^[4] Os,^[5] Rh,^[6] Ir^[7] and Pd,^[8] have been reported to be effective catalysts for this reaction. Despite the progress, the replacement of noblemetal catalysts with those derived from earth-abundant base metals is attractive, as it offers additional economic and ecological benefits.^[9] Recently, Milstein and co-workers reported a remarkable example of *Mn*-catalyzed α -olefination of nitriles with alcohols via acceptorless dehydrogenation.^[10] However, to the best of our knowledge, the α -alkylation of nitriles with alcohols catalyzed by base metals has not been reported. Herein, we present the first examples of iron-catalyzed aalkylation of nitriles with primary alcohols through a hydrogenborrowing strategy (Scheme 1). The iron pincer catalyst showed even better performance than some of the noble metal catalysts in terms of substrate scope and catalytic activity.

Iron pincer complexes with PNP ligands have proven to be efficient catalysts for dehydrogenation^[11] and hydrogenation^[12] of a range of substrates. The dehydrogenation and hydrogenation abilities of these complexes render them possible candidates for hydrogen-borrowing catalysts. However, iron complexes,^[9] and particularly the pincer variants,^[9e] have rarely been used as catalysts in hydrogen borrowing reactions. With these observations in mind, we examined Fe-PNP complexes for the alkylation of nitriles with alcohols, a reaction requiring both dehydrogenation and hydrogenation abilities of the catalyst.

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Scheme 1. The importance of nitrile compounds and past/present work on α -alkylation of nitriles with alcohols.

Iron complexes 1-4 were prepared and initially examined as catalyst candidates for the model alkylation of phenylacetonitrile 6 with 4-methylbenzyl alcohol 5 (Scheme 2). After screening a variety of conditions including these and other metal compounds (see SI for details), complex 3, with cyclohexyl substituents on the phosphorus, was found to be most effective in catalyzing the model reaction. Thus, under the catalysis of 3 (1 mol%) in the presence of the activating NaBHEt₃ (2 mol%) and NaOH (1 equivalent), 7a was obtained in an NMR yield of 99% in toluene at 130 °C under Ar in 6 h, and the substrate to catalyst ratio could be raised to 500 (Scheme 2). Slightly lower activities were observed by replacing the cyclohexyl substituent of 3 with phenyl (2) or isopropyl (4) variants. Complex 1, without the CO ligand, was essentially inactive. The structures of 1 and 3 were confirmed by X-ray diffraction.

With the optimized reaction conditions in hand, the scope of the alkylation reaction was explored (Scheme 3). The α alkylation of **6** with various alcohols was first examined with **3** as catalyst (1 mol%), NaBHEt₃ (2 mol%) as activating agent and NaOH as base (1 equivalent). In general, both benzylic and aliphatic alcohols reacted well to afford the corresponding alkylated products in good to excellent yields. For benzylic alcohols, electron-donating substituents tend to impart slightly better activity than electron-withdrawing ones (**7a**-**7k**), and good yields were still obtained for sterically bulky substrates (**7d**, **7e**). The presence of a morpholine moiety on the phenyl ring of benzyl alcohol is tolerated (**7k**). Aliphatic alcohols generally gave lower yields of the desired α -alkylated products (**7l**-**7v**) and

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Scheme 2. Fe-PNP complexes catalyzed α -Alkylation of nitriles with primary alcohols and the X-ray structures of 1 and 3. See SI for detailed conditions.

further optimization of reaction conditions was required in some cases (71, 7m, 7n, 7t). Despite extensive effort of optimization, the yield for the reaction of methanol with 2-naphthylacetonitrile was only 26% (7I); however, significantly higher yields were obtained with longer chain aliphatic alcohols (7m-7o). Interestingly, complex 2 gave better results than 3 for some of aliphatic alcohols (7n, 7t). These results indicate that fine tuning of the steric and electronic properties of the catalyst is necessary to suit reactivity of different substrates in hydrogen borrowing reactions, which require a subtle balance of the dehydrogenation/hydrogenation abilities of catalysts. Sterically bulkier aliphatic alcohols could also react (7p-7r), affording albeit a lower yield in the case of cyclopropylmethanol (7q). Notably, both unsaturated and amino alcohols are viable substrates, with the C=C double bond and amino unit remaining intact in the product (7u-7v). 7v could be hydrolyzed to an amino acid 7w in high yield (see SI), which is a unique gamma-aminobutyric-acid derivative and may find applications in biological studies.^[13]

The scope of the reaction was further examined by reacting other nitrile compounds with **5** (Scheme 3). A variety of arylacetonitriles containing both electron-withdrawing and donating substituents were successfully alkylated with **5** in good to excellent yields (**8a-8g**). 2-(Phenylsulfonyl)acetonitrile was also a viable substrate, the product of which (**8h**) could be further functionalized.^[14] However, aliphatic nitriles, such as acetonitrile and phenylpropanenitrile, gave poor yields in the alkylation reaction (**8i**, **8j**), probably as a result of the high pKa values of the protons adjacent to the cyano group (pKa = 31 for acetonitrile vs 22 for phenylacetonitrile in DMSO).

Another appealing feature of the Fe-catalyzed system is that heterocyclic substrates are well tolerated (Scheme 3). Thus, unprotected indole (**9a-9d**), furan (**9e**) and pyridine (**9f-9i**) were all proved to be viable. These substrates are problematic even for some noble metal catalysts.^[4-8]

The remarkable ability of the iron complexes in catalyzing the alkylation prompted us to look into the reaction mechanism. Monitoring of the alkylation of 6 with 5 catalyzed by complexes 2-4 revealed an olefin intermediate 10 and a kinetic profile



Scheme 3. α -Alkylation of nitriles (black) with primary alcohols (red). See SI for detailed conditions.

typical of a sequential reaction (Scheme 4). Based on the information gained from this scheme and the literature^[4-8], the alkylation is proposed to proceed via the dehydrogenation of 5 to give 4-methylbenzaldehyde, which condenses with 6 under basic conditions to form 10, hydrogenation of which affords 7a. As the alkylation is performed under a nitrogen atmosphere, the formation of 10 indicates that hydrogen gas is released. Indeed, hydrogen gas was detected from the head gas of the reaction of 5 with 6 catalyzed by 3 (See section 5.2 in the SI). Together with the faster initial rates for the formation of 10 than for 7a, the accumulation of 10 suggests that the turnover rate of the alkylation may be limited by the step of hydrogenation.

The proposition above is supported by further experiments. Thus, the isolated olefin intermediate **10'** was reduced by benzyl alcohol or H₂ under the catalysis of **3**, affording **7b** as expected from the intermediary role of **10'** (See section 5.3 in the SI). Comparing the alkylation of **6** by benzyl alcohol with that by α, α - COMMUNICATION

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d₂-benzyl alcohol revealed a significant kinetic isotope effect for the formation of **7b**, but only an insignificant one for that of its olefin intermediate (See section 5.4 in the SI), corroborating olefin hydrogenation as rate limiting step. Interestingly, it is noted that whilst the complexes **2-4** show similar initial rates in forming **7a**, **2** appears to be significantly less active in catalyzing the dehydrogenation of **5** from which **7a** results. Thus, the lower alkylation yield observed with **2** in Scheme 2 can be ascribed to its lower activity in alcohol dehydrogenation.



Scheme 4. Kinetic profiles for the reaction of 5 with 6 catalyzed by the Fe-PNP complexes 2, 3 and 4. See SI for detailed conditions.

A key mechanistic question is what happened to the Fe complex during the reaction. Toward this end, we carried out extensive studies by using NMR, IR and HRMS. In the catalytic reaction, the Fe catalyst was first activated by NaBHEt₃. As shown in Scheme S12 (SI), dissolving 3 in toluene afforded a clear blue solution, which gave an absorption peak at 1944 cm⁻¹. in the IR spectrum, corresponding to the stretching absorption of CO ligand, and a single peak at δ 60.7 ppm in the ³¹P NMR spectrum. Addition of 2 equivalents of NaBHEt₃ to this solution led to an immediate color change from blue to red. In the ¹H NMR spectrum, two sets of hydride signals were detected at δ -9.3 ppm (multiplet) and -25.1 ppm (Scheme S13, SI); the ³¹P NMR spectrum showed peaks at δ 106.5, 106.3 and 105.9 ppm. Based on the study of Hazari, Schneider^{[15]} and $\mathsf{Jones}^{[11c]}$ and their co-workers, these resonances can be tentatively assigned to the complexes 11a, 11b and 12 (Scheme 5). The ³¹P NMR spectrum also revealed a peak at δ 98.0 ppm, assignable to 13^[15], and a signal from the free ligand. IR and HRMS provided further support for the structures. Thus, the absorptions at 1795 and 1850 cm⁻¹ in the IR spectrum (Scheme S12) fit with the previously reported data for CO stretching in 13,[16] and peaks corresponding to 12 and 13 were detected by HRMS. In addition, HRMS indicated the formation of the species 18. Clearly, treatment of 3 with NaBHEt₃ affords a complex mixture.

More insightful observations were made upon introduction of the substrates. Thus, addition of alcohol **5**, after mixing **3** with NaBHEt₃ for 15 min in d₈-toluene, gave rise to only a major hydride peak at δ -23.3 ppm in the ¹H NMR spectrum (Scheme S13); the ³¹P NMR showed a peak at δ 84.8 ppm. In the IR

spectrum, a new CO stretching peak was observed at 1902 cm⁻¹ (Scheme S12). We tentatively attribute these observations to complex 15 resulting from the protonation of 12 by 5 (Scheme 5). However, the corresponding HRMS only showed peaks assignable to 12 and 13, presumably due to the instability of 15. Remarkably, introducing the nitrile 6, instead of 5, led to the formation of only one observable species 14, according to the ¹H NMR (δ -19.1 ppm), ³¹P NMR (δ 86.2 ppm), IR (1920 cm⁻¹) and HRMS ([M+H]+, 667.3595) (See Sections 5.5.1-5.5.4, SI).[17] Further ¹H NMR, ³¹P NMR and HRMS experiments confirmed that addition of 6 to the mixture of 11a/11b, 12, 13, 18 and free ligand, formed upon treatment of 3 with NaBHEt₃, resulted in the disappearance of all these species, affording 14 (See Section 5.5.5, SI). Being the only observable species in the presence of substrates, 14 could be the catalyst resting state. These observations indicate that coordinating substrates, particularly the nitriles, stabilize the iron-hydride intermediate and enhance its concentration. We note that this stabilizing effect of substrates has not been reported before in iron-catalyzed hydrogenation and dehydrogenation, which may have implications in the design and application of Fe-PNP catalysts.



Scheme 5. Proposed mechanism for the alkylation of nitriles, including various spectroscopically detected species (Ar = p-methylphenyl).

The mechanism of how 13 and 18 are formed is not yet clear. A tentative pathway is shown in Scheme 5. 11b may undergo reductive elimination of H_2 to afford a zero-valent complex 17, disproportionation of which would result in 13 and 18. The latter is not expected to be stable, decomposing to the free ligand and undefined iron species. On the other hand, the hydride in 11a/11b could be protonated by the neighboring N-H proton, affording 12. All these species are likely to be in equilibrium, and

when 6 (in large excess) is introduced, the equilibria are driven to favoring the formation of 14.

Based on the studies above and the literature, a proposed mechanism for the alkylation, exemplified by that of 5 with 6, is shown in Scheme 5. The activation of 3 in toluene with NaBHEt₃ results in the formation of a complex mixture, which is converted into the complex 14 upon introducing 6, with 14 in equilibrium with **12**. Protonation of the latter with **5** affords **15**, from which β hydrogen elimination takes place, releasing one molecule of benzaldehyde while generating **11a**.^[11c, 11d] The benzaldehyde condenses with 6 with the aid of a base to produce the olefin intermediate 10, which is reduced by 11a to give the alkylated product 7a, while regenerating 12. The species involved in the catalytic cycle are probably in equilibrium with each other via dissociation/association of substrates, aldehydes and H₂. As mentioned, the catalysis appears to be rate-limited by the step of hydrogenation of **10**. This remains, however, largely hypothetic, without measuring the rate constants and/or calculating the energy barriers of catalytic cycle.

In summary, the first Fe catalyzed α -alkylation of nitriles with primary alcohols via a hydrogen borrowing pathway has been developed. The catalytic system shows broad substrate scope and high activity. Mechanistic studies showed that the reaction proceeds sequentially, involving the intermediary of an olefin. Significantly, the commonly adopted procedure of catalyst activation with boron hydrides leads to a complex mixture of iron species, and it is the nitrile substrate that converts these species into an active hydride catalyst.

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Keywords: iron catalysis • alkylation • nitrile • alcohol • hydrogen transfer

- a) J.-T. Yu, F. Teng, J. Cheng, *Adv. Synth. Catal.* **2017**, *359*, 26-38; b) N. Kurono, T. Ohkuma, *ACS Catal.* **2016**, 6, 989-1023; c) R. López, C. [1] Palomo, Angew. Chem. Int. Ed. 2015, 54, 13170-13184
- F. F. Fleming, L. Yao, P. C. Ravikumar, L. Funk, B. C. Shook, J. Med. [2] Chem. 2010, 53, 7902-7917.
- a) G. Guillena, D. J. Ramón, M. Yus, Chem. Rev. 2009, 110, 1611-[3] 1641; b) T. D. Nixon, M. K. Whittlesey, J. M. J. Williams, Dalton Trans. 2009, 753-762; c) G. E. Dobereiner, R. H. Crabtree, Chem. Rev. 2010, 110, 681-703; d) A. J. A. Watson, J. M. J. Williams, Science 2010, 329, 635-636; e) J. Choi, A. H. R. MacArthur, M. Brookhart, A. S. Goldman, *Chem. Rev.* **2011**, *111*, 1761-1779; f) C. Gunanathan, D. Milstein, Science **2013**, *341*, 1229712; g) Y. Obora, ACS Catal. **2014**, *4*, 3972-3981; h) A. Nandakumar, S. P. Midya, V. G. Landge, E. Balaraman, Angew. Chem. Int. Ed. 2015, 54, 11022-11034; i) S. Werkmeister, J. Neumann, K. Junge, M. Beller, Chem. Eur. J. 2015, 21, 12226-12250; j) Neumann, K. Junge, M. Bener, *Chem. Eur. J.* 2015, *21*, 12226-12265 []
 Q. Yang, Q. Wang, Z. Yu, *Chem. Soc. Rev.* 2015, *44*, 2305-2329; k] J.
 Feng, Z. A. Kasun, M. J. Krische, *J. Am. Chem. Soc.* 2016, *138*, 5467-5478; I] C. Wang, J. Xiao, *Chem. Commun.* 2017, *53*, 3399-3411; m) R.
 H. Crabtree, *Chem. Rev.* 2017, *117*, 9228-9246.
 a) K. Motokura, D. Nishimura, K. Mori, T. Mizugaki, K. Ebitani, K.
 Kaneda, J. Am. Chem. Soc. 2004, *126*, 5662-5663; b) K. Motokura, N.
- [4] Fujita, K. Mori, T. Mizugaki, K. Ebitani, K. Jitsukawa, K. Kaneda, Chem. Eur. J. 2006, 12, 8228-8239; c) S. Burling, B. M. Paine, D. Nama, V. S.

Brown, M. F. Mahon, T. J. Prior, P. S. Pregosin, M. K. Whittlesey, J. M. J. Williams, *J. Am. Chem. Soc.* **2007**, *129*, 1987-1995; d) H. W. Cheung, J. Li, W. Zheng, Z. Zhou, Y. H. Chiu, Z. Lin, C. P. Lau, Dalton Trans. 2010, 39, 265-274; e) T. Kuwahara, T. Fukuyama, I. Ryu, Chem. Lett. **2013**, *42*, 1163-1165; f) J. Alós, T. Bolaño, M. A. Esteruelas, M. Oliván, E. Oñate, M. Valencia, *Inorg. Chem.* **2014**, *53*, 1195-1209; g) S. Thiyagarajan, C. Gunanathan, *ACS Catal.* **2017**, 7, 5483-5490. M. L. Buil, M. A. Esteruelas, J. Herrero, S. Izquierdo, I. M. Pastor, M.

- [5] Yus, ACS Catal. 2013, 3, 2072-2075.
- a) F. Li, X. Zou, N. Wang, Adv. Synth. Catal. 2015, 357, 1405-1415; b) [6] J. Li, Y. Liu, W. Tang, D. Xue, C. Li, J. Xiao, C. Wang, Chem. Eur. J. 2017, 23, 14445-14449.
- a) C. Löfberg, R. Grigg, M. A. Whittaker, A. Keep, A. Derrick, J. Org. [7] Chem. 2006, 71, 8023-8027; b) B. Anxionnat, D. Gomez Pardo, G.
 Ricci, J. Cossy, Org. Lett. 2011, 13, 4084-4087; c) T. Sawaguchi, Y.
 Obora, Chem. Lett. 2011, 40, 1055-1057; d) B. Anxionnat, D. Gomez
 Pardo, G. Ricci, J. Cossy, Eur. J. Org. Chem. 2012, 2012, 4453-4456. A. Corma, T. Ródenas, M. J. Sabater, J. Catal. 2011, 279, 319-327. [8]
- a) T. Yan, B. L. Feringa, K. Barta, Nat. Commun. 2014, 5, 5602; b) H.-J. [9] Pan, T. W. Ng, Y. Zhao, Chem. Commun. 2015, 51, 11907-11910; c) A. J. Rawlings, L. J. Diorazio, M. Wills, Org. Lett. 2015, 17, 1086-1089; d) E. Saravanakumar, S. Jean-Baptiste, B. Matthias, D. Christophe, Angew. Chem. Int. Ed. 2015, 54, 14483-14486; e) M. Mastalir, B. Stöger, E. Pittenauer, M. Puchberger, G. Allmaier, K. Kirchner, Adv. Synth. Catal. 2016, 358, 3824-3831.
- S. Chakraborty, U. K. Das, Y. Ben-David, D. Milstein, J. Am. Chem. Soc. [10] 2017, 139, 11710-11713
- a) S. Chakraborty, W. W. Brennessel, W. D. Jones, J. Am. Chem. Soc. 2014, 136, 8564-8567; b) A. Glüer, M. Förster, V. R. Celinski, J. Schmedt auf der Günne, M. C. Holthausen, S. Schneider, ACS Catal. [11] 2015, 5, 7214-7217; c) S. Chakraborty, P. O. Lagaditis, M. Förster, E. A. Bielinski, N. Hazari, M. C. Holthausen, W. D. Jones, S. Schneider, ACS Catal. 2014, 4, 3994-4003; d) P. J. Bonitatibus, S. Chakraborty, M. D. Doherty, O. Siclovan, W. D. Jones, G. L. Soloveichik, Proc. Nat. Acad. Sci. 2015, 112, 1687-1692.
- [12] a) C. Bornschein, S. Werkmeister, B. Wendt, H. Jiao, E. Alberico, W. Baumann, H. Junge, K. Junge, M. Beller, *Nat. Commun.* **2014**, *5*, 4111; b) S. Chakraborty, H. Dai, P. Bhattacharya, N. T. Fairweather, M. S. Gibson, J. A. Krause, H. Guan, J. Am. Chem. Soc. 2014, 136, 7869-7872; c) N. Gorgas, B. Stöger, L. F. Veiros, E. Pittenauer, G. Allmaier, K. Kirchner, Organometallics 2014, 33, 6905-6914; d) T. Zell, Y. Ben-David, D. Milstein, Catal Sci Technol 2015, 5, 822-826; e) F. Bertini, N. Gorgas, B. Stöger, M. Peruzzini, L. F. Veiros, K. Kirchner, L. Gonsalvi, ACS Catal. 2016, 6, 2889-2893; f) N. M. Rezayee, D. C. Samblanet, M. S. Sanford, ACS Catal. 2016, 6, 6377-6383; g) R. Xu, S. Chakraborty, S. M. Bellows, H. Yuan, T. R. Cundari, W. D. Jones, ACS Catal. 2016, 6, 2127-2135; h) A. Zirakzadeh, K. Kirchner, A. Roller, B. Stöger, M. Widhalm, R. H. Morris, Organometallics 2016, 35, 3781-3787; i) S. Chakraborty, G. Leitus, D. Milstein, Angew. Chem. Int. Ed. 2017, 56, 2074-2078; j) M. K. Karunananda, N. P. Mankad, ACS Catal. 2017, 7, 6110-6119.
- [13] Y. Perumal, V. R. Jegadeesan, S. Dharmarajan, Recent Patents on CNS Drug Discovery 2006, 1, 113-118.
- T. Niwa, H. Yorimitsu, K. Oshima, *Tetrahedron* **2009**, *65*, 1971-1976. E. A. Bielinski, P. O. Lagaditis, Y. Zhang, B. Q. Mercado, C. Würtele, W. [14] [15] H. Bernskoetter, N. Hazari, S. Schneider, J. Am. Chem. Soc. 2014, 136, 10234-10237
- [16] I. Koehne, T. J. Schmeier, E. A. Bielinski, C. J. Pan, P. O. Lagaditis, W. H. Bernskoetter, M. K. Takase, C. Würtele, N. Hazari, S. Schneider, Inorg. Chem. 2014, 53, 2133-2143.
- Further evidence supporting the formation of ${\bf 14}$ is found in Section [17] 5.5.6, SI.

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A Fe-PNP pincer complex catalyzes efficient α -alkylation of nitriles with primary alcohols via a hydrogen-borrowing pathway, with the turnover rate limited by the reduction of the olefin intermediate. The nitriles are important - not only being a substrate but also stabilizing active Fe-H species.

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Fe catalyzed alkylation of nitriles with alcohols