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"Naked" Iridium(IV) Oxide Nanoparticles as Expedient and Robust Catalysts for Hydrogenation of Nitrogen Heterocycles: Remarkable Vicinal Substitution Effect and Recyclability

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Abstract: Iridium(IV) oxide nanoparticles were facilely prepared from iridium trichloride hydrate and sodium hydroxide by a ball-milling reaction at room temperature. The "naked" iridium nanocatalyst showed high stability and activity for the hydrogenation of a series of nitrogen heterocycles, for the first time, under a hydrogen balloon at room temperature with a selectivity of higher than 99%. Besides, an unprecedented substitution-dependent effect was discovered, where substrates with vicinal substituents on 2-, 3-, or 8-positions exhibited distinctly higher reaction rates than unsubstituted or remote substituted ones. Extraordinary recyclability was discovered in the hydrogenation of 2-methylquinoline for 30 runs without loss of activity.

Keywords: catalytic hydrogenation; iridium oxide nanoparticles; naked nanocatalyst; nitrogen heterocycles; recyclability

The application of nanocatalysts facilitates more efficient organic transformations compared to that of bulky materials, and sometimes molecular complexes, and thus has attracted high interest from academic and industrial chemists for several decades.^[1] Due to the large surface-to-volume ratio, naked nanocatalysts usually exhibit higher catalytic efficiency. Nevertheless, they suffer from aggregation and poor reusability, which seriously restricts their developments. Thus, a variety of stabilization methods, using surfactants,^[2] organic ligands,^[3] polymers,^[4] dendrimers,^[5] metal organic frameworks (MOF)^[6] and ionic liquids,^[7] were developed to improve their relative properties. Our group has also advanced a series of dendrimers- and organic ligands-stabilized nanocatalysts for carboncarbon bond formation and hydrogenations.^[8] However, in comparison with the stabilized transition metal nanocatalysts, the naked/unsupported nanocatalysts offer an opportunity to understand the intrinsic catalytic activity more easily by elimination of the support effect. Moreover, the blooming of stabilized nanocatalysts still suffers from the catalytic mechanism, where the true metal species in catalytic cycles remain obscure so far depending on the nature of the particles and/or reactions, which were widely accepted as "semi-heterogeneous".^[9,1g] From this point of view, naked/unsupported nanocatalysts have been considered a hot research area in recent years. Naked silver, gold, nickel and platinum nanocatalysts were systematically prepared and investigated in various organic reactions.^[10] In Jin's work, for instance, the unsupported nanoporous gold catalyst exhibited high selectivity in the hydrogenation of alkynes and quinolines with organosilane and water as a hydrogen source.[10f] Quite interestingly, although supported iridium oxide nanoparticles possess special activities in several chemical transformations including hydrogenation,^[11] catalytic water oxidation^[12] and CO₂ reduction^[13] etc., the catalytic application of their naked form was rarely reported.^[14] For an example, Diao's group produced iridium oxide nanoparticles via photochemical hydrolysis of iridium chloride in alkaline medium at room temperature with an average diameter of $1.7\pm$ 0.3 nm. Furthermore, a partially reduced Ir/IrO_x nanocomposite exhibited good catalytic performance

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toward the reduction of 4-nitrophenol.^[14a] To the best of our knowledge, however, the hydrogenation of nitrogen heterocycles catalyzed by naked iridium oxide nanoparticles has not been established yet.

1,2,3,4-Tetrahydroquinoline and derivatives as representative nitrogen heterocycles are a ubiquitous class of building blocks in naturally-occurring and synthetic compounds, which have wide applications in fine chemicals, pharmaceuticals and agrochemicals.^[15] In terms of simplicity and atom efficiency, the hydrogenation of readily available quinoline derivatives has been recognized as a promising approach (Scheme 1).



Scheme 1. Hydrogenation of quinolines *via* homogeneous and heterogeneous systems, and this work.

To date, various homogeneous and heterogeneous protocols catalyzed by transition metals or in a metalfree manner were applied for the hydrogenation of quinolines and their derivatives.^[16,17,18] Recently, an elegant study on a heterogeneous protocol was reported by Beller and co-workers, who developed core-shell cobalt oxide/cobalt nanoparticles modified by nitrogen-doped graphene layers on alumina. This heterogeneous catalyst enabled good activity and high selectivity in hydrogenation of nitrogen heteroarenes including quinolines, acridines and unprotected indoles, however, with a temperature of 120°C and time of up to 60 hours.^[17e] It should be noted that current hydrogenations of nitrogen heterocycles are associated with one or more shortcomings, including complicated catalyst preparation, high reaction pressure/temperature, high catalyst loading, air-sensitive ligands, additives, metal leaching, recyclability issues and so on. Consequently, we envisioned that naked/unsupported metal nanoparticles might match with the high demand of combining the merits of homogeneous and heterogeneous catalysts to address the above disadvantages. Herein, we reveal a facile preparation of naked iridium(IV) oxide nanoparticles, along with their first applications in the heterogeneous hydrogenation of nitrogen heterocycles with high efficiency and extraordinary recyclability under mild conditions.

Our studies started with the preparation of naked iridium(IV) oxide nanoparticles. Previous works have revealed the synthesis of iridium oxide nanoparticles *via* photochemical or thermal hydrolysis of Ir(IV)/Ir(III) precursors under basic aqueous conditions.^[14] In comparision, we herein disclose an operationally simple and greener ball-milling protocol without solvent or illumination. For a typical procedure, iridium chloride hydrate and sodium hydroxide were mixed (molar ratio of 1:4) and ground together in an agate mortar for 30 minutes at room temperature. The reaction started readily during the mixing process, accompanied by the release of heat. The mixture was rinsed with distilled water, and then dried at 80 °C for 4 hours The equation of the reaction is as follows:

4 IrCl₃·3 H₂O + 12 NaOH + O₂ = 4 IrO₂·x H₂O + 12 NaCl + (18-4x) H₂O

The resulting black powder indicated the formation of iridium(IV) oxide nanoparticles. The prepared IrO_2 NPs were absolutely insoluble in common solvents, such as THF, dichloromethane, ether, hexane, methanol, DMF and water, albeit slightly soluble in heated DMSO. This solubility provided for unambiguous heterogeneous catalysis and facile solvent precipitation for catalyst recovery.

Further characterization was conducted by transmission electron microscopy (TEM). The TEM image and size distribution of particles are shown in Figure 1, which revealed an average diameter of $2.0\pm$ 0.5 nm. X-ray photoelectron spectroscopy (XPS) measurement showed the Ir $4f_{7/2}$ and Ir $4f_{5/2}$ signals with binding energies E_b at 62.1 eV and 65.1 eV, respectively (Figure 1c). The XPS spectrum exemplified that the resulting iridium nanoparticles were assigned to the Ir(IV) state. These values were consistent with the literature report.^[19] To gain further insights into the chemical composition of the obtained iridium(IV) oxide nanoparticles, thermogravimetry (TG), X-ray diffraction (XRD) and Raman spectroscopy have been performeded. The total mass loss of the iridium(IV) oxide sample, as shown on the TG curves (Figure 2a), was up to 24.0%. Since no organic components were used for the whole preparation process, this mass loss might be contributed to the existence of crystalline water. Thus, the molecular formula of nanoparticles can be deduced as IrO2·4H2O. The XRD analysis was performed on a Rigaku Miniflex 600 with Cu ($\lambda = 1.54178$ Å) irradiation at the scanning rate of 10°m⁻ in the 20 range of 20-80° operating at 40 kV and 40 mA. Two board humps were observed at 33° and 56° (Figure 2b) corresponding to

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Figure 1. (a) TEM image of IrO_2 NPs (scale bar=10 nm); (b) the corresponding particle size distribution; (c) XPS spectrum of IrO_2 NPs.

(101) and (211) planes of IrO₂ in the tetragonal phase.^[19] Raman bands measured at 549 and 716 cm⁻¹ can be readily assigned to the first order E_g and B_{2g} phonon bands of rutile IrO₂ (Figure 2c).^[20]

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400 600 800 1000

Raman shift / cm⁻¹

Figure 2. (a) TG spectrum of IrO_2 NPs; (b) XRD spectrum of IrO_2 NPs; (c) Raman spectrum of IrO_2 NPs.

With this heterogeneous nanocatalyst in hand, we first examined the feasibility and efficiency of iridium (IV) oxide in the catalytic hydrogenation of 2-methylquinoline. Using 2 mol% iridium (IV) oxide nanoparticles, the desired product 1,2,3,4-tetrahydro-2-methyl-

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2-methylquinolir	ne. ^[a]	
	2 mol% IrO ₂ NPs	\sim
Ľ ∧ ∧	H ₂ balloon, solvent, r.t., 24 h	
19		29 H

Table 1. The effect of the solvents on the hydrogenation of

14		24
Entry	Solvent	Yield (2a [%]) ^[b]
1	toluene	20
2	dichloromethane	44
3	THF	17
4	1,4-dioxane	20
5	MeCN	32
6	EtOAc	36
7	EtOH	63
8	МеОН	>95 (98)
9	2,2,2-trifluoroethanol	>95 (97)
10	H_2O	<5
11 ^[c]	MeOH	46

[a] Reaction conditions: 0.2 mmol 2-methylquinoline, 2 mL solvent, 2.0 mol% catalyst, H₂ balloon, room temperature, 24 h.

^[c] Commercial IrO₂.

Table 2. IrO₂ nanoparticles-catalyzed hydrogenation of nitrogen heterocycles: vicinal substitutions.^[a]



 ^[a] Reaction conditions A: nitrogen heterocycle (0.2 mmol), MeOH (2 mL), IrO₂ NPs (1.2 mg, 0.04 mmol), H₂ balloon, room temperature, 24 h.

^[b] Isolated yield.

^[c] The product – with repetition for three times – was identified as 1,2,3,4-tetrahydroquinoline.

corresponding adducts in high yields and selectivities. Substrate with a methyl group on the 3-position of

substrate also reacted smoothly, although it is widely

quinoline was obtained in 20% yield with toluene as solvent under a hydrogen balloon at room temperature for 24 hours (Table 1, entry 1). As shown in Table 1, the conversions were strongly dependent on the solvents. Non-polar solvents such as dichloromethane, THF, 1,4-dioxane, acetonitrile and ethyl acetate gave yields of less than 50%. In sharp contrast, the conversions were dramatically enhanced in alcoholic solvents. Yields of more than 95%, along with 99% selectivity, were obtained in methanol and 2,2,2-trifluoroethanol (entries 8 and 9). However, the substrate remained intact in water (entry 10). To our delight, a significantly differentiated reactivity of iridium(IV) oxide nanoparticles and commercial IrO₂ was observed, where the bulky commercial IrO₂ only afforded a lower yield of 46% (entry 11). As illustrated in the optimizations, a high pressure of molecular hydrogen, elevated temperatures or high catalyst loadings are simultaneously avoided without impairing the catalytic efficiency. Moreover, the nanocatalyst could be removed by decantation or centrifugation, leaving the hydrogenation product alone after evaporation of the methanol. Thus, to the best of our knowledge, this is the operationally simplest protocol under mild conditions for heterogeneous hydrogenation of 2-methylquinoline reported so far.

The substrate scopes of various substituted quinolines and other nitrogen heterocycles were further investigated under the optimized conditions (Table 2). In general, quinoline derivatives with vicinal functional groups (2, 3, 8 positions) are hydrogenated to the accepted as a tough substrate, usually applied with high pressure and/or temperature.^[16e] More interestingly, the presence of electron-deficient bromo substituents on the 6 or 8 positions of quinoline moiety did not retard the hydrogenation process. Besides, no hydrodehalogenation products were detected under the current conditions (entries 6 and 7), whereas the cleavage of C-Br bond is a common event for iridium and other transition metal complexes/nanoparticles.^[21,8e,f] These results further testified the mild and highly regioselective properties of our protocol. To be noted, an unanticipated C-N bond cleavage was observed for 2-aminoquinoline (1c, entry 3). Vicinal substituted quinoxanes (1h-1j) are also applicable under the standard conditions with excellent yields and selectivities. Further efforts on the hydrogenation of vicinal substituted benzothiazoles, benzofurans and indoles gave negative results, which implied the substrate structure dependence of our iridium(IV) oxide nanoparticles. It is worthy to mention that the above excellent re-

It is worthy to mention that the above excellent results were obtained with substrates bearing vicinal substitutions. Otherwise, the hydrogenation turned to be sluggish. As depicted in Table 3, quinoline and other nitrogen heterocycles with remote substitutions (4, 5, 6, 7 positions) required higher reaction temperature and hydrogen pressure to enable statisfactory

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^[b] Determined by ¹H-NMR (isolated yield in brackets).

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Table 3. IrO2	nanoparticles-catalyzed	hydrogenation	of	ni
trogen hetero	cycles: none or remote s	ubstitutions. ^[a]		

R ¹	Z N k-1t	−R ² + H ₂ (60 atm)	IrO ₂ NPs (2 mol%) MeOH, 24 h, 60 °C	$R^{1} \xrightarrow[H]{} Z_{H} R^{2}$ $R^{2} \xrightarrow[H]{} R^{2}$ $2k-2t$
Entry	Z	\mathbb{R}^1	R ²	Yield (2 [%]) ^[b]
1	Н	Н	H (1k)	98 (<5)
2	Н	Н	2-Ph (11)	97 (43)
3	Н	Н	4-Me (1m)	42 (0)

3	п	п	4-IVIC (1111)	42 (0)
4	Η	Н	6-Me (1n)	98 (<5)
5	Н	Н	6-MeO (10)	97 (<5)
6	Η	$6-NH_2$	Н (1р)	96 (0)
7	Н	Н	7-Me (1q)	97 (18)
8	Н	8-Cl	H (1 r)	95 (31)
9	Ν	Н	H (1s)	98 (<5)
10	Ν	Н	2-Ph (1t)	96 (<5)

[[]a] Reaction conditions B: nitrogen heterocycle (0.2 mmol), MeOH (2 mL) and IrO₂ NPs (1.2 mg, 0.04 mmol), 60 atm H₂, 60 °C, 24 h.

conversion. For instance, the hydrogenation of quinoline gave >95% yield upon heating up to 60°C under 60 atm hydrogen pressure (conditions B, entry 1), whereas only a <5% yield was detected with the former optimized conditions A (hydrogen balloon, room temperature). Moreover, the rest of substrates possessing remote substitutions or vicinal phenyl groups furnished much lower yields ranging from 0-43% under conditions A. It is well known that orthosubstitution sometimes diminished the efficiency of catalytic hydrogenation due to the steric hindrance.^[22] However, this type of reverse substitution-dependent effect is impressive and unprecedented in catalytic hydrogenation. Furthermore, a competing hydrogenation of 2-methylquinoline and 4-methylquinoline was conducted under the standard conditions A in Scheme 2. A 100:0 (2a:2m) ratio of hydrogenated products was indentified by ¹H-NMR, further exemplifing the positive effect of vicinal substitution. We hypothesize that the homolytic hydrogen would be stabilized by the iridium oxide and activate the pyridine moiety, which synergistically enables a weak hydrogen-bonding interaction of the vicinal (methyl)C-H with an oxygen atom on the surface of iridium oxide nanoparticles toward higher efficiency.^[23] It is noticed that 2-phenyl-substituted substrates (11, 1t) proceeded sluggishly under conditions A, but were converted into hydrogenated products with excellent yields under conditions B. This comparison is consistent with the fact that larger conjugation would retard the hydrogenation efficiency.^[16e]



Scheme 2. The competing hydrogenation reaction and the proposed C-H···O(=Ir=O) hydrogen bonding interaction.

Finally, the reusability of this nanocatalyst was evaluated with 2-methylquinoline as the model substrate. Figure 3 depicts the recovery and reusability of our "naked" iridium(IV) oxide catalyst. After the reaction completion, the catalyst was collected by centrifugation, and the products were separated by simple decantation and evaporation. By adding a new batch of methanol and 2-methylquinoline, the recovered nanocatalyst can be used directly for the next run. This recycling protocol enabled the iridium oxide nanoparticles to be used for 30 runs furnishing quantitative conversion of substrates without loss of activity and selectivity. This remarkable stability for "naked" nanoparticles is intriguing and unprecedented, since aggregations always lead to deactivation of catalytic sites without the protection of stabilizors. TEM images of iridium oxide nanoparticles after 30 runs exhibited a similar size distribution compared to the freshly prepared ones. Meanwhile, the XPS spectrum indicated the sole component of Ir(IV), no Ir(0) species was formed after hydrogenation and recovery. Furthermore, ICP-OES was applied to detect the leaching of iridium in the organic phase for 1st, 2nd and 30th cycles, which all gave values below the detection threshold. The above observations collectively point to a heterogeneous process, and completely rule out the "semi-heterogeneous" manner for this protocol.

In summary, we have revealed here an expedient preparation of "naked" iridium(IV) oxide nanoparticles from iridium trichloride hydrate and sodium hydroxide via a ball-milling reaction. This heterogeneous nanocatalyst was applied, for the first time, in the hydrogenation of a series of nitrogen heterocycles with a hydrogen balloon at room temperature. The catalyst showed high stability and activity, along with a selectivity higher than 99%. An unprecedented sub-

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[[]b] Isolated yields (yields under reaction conditions A in brackets).









Figure 3. (a) The recycling runs; (b) TEM image (scale bar=5 nm) and particle size distribution of the nanocatalyst after 30 runs.

stitution-dependent effect was discovered, where substrates with vicinal substituents on 2, 3, or 8 positions exhibited distinctly higher reaction rates than unsubstituted or remotely substituted ones. Moreover, extraordinary recyclability was discovered in the hydrogenation of 2-methylquinoline for 30 runs without loss of activity or metal leaching. **Experimental Section**

Typical Procedures for Preparation of "Naked" Iridium Oxide Nanoparticles

Iridium chloride trihydrate and sodium hydroxide were premixed with a molar ratio of 1:4, and then the mixture was ground by ball-milling in an agate mortar for 30 min at room temperature. The reaction started readily during the mixing process, accompanied by the release of heat. The product was rinsed with distilled water then oven dried at 80 °C for 4 hours to afford black powder ready for catalytic use directly.

Typical Procedure for Catalytic Hydrogenation of Nitrogen Heterocycles with "Naked" Iridium Oxide Nanoparticles

2-Methylquinoline (28.6 mg, 0.2 mmol), IrO_2 NPs (1.2 mg, 2 mol%), and 2 mL methanol were charged into a reaction tube, purged with hydrogen for three times and then pressurized with a hydrogen balloon. The reaction mixture was stirred at room temperature for 24 hours. After completion, the catalyst was recovered by decantation or centrifugation at 15,000 rpm, and then washed with methanol for 3 times (1 mL×3). The organic phases were combined and concentrated to afford the hydrogenated product (**2a**). The recovered nanocatalysts can be used directly for the next run.

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References

- For selected books and reviews, see: a) D. Astruc, Nanoparticles and Catalysis, Wiley-VCH, 2008; b) C. Deraedt, D. Astruc, Acc. Chem. Res. 2014, 47, 494; c) P. Hervés, M. PérezLorenzo, L. M. LizMarzán, J. Dzubiella, Y. Lu, M. Ballauff, Chem. Soc. Rev. 2012, 41, 5577; d) N. Yan, C. Xiao, Y. Kou, Coord. Chem. Rev. 2010, 254, 1179; e) A. Corma, H. Garcia, Chem. Soc. Rev. 2008, 37, 2096; f) D. Astruc, Inorg. Chem. 2007, 46, 1884; g) D. Astruc, F. Lu, J. R. Aranzaes, Angew. Chem. 2005, 117, 8062; Angew. Chem. Int. Ed. 2005, 44, 7852; h) A. T. Bell, Science 2003, 299, 1688; i) M. A. El-Sayed, Acc. Chem. Res. 2001, 34, 257.
- [2] a) S. R. Isaacs, E. C. Cutler, J. S. Park, T. R. Lee, Y. S. Shon, *Langmuir* 2005, *21*, 5689; b) B. H. Yoon, H. Kim, C. M. Wai, *Chem. Commun.* 2003, 1040.
- [3] a) A. Ferry, K. Schaepe, P. Tegeder, C. Richter, K. M. Chepiga, B. J. Ravoo, F. Glorius, ACS Catal. 2015, 5, 5414; b) J. F. Sonnenberg, N. Coombs, P. A. Dube,

Adv. Synth. Catal. 0000, 000, 0-0

These are not the final page numbers! **77**

.

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R. H. Morris, J. Am. Chem. Soc. 2012, 134, 5893; c) M.
Montalti, N. Zaccheroni, L. Prodi, N. O'Reilly, S. L.
James, J. Am. Chem. Soc. 2007, 129, 2418; d) S. Jansat,
M. Gómez, K. Philippot, G. Muller, E. Guiu, C. Claver,
S. Castillón, B. Chaudret, J. Am. Chem. Soc. 2004, 126, 1592.

- [4] a) Q. M. Kainz, O. Reiser, Acc. Chem. Res. 2014, 47, 667; b) G. Yun, Z. Hassan, J. Lee, J. Kim, N. S. Lee, N. H. Kim, K. Baek, I. Hwang, C. G. Park, K. Kim, Angew. Chem. 2014, 126, 6532; Angew. Chem. Int. Ed. 2014, 53, 6414; c) Y. M. A. Yamada, T. Arakawa, H. Hocke, Y. Uozumi, Angew. Chem. 2007, 119, 718; Angew. Chem. Int. Ed. 2007, 46, 704; d) M. S. Kwon, N. Kim, S. H. Seo, I. S. Park, R. K. Cheedrala, J. Park, Angew. Chem. 2005, 117, 7073; Angew. Chem. Int. Ed. 2005, 44, 6913; e) B. P. S. Chauhan, J. S. Rathore, T. Bandoo, J. Am. Chem. Soc. 2004, 126, 8493.
- [5] a) C. Deraedt, N. Pinaud, D. Astruc, J. Am. Chem. Soc. 2014, 136, 12092; b) C. Deraedt, L. Salmon, L. Etienne, J. Ruiz, D. Astruc, Chem. Commun. 2013, 49, 8169; c) V. S. Myers, M. G. Weir, E. V. Carino, D. F. Yancey, S. Pande, R. M. Crooks, Chem. Sci. 2011, 2, 1632; d) X. Peng, Q. Pan, G. L. Rempel, Chem. Soc. Rev. 2008, 37, 1619.
- [6] a) M. Zhao, K. Deng, L. He, Y. Liu, G. Li, H. Zhao, Z. Tang, J. Am. Chem. Soc. 2014, 136, 1738; b) Q.-L. Zhu, J. Li, Q. Xu, J. Am. Chem. Soc. 2013, 135, 10210; c) A. Dhakshinamoorthy, H. Garcia, Chem. Soc. Rev. 2012, 41, 5262, and references cited therein.
- [7] a) J. D. Scholten, B. C. Leal, J. Dupont, ACS Catal.
 2012, 2, 184; b) C. Vollmer, C. Janiak, Coord. Chem. Rev. 2011, 255, 2039, and references cited therein.
- [8] a) L. Wu, J. Ling, Z.-Q. Wu, Adv. Synth. Catal. 2011, 353, 1452; b) L. Wu, X. Zhang, Z. Tao, Catal. Sci. Technol. 2012, 2, 707; c) L. Wu, Y. Zhang, Y.-G. Ji, Curr. Org. Chem. 2013, 17, 1288; d) Y. G. Ji, L. Wu, Q.-H. Fan, Acta Chim. Sin. (Engl. Ed.) 2014, 72, 798; e) Y. Zhang, M. Mao, Y.-G. Ji, J. Zhu, L. Wu, Tetrahedron Lett. 2016, 57, 329; f) Y. Zhang, J. Zhu, Y.-T. Xia, X.-T. Sun, L. Wu, Adv. Synth. Catal. 2016, 358, 3039.
- [9] A. Schätz, O. Reiser, W. J. Stark, Chem. Eur. J. 2010, 16, 8950.
- [10] a) S. Giuffrida, G. Ventimiglia, S. Sortino, Chem. Commun. 2009, 4055; b) G. Merga, R. Wilson, G. Lynn, B. H. Milosavljevic, D. Meisel, J. Phys. Chem. C 2007, 111, 1220; c) M. Boronat, A. Corma, J. Catal. 2011, 284, 138; d) C. Moreno, N. J. Divins, J. Gázquez, M. Varela, I. Angurell, J. Llorca, Nanoscale 2012, 4, 2278; e) G. L. HallettTapley, C. D'Alfonso, N. L. Pacioni, C. D. McTiernan, M. González-Béjar, O. Lanzalunga, E. I. Alarcon, J. C. Scaiano, Chem. Commun. 2013, 49, 10073; f) M. Yan, T. Jin, Q. Chen, H. E. Ho, T. Fujita, L. Y. Chen, M. Bao, M. W. Chen, N. Asao, Y. Yamamoto, Org. Lett. 2013, 15, 1484; g) M. Shah, Q. X. Guo, Y. Fu, Catal. Commun. 2015, 65, 85; h) B. Gralec, A. Lewera, App. Catal. B: Environ. 2016, 192, 304.
- [11] C. Hammond, M. T. Schümperli, S. Conrad, I. Hermans, *ChemCatChem* 2013, 5, 2983.
- [12] a) J. C. HidalgoAcosta, M. A. Méndez, M. D. Scanlon, H. Vrubel, V. Amstutz, W. Adamiak, M. Opallo, H. H. Girault, *Chem. Sci.* 2015, *6*, 1761; b) R. D. L. Smith, B. Sporinova, R. D. Fagan, S. Trudel, C. P. Berlinguette,

Adv. Synth. Catal. 0000, 000, 0-0

These are not the final page numbers! **77**

7

Chem. Mater. **2014**, *26*, 1654; c) D. B. Grotjahn, D. B. Brown, J. K. Martin, D. C. Marelius, M. C. Abadjian, H. N. Tran, G. Kalyuzhny, K. S. Vecchio, Z. G. Specht, S. A. Cortes-Llamas, V. MirandaSoto, C. van Niekerk, C. E. Moore, A. L. Rheingold, *J. Am. Chem. Soc.* **2011**, *133*, 19024.

- [13] Q.-Y. Bi, J.-D. Lin, Y.-M. Liu, S.-H. Xie, H.-Y. He, Y. Cao, Chem. Commun. 2014, 50, 9138.
- [14] a) D. Xu, P. Diao, T. Jin, Q. Wu, X. Liu, X. Guo, H. Gong, F. Li, M. Xiang, R. Yu, ACS Appl. Mater. Interfaces 2015, 7, 16738; b) K. Chakrapani, S. Sampath, Chem. Commun. 2015, 51, 9690; c) Y. Zhao, E. A. HernandezPagan, N. M. Vargas-Barbosa, J. L. Dysart, T. E. Mallouk, J. Phys. Chem. Lett. 2011, 2, 402.
- [15] For selected reviews: a) V. Sridharan, P. A. Suryavanshi, J. C. Menéndez, *Chem. Rev.* 2011, *111*, 7157;
 b) J. D. Scott, R. M. Williams, *Chem. Rev.* 2002, *102*, 1669.
- [16] For selected homogeneous protocols with transition metals, see: a) W.-B. Wang, S.-M. Lu, P.-Y. Yang, X.-W. Han, Y.-G. Zhou, J. Am. Chem. Soc. 2003, 125, 10536; b) H. Zhou, Z. Li, Z. Wang, T. Wang, L. Xu, Y. He, Q.-H. Fan, J. Pan, L. Gu, A. S. C. Chan, Angew. Chem. 2008, 120, 8592; Angew. Chem. Int. Ed. 2008, 47, 8464; c) R. Yamaguchi, C. Ikeda, Y. Takahashi, K. I. Fujita, J. Am. Chem. Soc. 2009, 131, 8410; d) G. E. Dobereiner, A. Nova, N. D. Schley, N. Hazari, S. J. Miller, O. Eisenstein, R. H. Crabtree, J. Am. Chem. Soc. 2011, 133, 7547; e) T. Wang, L.-G. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. C. Chan, J. Am. Chem. Soc. 2011, 133, 9878; f) D.-S. Wang, Q.-A. Chen, S.-M. Lu, Y.-G. Zhou, Chem. Rev. 2012, 112, 2557, and references cited herein.
- [17] For selected heterogeneous protocols with transition metals, see: a) H. U. Blaser, U. Siegrist, H. Steiner, M. Studer, in: Fine Chemicals through Heterogeneous Catalysis, (Eds.: R. A.Sheldon, H. van Bekkum), Wiley-VCH, Weinheim, 2001; b) N. A. Beckers, S. Huynh, X. Zhang, E. J. Luber, J. M. Buriak, ACS Catal. 2012, 2, 1524; c) M. Fang, N. Machalaba, R. A. SanchezDelgado, Dalton Trans. 2011, 40, 10621; d) M. Fang, R. A. SanchezDelgado, J. Catal. 2014, 311, 357; e) F. Chen, A. E. Surkus, L. He, M. M. Pohl, J. Radnik, C. Topf, K. Junge, M. Beller, J. Am. Chem. Soc. 2015, 137, 11718; f) M. Niu, Y. Wang, P. Chen, D. Du, J. Jiang, Z. Jin, Catal. Sci. Technol. 2015, 5, 4746; g) A. Karakulina, A. Gopakumar, İ. Akçok, B.L. Roulier, T. LaGrange, S. A. Katsyuba, S. Das, P. J. Dyson, Angew. Chem. 2016, 120, 300; Angew. Chem. Int. Ed. 2016, 55, 292.
- [18] For representative metal-free protocols, see: a) Y.-T. Xia, X.-T. Sun, L. Zhang, K. Luo, L. Wu, Chem. Eur. J. 2016, 22, 17151; b) C. Wang, C. Li, X. Wu, A. Pettman, J. Xiao, Angew. Chem. 2009, 121, 6646; Angew. Chem. Int. Ed. 2009, 48, 6524; c) M. Rueping, T. Theissmann, Chem. Sci. 2010, 1, 473; d) M. Rueping, A. P. Anton-chick, T. Theissmann, Angew. Chem. 2006, 118, 3765; Angew. Chem. Int. Ed. 2006, 45, 3683; e) C. Zheng, S.-L. You, Chem. Soc. Rev. 2012, 41, 2498.
- [19] K. Chakrapani, S. Sampath, Chem. Commun. 2015, 51, 9690.

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- [20] J. H. Shim, Y. Lee, M. Kang, L. Jaeyeon, M. B. Jeong, L. Youngmin, L. Chongmok, H. K. Myung, *Anal. Chem.* 2012, 84, 3827.
- [21] a) F. Alonso, I. P. Beletskaya, M. Yus, *Chem. Rev.* 2002, 102, 4009; b) J. Yang, M. Brookhart, *J. Am. Chem. Soc.* 2007, 129, 12656; c) R. Nakao, H. Rhee, Y. Uozomi, *Org. Lett.* 2005, 7, 163.
- [22] For steric hindrance to retard catalytic hydrogenation, see: a) A. Togni, C. Breutel, A. Schnyder, F. Spindler,

H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, *116*, 4062; b) Y. Wei, C. Wang, X. Jiang, D. Xue, J. Li, J. Xiao, *Chem. Commun.* **2013**, *49*, 5408.

[23] For activated C-H…O(=C) hydrogen bonding interaction, see: a) Y. Gu, T. Kar, S. Scheiner, J. Am. Chem. Soc. 1999, 121, 9411; b) C. R. Jones, P. K. Baruah, A. L. Thompson, S. Scheiner, M. D. Smith, J. Am. Chem. Soc. 2012, 134, 12064; c) R. C. Johnston, P. H.-Y. Cheong, Org. Biomol. Chem. 2013, 11, 5057.

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COMMUNICATIONS

"Naked" Iridium(IV) Oxide Nanoparticles as Expedient and Robust Catalysts for Hydrogenation of Nitrogen Heterocycles: Remarkable Vicinal Substitution Effect and Recyclability

Adv. Synth. Catal. 2017, 359, 1-9

🛄 Yi-Gang Ji, Kai Wei, Teng Liu, Lei Wu,* Wei-Hua Zhang*



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- Facile Ball-Milling Preparation of IrO₂ NPs
- The First Application of "Naked" IrO₂ NPs in Hydrogenation of N-heterocycles
- Mild Conditions with Hydrogen Balloon at Room Temperature
- Reaction Rate: Vicinal Substitutions >> None or Remote Substitutions
- Extraordinary Recyclability with 30 runs

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