Organic & Biomolecular Chemistry

COMMUNICATION

RSCPublishing

View Article Online View Journal | View Issue

Cite this: Org. Biomol. Chem., 2013, 11, 7653

Received 12th September 2013, Accepted 30th September 2013

DOI: 10.1039/c3ob41872c

www.rsc.org/obc

Efficient and regioselective nickel-catalyzed [2 + 2 + 2] cyclotrimerization of ynoates and related alkynes†

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A nickel-based catalytic system has been developed for [2 + 2 + 2] cyclotrimerization of various alkynes, especially ynoates. This catalytic system enables facile construction of substituted aromatic compounds in excellent yields with high regioselectivity.

Transition-metal-catalyzed [2 + 2 + 2] cycloaddition of alkynes represents a versatile method for the construction of benzene rings.¹ It is especially useful when the desired substitution pattern is not easily built via conventional aromatic substitution reactions. The challenge of implementing this cyclization strategy, however, arises in performing the reactions of unsymmetrical alkynes due to the formation of different regioisomers. Typically, [2 + 2 + 2] cycloaddition of a divne and an alkyne² or intramolecular cycloaddition of a triyne³ is more regioselective, and therefore it has been more widely utilized in organic synthesis.¹ Nevertheless, over the past two decades, a plethora of transition metal systems (e.g., Ti,⁴ Co,⁵ Ni,⁶ Ru,⁷ Rh,⁸ Pd⁹ and other metals¹⁰) have been developed specifically to catalyze intermolecular [2 + 2 + 2] cycloaddition of three individual alkyne molecules. Despite the progress, many challenges remain, particularly to increase catalytic efficiency and improve regioselectivity. While the majority of known protocols employ 5-10 mol% of metal catalysts (with respect to the total alkynes), there are a few cases where a catalyst loading as low as 1 mol% is sufficient to convert alkynes to substituted benzenes in high yield with high regioselectivity.^{4c,7e,8b,10d} One notable example, and arguably the most active catalytic system reported to date, involves cyclopentadienyl-ruthenium-based complexes,^{7e} which promote the cyclotrimerization of alkynes

^bSchool of Chemistry & Materials Science, Rochester Institute of Technology, Rochester, NY 14623, USA. E-mail: mgcsch@rit.edu; Fax: (+1) 585-475-7800; Tel: (+1) 585-475-5108 with turnover numbers (TONs) up to 196 and isomeric ratios greater than 90:10.

During the course of developing a nickel-based catalytic system for regioselective reductive coupling of ynoates and aldehydes (Scheme 1),¹¹ we found that in order to achieve high yields for the desired silyl-protected γ -hydroxy- α , β -enoates, the ynoate substrate must be added very slowly to the reaction mixture. Close inspection of the byproducts revealed that one of the competing pathways was the cyclotrimerization of ynoates to generate benzene-1,2,4-tricarboxylates as the major isomers. Nickel-catalyzed oligomerization of ynoates is known in the literature, but in most cases tetra-substituted cyclooctatetraenes are the cycloaddition products.¹² A study done in the early sixties using $Ni(PPh_3)_2(CO)_2$ as the catalyst showed that oligomerization of ethyl propiolate produced 1,2,4- and 1,3,5substituted aromatic compounds in 89% and 6% yields, respectively.13 Given that these benzene derivatives could be used as new branching or cross-linking agents for polymers¹⁴ and as precursors for synthesizing organic light-emitting diode materials,¹⁵ we became interested in optimizing the conditions for the cyclotrimerization of ynoates and related alkynes. In this paper, we will report these results and illustrate that such a process can be readily catalyzed by $Ni(COD)_2/$ PPh₃ or Ni(COD)₂/NHC (NHC is an N-heterocyclic carbene). The advantages of using this methodology are several fold. First of all, catalysts can be easily generated in situ by mixing commercially available reagents. More importantly, the catalytic process is quite efficient; TONs as high as 2000 can be



Scheme 1 Nickel-catalyzed reductive coupling reactions.

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[†]Electronic supplementary information (ESI) available: Experimental procedures and spectroscopic characterization data for compounds **2a–p**, **3d**, and **3p**. CCDC 948437 (**2f**) and 948438 (**2m**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ob41872c

achieved, allowing the synthesis to be carried out on the gram scale. Moreover, the observed regioselectivity is typically high and in a number of cases only one regioisomer is formed.

We commenced our study with the identification of optimal conditions for the cyclotrimerization reaction using ethyl propiolate 1a as the substrate. The results are summarized in Table 1. In agreement with our previous procedures for reductive coupling of ynoates and aldehydes,¹¹ the first set of experiments (entries 1-3) was to test the catalytic performance of $Ni(COD)_2$ (10 mol%) combined with an equimolar amount of a phosphine ligand. In the presence of $Ni(COD)_2/P^nBu_3$, only a negligible amount of product formed after 1 h at room temperature, as determined by GC-MS (entry 1). While replacing $P^n Bu_3$ with PCy₃ increased the yield to 20% (entry 2), the use of PPh₃ led to a more significant improvement with GC yield reaching 82% (entry 3). Encouraged by this result, we were curious to see if the commercially available Ni(PPh₃)₄ would catalyze the same reaction. With 1 mol% of $Ni(PPh_3)_4$ (entry 4), a quantitative conversion of 1a to aromatic compounds 2a and 3a (with a ratio of 97:3) was observed within 1 h. Although $Ni(PPh_3)_4$ proved to be an effective catalyst, it is a relatively expensive reagent. We thus decided to replace it with the much cheaper $Ni(COD)_2$ along with 4 equivalents of PPh₃.¹⁶ The *in situ* generated catalyst turned out to be as efficient as pure $Ni(PPh_3)_4$ in promoting the cyclotrimerization reaction without compromising the level of regioselectivity (entry 5). Additional optimization studies suggested that the amount of PPh₃ could be reduced to 3 equivalents relative to $Ni(COD)_2$ (entry 6). However, reducing the PPh₃/Ni(COD)₂ ratio further resulted in diminished yields (entries 7 and 8). We also tested different solvents for the cyclotrimerization reaction. Among the solvents tested, toluene was found to be a much

Table 1 Optimization of the reaction conditions ^a							
Ξ	CO₂Et <u>co₂</u> Et <u>catalyst</u> 1a	CO ₂ Et CO ₂ Et CO ₂ Et 2a	Et + EtO ₂ C	CO ₂ Et	D ₂ Et		
Entry	Catalyst	Cat. (mol%)	Solvent	Yield ^b (%)	2a : 3a ^c		
1	$Ni(COD)_2: P^n Bu_3(1:1)$	10	Toluene	2	n.d.		
2	$Ni(COD)_2 : PCy_3(1:1)$	10	Toluene	20	n.d.		
2	Ni(COD), $DDh(1,1)$	10	Toluene	00	n d		

3	$Ni(COD)_2: PPh_3(1:1)$	10	Toluene	82	n.d.
4	$Ni(PPh_3)_4$	1	Toluene	100	97:3
5	$Ni(COD)_2 : PPh_3 (1:4)$	1	Toluene	100	97:3
6	$Ni(COD)_2 : PPh_3 (1:3)$	1	Toluene	100	97:3
7	$Ni(COD)_2 : PPh_3(1:2)$	1	Toluene	57	n.d.
8	$Ni(COD)_2 : PPh_3(1:1)$	1	Toluene	36	n.d.
9	$Ni(COD)_2$: PPh ₃ (1:3)	1	THF	42	n.d.
10	$Ni(COD)_2: PPh_3(1:3)$	1	CH_3CN	72	n.d.

^{*a*} Conditions: **1a** (0.25 mmol), nickel catalyst and *n*-decane (internal standard, 0.04 mmol) in 2 mL of solvent. ^{*b*} Combined (**2a** + **3a**) yield determined by GC-MS. ^{*c*} Ratio determined by ¹H NMR (n.d. = not determined).

better medium to carry out the reaction than the more polar solvents such as THF and CH_3CN (entries 9 and 10).

It should be mentioned that there are literature precedents for $Ni(COD)_2/PPh_3$ -catalyzed [2 + 2 + 2] cycloaddition of alkynes. The Mori group has reported cocyclization of diynes and acetylene catalyzed by 30 or 40 mol% of Ni(COD)₂/PPh₃ (1:4).¹⁷ Saito, Yamamoto, and co-workers have used the same catalytic mixture (10 mol%) for regioselective cyclotrimerization of 1-perfluoroalkylenynes.^{6b} Ikeda et al. have employed 5 mol% of Ni(COD)₂/PPh₃ (1:2) for cross-cyclotrimerization of two different alkynes.^{6a} A more recent study by the Baran group has demonstrated that 10 mol% of $Ni(COD)_2/PPh_3$ (1:1) is an effective catalyst for co-oligomerization of 1,3-dienes and alkynes, but for some alkyne substrates, benzene derivatives are the main products.¹⁸ One common feature of the abovementioned catalytic processes as well as other Ni(COD)2-catalyzed reactions is the high catalyst loading, which is, in part, due to the low thermal stability of the Ni(0) species.¹⁹ In this regard, the relatively low catalyst loading needed in our system is quite unusual. As a matter of fact, even with 0.05 mol% of the nickel catalyst, cyclotrimerization of 1a was found to be complete within 2 h (eqn (1)). The calculated TON of 2000, to the best of our knowledge, is the highest for any transitionmetal-catalyzed cyclotrimerization reaction.



To explore the scope of the cyclotrimerization reaction, we applied the optimized conditions to a variety of ynoates. As shown in Table 2, methyl, ethyl, or tert-butyl propiolate (entries 1-3) underwent facile cyclotrimerization to afford the corresponding benzene-1,2,4-tricarboxylate as the major product. The observed regioselectivity (97:3) appeared to be unaffected by the size of the alkyl groups. However, the reaction of 2-naphthyl propiolate was less selective, resulting in an 88:12 mixture of 1,2,4- and 1,3,5-isomers (entry 4). Attempts to improve the regioselectivity by replacing 3 equiv. of PPh₃ with 1 equiv. of an NHC ligand (Fig. 1) were unsuccessful (entries 5 and 6). Ynoates with an internal C=C bond also proved to be viable substrates, although a longer reaction time or a higher temperature was necessary. For example, cyclotrimerization of diethyl acetylenedicarboxylate 1e took 5 h to complete, providing a hexa-substituted benzene in nearly quantitative yield upon isolation (entry 7). In contrast, no reaction was observed for 1f after 24 h at room temperature. Yang and co-workers had encountered a similar challenge¹⁵ when using Hilt's cobalt diimine catalyst^{5c} to effect the cyclotrimerization of 1f. Fortunately, at 80 °C, nickel-catalyzed cyclotrimerization proceeded smoothly to yield the unsymmetrical cyclotrimer 2f as the major isomer, albeit with a modest selectivity of 80:20 (entry 8). The regioselectivity was, however,

Table 2 Cyclotrimerization of various ynoates^a



Entry	Ynoate	Cat.	Time (h)	Temp. (°C)	$\operatorname{Yield}^{b}(\%)$	$2:3^{d}$
1	───CO₂Et (1a)	А	1	23	90	97:3
2	CO ₂ Me (1 b)	А	1	23	91	97:3
3	───CO ₂ ^t Bu (1c)	А	1	23	88	97:3
4	CO ₂ (2-Np)	А	1	23	86 ^c	88:12
5	(1d)	В	1	23	n.d.	75:25
6		С	1	23	n.d.	75:25
7	EtO_2C — CO_2Et	А	5	23	96	—
8	EtO ₂ C— <u> Ph</u>	А	12	80	94^c	80:20
9	(1f)	В	24	23	92	97:3
10	EtO_2C — — — Me	А	24	23	74	80:20
11		В	24	23	n.d.	85:15
12		С	24	23	84	90:10
13	MeO ₂ C	А	24	23	71	80:20
14		В	24	23	94	>99:1
15	MeO ₂ C—— ⁿ Hex	В	24	23	89	>99:1
16	$EtO_2C TMS$	В	24	23	92	>99:1

^{*a*} Abbreviations: 2-Np = 2-naphthyl, ^{*n*}Pr = *n*-propyl, ^{*n*}Hex = *n*-hexyl; reaction conditions: 1.5 mmol of 1 in 2 mL of toluene (for cat. **A**) or THF (for cat. **B** and **C**), cat. **A** = 1 mol% Ni(COD)₂/PPh₃ (1:3), cat. **B** = 1 mol% Ni(COD)₂/SIPr (1:1), cat. **C** = 1 mol% Ni(COD)₂/SIMes (1:1). ^{*b*} Isolated yield for 2. ^{*c*} Combined isolated yield for 2 and 3. ^{*d*} Ratio determined by ¹H NMR or GC-MS.



Fig. 1 NHCs employed in this study.

substantially higher when SIPr was used in place of PPh₃ (entry 9). The substitution pattern of 2**f** was further established by X-ray crystallography (Fig. 2, see ESI[†]).[‡] Worthy of particular note is that 2**f** has been previously sought after as a precursor to isotruxene,¹⁵ a potential building block for synthesizing various π -conjugated systems.²⁰ Thus, the method developed here could be a convenient synthetic route to these types of molecules. Interestingly, Ni(COD)₂/PPh₃-catalyzed cyclotrimerization of **1g** (entry 10) and **1h** (entry 13) took place at room temperature, but displayed modest regioselectivity (80:20). These results were somewhat surprising; in our previous study of reductive coupling of ynoates and aldehydes,¹¹ the reaction of **1h** was found to be much more regioselective than that of



Fig. 2 X-ray structure of compound 2f (50% probability level).

1a or **1b**. For related reactions including the cyclotrimerization of alkynes, metallacyclopentadiene intermediates are usually generated *via* reductive coupling of alkynes,¹ and the regioselectivity in metallacycle formation is often influenced by polarization of the triple bonds.²¹ Given the disparity of

electronic properties between an ester group and an alkyl group, we had anticipated a high regioselectivity for 1g and 1h. Perhaps in these cases, steric effects are also important. We then decided to switch to NHC ligands with the aim to improve the regioselectivity. In the presence of a 1:1 catalytic mixture of $Ni(COD)_2$ and SIPr, the ratio of 2g to 3g was increased slightly to 85:15 (entry 11). The use of SIMes resulted in a further improvement of selectivity to 90:10, and 2g could be separated from the mixture in 84% yield (entry 12). In the case of 1h, the employment of SIPr as an ancillary ligand led to the exclusive formation of 2h (entry 14). The sterically more demanding ynoates 1i and 1j did not react at room temperature or 80 °C when using Ni(COD)₂/PPh₃ as the catalyst. On the other hand, cyclotrimerization of both substrates was smoothly catalyzed by Ni(COD)₂/SIPr, giving 2i and 2j as the predominant products (entries 15 and 16).

The success of ynoate cyclotrimerization prompted us to examine the reactivity of alkynes without the ester functionality (Table 3). At room temperature in the presence of 1 mol% of Ni (COD)₂ and 3 mol% of PPh₃, phenylacetylene **1k** was regioselectively converted to **1**,2,4-triphenyl benzene **2k** in 90% yield (entry 1). Similarly high yields and regioselectivity were obtained for the cyclotrimerization of **1l** and **1m** (entries 2 and 3), and one of the products **2m** was also crystallographically characterized (see ESI[†]). The reaction of **1n**, an internal alkyne, required an elevated temperature; no reactivity was observed at room temperature (entry **4**). Compounds **1o** and **1p** have been rarely tested for cyclotrimerization reactions. The pyridyl group in **1o** may potentially poison the catalyst by binding to nickel, while



^{*a*} Conditions: **1** (1.5 mmol), Ni(COD)₂ (0.015 mmol) and PPh₃ (0.045 mmol) in 2 mL of toluene. ^{*b*} Isolated yield for **2**. ^{*c*} Combined isolated yield for **2p** and **3p**. ^{*d*} Ratio determined by ¹H NMR.

the cyclopropyl group in **1p** may undergo a ring-opening reaction. We were pleased to find that neither process was operating under our catalytic conditions. Analogous to the reaction of other terminal alkynes, 1,2,4-trisubstituted benzene derivatives formed as the major isomers (entries 5 and 6).

To further demonstrate the synthetic utility of the cyclotrimerization reaction, we conducted a gram-scale synthesis of **2b** using 0.05 mol% of nickel catalyst (eqn (2)). The regioselectivity remained high (97:3) favoring the unsymmetrical isomer **2b**, which was isolated in high yield.



In conclusion, we have described an effective nickel system for the catalytic cyclotrimerization of ynoates and related alkynes. This methodology provides access to a diverse array of tri- or hexa-substituted benzene derivatives in an efficient and highly regioselective manner. The ester-containing products **2a–j** may find many applications in materials chemistry. Preliminary studies have also shown that compounds **2d/3d**, **2l**, **2m** and **2o** display interesting photoluminescent properties. These results will be reported elsewhere.

Acknowledgements

We thank the U.S. National Science Foundation (CHE-0952083) for support of this research and Dr Allen G. Oliver (University of Notre Dame, Department of Chemistry & Biochemistry) for the data collection using the Bruker ApexII DUO.

Notes and references

‡Crystal data for **2f**: $C_{33}H_{30}O_6$, M = 522.57, orthorhombic, a = 11.6106(2), b = 12.5495(2), c = 18.7424(4) Å, V = 2730.9(9) Å³, T = 150 K, space group $Pna2_1$, Z = 4, $\lambda = 1.54178$ Å, reflections measured 28 929, 5161 unique ($R_{int} = 0.0323$) which were used in the calculations. The final R_1 was 0.0539 and the final wR_2 (F^2) was 0.1470 (all data).

Crystal data for **2m**: $C_{30}H_{24}O_6$, M = 480.49, orthorhombic, a = 11.3776(2), b = 15.9590(3), c = 26.0724(4) Å, V = 4734.10(14) Å³, T = 150 K, space group *Pbca*, Z = 8, $\lambda = 1.54178$ Å, reflections measured 68 457, 4563 unique ($R_{int} = 0.0588$) which were used in the calculations. The final R_1 was 0.0454 and the final wR_2 (F^2) was 0.0988 (all data).

 For representative reviews and book chapters, see: (a) S. Saito and Y. Yamamoto, Chem. Rev., 2000, 100, 2901– 2915; (b) S. Kotha, E. Brahmachary and K. Lahiri, Eur. J. Org. Chem., 2005, 4741–4767; (c) V. Gandon, C. Aubert and M. Malacria, Chem. Commun., 2006, 2209– 2217; (d) P. R. Chopade and J. Louie, Adv. Synth. Catal., 2006, 348, 2307–2327; (e) B. R. Galan and T. Rovis, Angew. Chem., Int. Ed., 2009, 48, 2830–2834; (f) D. B. Grotjahn, in Comprehensive Organometallic Chemistry II, ed. E. W. Abel,

(1p)

F. G. A. Stone and G. Wilkinson, Elsevier, Oxford, 1995, ch. 7.3, vol. 12, pp. 741–770; (*g*) N. E. Schore, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, ch. 9.4, vol. 5, pp. 1129–1162.

- 2 For recent representative examples of [2 + 2 + 2] cycloaddition of a diyne and an alkyne, see: (a) Y. Yamamoto, A. Nagata, H. Nagata, Y. Ando, Y. Arikawa, K. Tatsumi and K. Itoh, *Chem.-Eur. J.*, 2003, 9, 2469–2483; (b) N. Saino, F. Amemiya, E. Tanabe, K. Kase and S. Okamoto, *Org. Lett.*, 2006, 8, 1439–1442; (c) J. A. Teske and A. Deiters, *J. Org. Chem.*, 2008, 73, 342–345; (d) J. A. Teske and A. Deiters, *Org. Lett.*, 2008, 10, 2195–2198.
- 3 For recent representative examples of intramolecular cyclotrimerization of a triyne, see: (a) E. A. Anderson, E. J. Alexanian and E. J. Sorensen, Angew. Chem., Int. Ed., 2004, 43, 1998–2001; (b) G. Chouraqui, M. Petit, C. Aubert and M. Malacria, Org. Lett., 2004, 6, 1519–1521; (c) N. Saino, D. Kogure and S. Okamoto, Org. Lett., 2005, 7, 3065–3067; (d) K. Tanaka, H. Sagae, K. Toyoda, K. Noguchi and M. Hirano, J. Am. Chem. Soc., 2007, 129, 1522–1523; (e) N. Nicolaus, S. Strauss, J.-M. Neudörfl, A. Prokop and H.-G. Schmalz, Org. Lett., 2009, 11, 341–344; (f) T. Welsch, H.-A. Tran and B. Witulski, Org. Lett., 2010, 12, 5644–5647.
- 4 (a) E. S. Johnson, G. J. Balaich, P. E. Fanwick and I. P. Rothwell, J. Am. Chem. Soc., 1997, 119, 11086–11087;
 (b) O. V. Ozerov, F. T. Ladipo and B. O. Patrick, J. Am. Chem. Soc., 1999, 121, 7941–7942;
 (c) O. V. Ozerov, B. O. Patrick and F. T. Ladipo, J. Am. Chem. Soc., 2000, 122, 6423–6431;
 (d) F. T. Ladipo, V. Sarveswaran, J. V. Kingston, R. A. Huyck, S. Y. Bylikin, S. D. Carr, R. Watts and S. Parkin, J. Organomet. Chem., 2004, 689, 502–514;
 (e) N. Morohashi, K. Yokomakura, T. Hattori and S. Miyano, Tetrahedron Lett., 2006, 47, 1157–1161.
- 5 (a) M. S. Sigman, A. W. Fatland and B. E. Eaton, J. Am. Chem. Soc., 1998, 120, 5130-5131; (b) L. Yong and H. Butenschön, Chem. Commun., 2002, 2852-2853;
 (c) G. Hilt, T. Vogler, W. Hess and F. Galbiati, Chem. Commun., 2005, 1474-1475; (d) G. Hilt, W. Hess, T. Vogler and C. Hengst, J. Organomet. Chem., 2005, 690, 5170-5181;
 (e) M. Lombardo, F. Pasi, C. Trombini, K. R. Seddon and W. R. Pitner, Green Chem., 2007, 9, 321-322;
 (f) C. C. Eichman, J. P. Bragdon and J. P. Stambuli, Synlett, 2011, 1109-1112; (g) L. Xu, R. Yu, Y. Wang, J. Chen and Z. Yang, J. Org. Chem., 2013, 78, 5744-5750.
- 6 (a) N. Mori, S. Ikeda and K. Odashima, *Chem. Commun.*, 2001, 181–182; (b) S. Saito, T. Kawasaki, N. Tsuboya and Y. Yamamoto, *J. Org. Chem.*, 2001, 66, 796–802; (c) C. Müller, R. J. Lachicotte and W. D. Jones, *Organometallics*, 2002, 21, 1975–1981.
- 7 (a) E. Rüba, R. Schmid, K. Kirchner and M. J. Calhorda, J. Organomet. Chem., 2003, 682, 204–211; (b) Y. Ura, Y. Sato, M. Shiotsuki, T. Kondo and T. Mitsudo, J. Mol. Catal. A: Chem., 2004, 209, 35–39; (c) Y. Yamamoto, J. Ishii, H. Nishiyama and K. Itoh, J. Am. Chem. Soc., 2004, 126, 3712–3713; (d) V. Cadierno, S. E. García-Garrido and J. Gimeno, J. Am. Chem. Soc., 2006, 128, 15094–15095;

(e) B. Dutta, B. F. E. Curchod, P. Campomanes, E. Solari, R. Scopelliti, U. Rothlisberger and K. Severin, *Chem.-Eur. J.*, 2010, **16**, 8400–8409; (f) M. Kawatsura, M. Yamamoto, J. Namioka, K. Kajita, T. Hirakawa and T. Itoh, *Org. Lett.*, 2011, **13**, 1001–1003.

- 8 (a) I. Amer, T. Bernstein, M. Eisen, J. Blum and K. P. C. Vollhardt, *J. Mol. Catal.*, 1990, **60**, 313–321;
 (b) K. Tanaka and K. Shirasaka, *Org. Lett.*, 2003, 5, 4697– 4699; (c) K. Tanaka, K. Toyoda, A. Wada, K. Shirasaka and M. Hirano, *Chem.-Eur. J.*, 2005, **11**, 1145–1156;
 (d) K. Yoshida, I. Morimoto, K. Mitsudo and H. Tanaka, *Tetrahedron*, 2008, **64**, 5800–5807.
- 9 (a) A. K. Jhingan and W. F. Maier, J. Org. Chem., 1987, 52, 1161–1165; (b) V. Gevorgyan, U. Radhakrishnan, A. Takeda, M. Rubina, M. Rubin and Y. Yamamoto, J. Org. Chem., 2001, 66, 2835–2841; (c) J. Li, H. Jiang and M. Chen, J. Org. Chem., 2001, 66, 3627–3629; (d) M. F. N. N. Carvalho, F. M. T. Almeida, A. M. Galvão and A. J. L. Pombeiro, J. Organomet. Chem., 2003, 679, 143–147; (e) J.-S. Cheng and H.-F. Jiang, Eur. J. Org. Chem., 2004, 643–646; (f) F. Inagaki, M. Mizutani, N. Kuroda and C. Mukai, J. Org. Chem., 2009, 74, 6402–6405.
- 10 (a) Fe: Y. Liu, X. Yan, N. Yang and C. Xi, *Catal. Commun.*, 2011, 12, 489–492; (b) Ln/Fe: X. Bu, Z. Zhang and X. Zhou, *Organometallics*, 2010, 29, 3530–3534; (c) Mo: N. Kaneta, T. Hirai and M. Mori, *Chem. Lett.*, 1995, 627–628; (d) Ir: R. Takeuchi and Y. Nakaya, *Org. Lett.*, 2003, 5, 3659–3662.
- 11 S. K. Rodrigo and H. Guan, *J. Org. Chem.*, 2012, 77, 8303–8309.
- 12 (a) J. R. Leto and M. F. Leto, J. Am. Chem. Soc., 1961, 83, 2944–2951; (b) R. Diercks and H. tom Dieck, Chem. Ber., 1985, 118, 428–435.
- 13 L. S. Meriwether, E. C. Colthup, G. W. Kennerly and R. N. Reusch, *J. Org. Chem.*, 1961, 26, 5155–5163.
- 14 M. G. McKee, G. L. Wilkes, R. H. Colby and T. E. Long, *Macromolecules*, 2004, 37, 1760–1767.
- 15 J.-S. Yang, H.-H. Huang and S.-H. Lin, *J. Org. Chem.*, 2009, 74, 3974–3977.
- 16 Prices listed by Sigma-Aldrich: Ni(PPh₃)₄, \$87 per mmol;
 Ni(COD)₂, \$8.4 per mmol; PPh₃, \$0.046 per mmol.
- 17 Y. Sato, T. Nishimata and M. Mori, *J. Org. Chem.*, 1994, **59**, 6133–6135.
- 18 D. Holte, D. C. G. Götz and P. S. Baran, J. Org. Chem., 2012, 77, 825–842.
- 19 P. A. Wender and T. E. Smith, bis(1,5-cyclooctadiene)nickel
 (0), in *Encyclopedia of Reagents for Organic Synthesis*,
 ed. L. A. Paquette, D. Crich, P. L. Fuchs and G. A. Molander,
 Wiley, Chichester, UK, 2nd edn, 2009, vol. 2, pp. 906–912.
- 20 (a) J.-S. Yang, Y.-R. Lee, J.-L. Yan and M.-C. Lu, Org. Lett., 2006, 8, 5813–5816; (b) S. Diring and R. Ziessel, Tetrahedron Lett., 2009, 50, 1203–1208; (c) H.-H. Huang, C. Prabhakar, K.-C. Tang, P.-T. Chou, G.-J. Huang and J.-S. Yang, J. Am. Chem. Soc., 2011, 133, 8028–8039.
- 21 (a) A. Stockis and R. Hoffmann, J. Am. Chem. Soc., 1980, 102, 2952–2962; (b) N. Mori, S. Ikeda and Y. Sato, J. Am. Chem. Soc., 1999, 121, 2722–2727.