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Iron carbonyl cluster-incorporated Cu(I) NHC complexes in homocoupling of arylboronic acids: an effective $[TeFe_3(CO)_9]^{2-}$ ligand†

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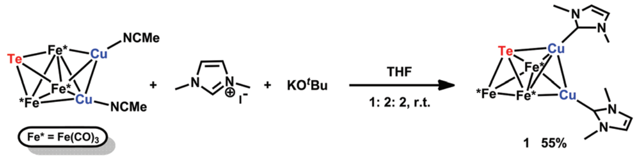
A new type of $TeFe_3(CO)_9$-incorporated dicopper NHC complex was obtained directly from one-pot reactions. By the introduction of the cluster anion $[TeFe_3(CO)_9]^{2-}$ and NHCs as the ligands, these di-Cu(I)-based complexes exhibited pronounced catalytic activities toward the homocoupling of arylboronic acids with low Cu loadings and high yields (up to 98%).

Heterometallic clusters, comprising two or more different transition metals, are of great interest because of their special properties[1] and applications in magnetism,[1,2] nanoscience,[1,2b,3] and catalysis.[1,4] Recently, the study of N-heterocyclic carbenes (NHCs) as ancillary ligands in organometallic catalysis has become a flourishing field of research.[5] On the other hand, many bulky metal carbonyl clusters with π-accepting CO groups are known as electron reservoirs[2b,c,6] and are expected to act as potential ligands to modulate electronic structures of their resultant catalysts. Although quite a few metal carbonyl NHC clusters have been reported,[7] only some heterometallic ones were characterized, presumably due to the lack of systematic syntheses.[7d–h] Until now, transition metal carbonyl NHC clusters are yet to be used as catalysts for organic reactions.

Symmetrical biaryls are important organic compounds for synthetic and medicinal chemistry.[8] A convenient synthetic route to symmetrical biaryls was *via* the Suzuki homocoupling reaction.[9] Despite the fact that some precious metal(Pd,[9,10] Rh,[9,11] Au[9,12])-mediated Suzuki homocoupling reactions have been reported with good catalytic activities, additional additives or ligands are usually required in these catalytic systems. Recently, an alternative route was achieved by the use of inexpensive Cu-catalysts without the need for additives.[8a,b,9,13] The mechanism for Cu-catalyzed homocoupling reactions of arylboronic acids is not yet obvious, but, a plausible mechanism that involves the formation of an unstable Cu(III) state under an atmosphere of O_2 has been proposed.[8a,13a–c] With our interest in anionic iron carbonyl chalcogenides,[2c] we attempted to introduce the electron-donating and bulky cluster anion $[TeFe_3(CO)_9]^{2-}$ (ref. 14) or/and NHCs as the ligands for the catalytic center Cu(I) to study the ligand effect. Herein, we report our design of a series of $TeFe_3(CO)_9$-incorporated mono- or bidentate-NHC di-Cu(I) complexes, forming a new type of ternary Te–Fe–Cu NHC carbonyl complex, such as $[(\mu_4\text{-Te})Fe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**), $[(\mu_3\text{-Te})Fe_3(CO)_9Cu_2(MeImCH_2ImMe)]$ (**2**), $[(\mu_4\text{-Te})Fe_3(CO)_9Cu_2(MeIm(CH_2)_2ImMe)]$ (**3**), and $[(\mu_4\text{-Te})Fe_3(CO)_9Cu_2(MeIm(CH_2)_3ImMe)]$ (**4**), which were first used as Cu(NHC)-containing catalysts in the homocoupling of arylboronic acids with low Cu loadings (0.5 or 1.0 mol%) and high turnovers per copper (54–196). These were the highest values compared with other reported homocouplings of arylboronic acids (TONs per copper <50) when using homogeneous Cu-based catalysts, and the value of 196 was the highest among metal-based cases.[8b,9–13]

A one-pot synthesis of the NHC-incorporated $TeFe_3Cu_2$-based complex $[(\mu_4\text{-Te})Fe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**) was achieved from the reaction of $[(\mu_3\text{-Te})Fe_3(CO)_9Cu_2(MeCN)_2]$[15] and 1,3-dimethylimidazolium iodide ($Me_2Im{\cdot}HI$) along with KO^tBu in a 1 : 2 : 2 ratio in THF at room temperature (Scheme 1). As shown in Fig. 1, complex **1** consisted of a distorted $TeFe_3(CO)_9Cu$ trigonal-bipyramidal core with a $TeFe_2$ ring in the equatorial plane, in which the Fe_2Cu triangular plane was further capped



Scheme 1 One-pot synthesis of the monodentate-NHC complex **1**.

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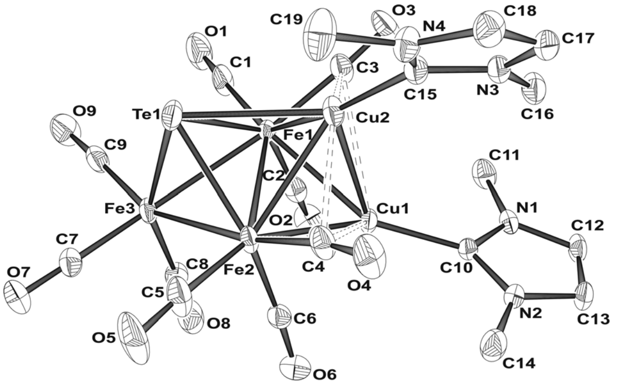
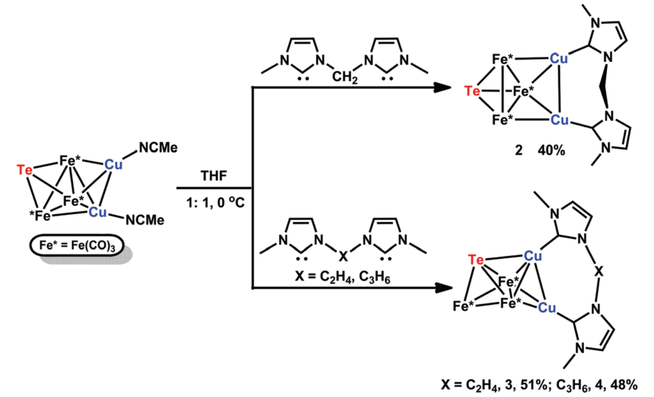


Fig. 1 ORTEP of **1** at 30% probability; hydrogen atoms are omitted for clarity.



Scheme 2 The synthesis of bidentate-NHC complexes **2–4**.

by another copper atom with the two Cu atoms covalently bonded (2.5949(9) Å). Each of the two copper atoms coordinated with a Me_2Im ligand with an average Cu–$C_{carbene}$ bond of 1.933(5) Å which was within the range of the reported Cu–$C_{carbene}$ bonds (*ca.* 1.80–2.20 Å) in Cu(I)–NHC complexes.[16] $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ was slightly air-sensitive, but complex **1** could survive in air for 10 days, which was confirmed by powder X-ray diffraction (PXRD) (Fig. S1, ESI†), indicating that the NHC ligand could help stabilize the $TeFe_3(CO)_9Cu_2$ core.

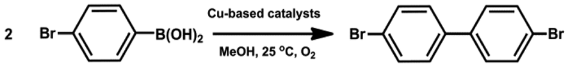
Further, a similar methodology was also applied to the construction of the bidentate-NHC complexes, $[(\mu_3\text{-Te})Fe_3(CO)_9Cu_2(MeImCH_2ImMe)]$ (**2**), $[(\mu_4\text{-Te})Fe_3(CO)_9Cu_2(MeIm(CH_2)_2ImMe)]$ (**3**), and $[(\mu_4\text{-Te})Fe_3(CO)_9Cu_2(MeIm(CH_2)_3ImMe)]$ (**4**), by the treatment of $[(\mu_3\text{-Te})Fe_3(CO)_9Cu_2(MeCN)_2]$ with diimidazolium salts, 1,1′-dimethyl-3,3′-methylene-diimidazolium diiodide ($MeImCH_2ImMe{\cdot}H_2I_2$), 1,1′-dimethyl-3,3′-ethylene-diimidazolium dibromide ($MeIm(CH_2)_2ImMe{\cdot}H_2Br_2$), and 1,1′-dimethyl-3,3′-propylene-diimidazolium diiodide ($MeIm(CH_2)_3ImMe{\cdot}H_2I_2$), and KO^tBu in a 1 : 1 : 2 ratio at room temperature in 11–21% yields. The yields of **2–4** could be improved to 40–51% if $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ was treated with $MeIm(CH_2)_nImMe$ carbenes (n = 1–3) *in situ* from the deprotonation reaction of diimidazolium salts with KO^tBu in THF (Scheme 2). Similar to **1**, complexes **2–4** each possessed a $TeFe_3(CO)_9Cu_2$ core with the Cu–Cu bond further bridged with $MeIm(CH_2)_nImMe$ (n = 1–3) (Fig. S2–S4, ESI†). According to the data available at the Cambridge Crystallographic Data Centre,[17] complexes **1–4** represented the first examples of NHC-containing mixed-metal carbonyl chalcogenide complexes.

To study the catalytic activity of $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ and **1–4** toward arylboronic acids, 4-bromophenylboronic acid was chosen as a model substrate. All reactions were monitored by TLC to ensure complete conversion of the starting materials. The reaction conditions were optimized to include the use of 1.0 mol% of Cu loading, methanol as the solvent, room temperature, an atmosphere of O_2, and without any additives such as bases, ligands, or other oxidants (Table 1 and Table S1, ESI†). For comparison, the di-$MeIm(CH_2)_2$-ImMe-bridged dicopper(I) complex, $[Cu_2(MeIm(CH_2)_2ImMe)_2][PF_6]_2$,[18] was synthesized and its catalysis toward homocoupling of 4-bromophenylboronic acid was performed as well.

As shown in Table 1, $[Et_4N]_2[TeFe_3(CO)_9]$ (entry 1) exhibited no activity toward 4-bromophenylboronic acid. However, when $[Cu(MeCN)_4][BF_4]$[19] (entry 2) was employed, 47% yield of 4,4′-dibromobiphenyl was obtained, revealing that Cu was essential for the catalytic performance. Interestingly, $[Cu_2(MeIm(CH_2)_2ImMe)_2][PF_6]_2$ and $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ (entries 3 and 4) exhibited excellent catalytic yields (85%, 8 h; 85%, 3 h), respectively, which showed that bidentate-NHC and $[TeFe_3(CO)_9]^{2-}$ were good ancillary ligands for these di-Cu-based catalysts. Although having similar TONs, $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ had higher turnover frequency (TOF = 28.3 h^{-1}) than that for $[Cu_2(MeIm(CH_2)_2ImMe)_2][PF_6]_2$ (10.6 h^{-1}), indicating that $[TeFe_3(CO)_9]^{2-}$ functioned as a better ligand than the bidentate-NHC ligand ($MeIm(CH_2)_2ImMe$) in this catalytic reaction. When both NHC and $[TeFe_3(CO)_9]^{2-}$ were introduced, the catalytic efficiencies (~44.0 h^{-1}) of catalysts **1–4** (entries 5–8) were significantly higher than $[Cu_2(MeIm(CH_2)_2ImMe)_2][PF_6]_2$ (10.6 h^{-1}) (entry 3), but only slightly better than $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ (28.3 h^{-1}) (entry 4), showing the importance of the $TeFe_3$ core effect. In addition, these catalysts with the mono- or bidentate-NHC attached to the $TeFe_3(CO)_9Cu_2$ core exhibited comparable efficiencies (~44.0 h^{-1}) (entries 5–8), demonstrating again that the catalyst activities were associated with the $TeFe_3$ core. As the Cu loading of catalysts **1–4** was lowered from 1.0 to 0.5 mol%, the yields remained almost the same but with increased TONs and decreased TOFs (entries 5–8 and 9–12). These results indicated that these $TeFe_3(CO)_9$-incorporated dicopper complexes **1–4** exhibited similar and pronounced catalytic activities which were better than other conventional catalysts such as Au, Fe, Pd, and Cu in homocoupling of 4-bromophenylboronic acid, which required higher temperature, additional base, external additives, longer reaction time, and higher loading of the catalyst (Table S2, ESI†).

The homocoupling mechanism of $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ and **1–4** was proposed to occur *via* a Cu(I)/Cu(III) catalytic cycle,[8a,13a] in which these catalysts underwent transmetalation with arylboronic acid under aerobic conditions, which involved

Table 1 Homocoupling of 4-bromophenylboronic acid with different catalysts[a]



Entry	Catalyst	Cu (mol%)	Time (h)	Yield[b,c] (%)	TON[d]	TOF[e] (h^{-1})
1	$[Et_4N]_2[TeFe_3(CO)_9]$	0[f]	12	0	—	—
2	$[Cu(MeCN)_4][BF_4]$	1.0	60	47	47	0.8
3	$[Cu_2(MeIm(CH_2)_2ImMe)]_2[PF_6]_2$	1.0	8	85	85	10.6
4	$[TeFe_3(CO)_9Cu_2(MeCN)_2]$	1.0	3	85	85	28.3
5	$[TeFe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**)	1.0	2	88	88	44.0
6	$[TeFe_3(CO)_9Cu_2(MeImCH_2ImMe)]$ (**2**)	1.0	2	87	87	43.5
7	$[TeFe_3(CO)_9Cu_2(MeIm(CH_2)_2ImMe)]$ (**3**)	1.0	2	88	88	44.0
8	$[TeFe_3(CO)_9Cu_2(MeIm(CH_2)_3ImMe)]$ (**4**)	1.0	2	88	88	44.0
9	$[TeFe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**)	0.5	12	82	164	13.7
10	$[TeFe_3(CO)_9Cu_2(MeImCH_2ImMe)]$ (**2**)	0.5	12	84	168	14.0
11	$[TeFe_3(CO)_9Cu_2(MeIm(CH_2)_2ImMe)]$ (**3**)	0.5	12	80	160	13.3
12	$[TeFe_3(CO)_9Cu_2(MeIm(CH_2)_3ImMe)]$ (**4**)	0.5	12	78	156	13.0

[a] Reaction conditions: 4-bromophenylboronic acid (1.0 mmol), MeOH (3.0 mL), 25 °C, O_2 (1 atm, balloon). [b] The isolated yield as an average of three runs. [c] All reactions were monitored by TLC. [d] Turnover number per copper for the biaryl product. [e] TON per hour. [f] 3.0 mol% of Fe loading.

weak Cu–Cu bond cleavages (Wiberg bond indices, 0.028–0.035, Table S3, ESI†) to make the Cu atoms more spatially open toward arylboronic acid, accompanied with the oxidation of the $TeFe_3Cu_2$ core, followed by reductive elimination to release the biaryl products (Fig. S5, ESI†).

In order to understand the oxidative behavior of $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ and **1–4**, differential pulse voltammetry (DPV) was measured and each showed two one-electron quasi-reversible oxidations between 0.015 and 0.286 V *vs.* SCE (Fig. 2, and Table S4, ESI†), which was assigned to the oxidation of the $TeFe_3Cu_2$ core, according to the HOMOs in DFT calculations (Fig. S6, ESI†). For comparison, the DPVs for $[Cu(MeCN)_4][BF_4]$ and $[Cu_2(MeIm(CH_2)_2ImMe)_2][PF_6]_2$ were also studied. It was interesting to find that the ease of their first oxidation nearly paralleled the increased catalyst activities ($[TeFe_3(CO)_9Cu_2(MeCN)_2]$ and **1–4** (0.015–0.134 V; 85–88%, 28.3–44.0 h^{-1}); $[Cu_2(MeIm(CH_2)_2ImMe)_2][PF_6]_2$ (0.399 V; 85%, 10.6 h^{-1}); $[Cu(MeCN)_4][BF_4]$ (1.004 V; 47%, 0.8 h^{-1})) (Table S4, ESI†), which substantiated that the oxidation of Cu(I) coupled with the $TeFe_3(CO)_9$ fragment played a key role in the catalytic mechanism of these $TeFe_3(CO)_9$-incorporated copper complexes.

To further explore the scope and generality of the present protocol under the optimized conditions, the homocoupling of arylboronic acids by catalyst **1** was examined and summarized in Table 2. Our studies showed that the homocoupling of *ortho*-bromophenylboronic acid gave the corresponding biaryls in lower yields (54%, entry 1) than those (68%, entry 2; 88%, entry 3) with *meta* and *para* substituents because of the notable steric hindrance. Also, the *meta*- and *para*-substituted arylboronic acids bearing a stronger electron-withdrawing

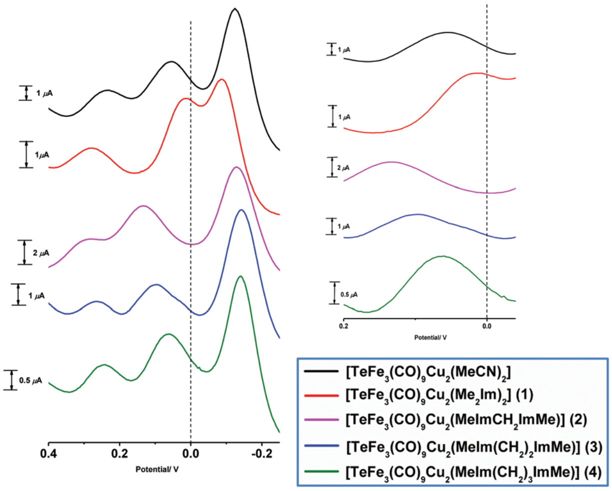
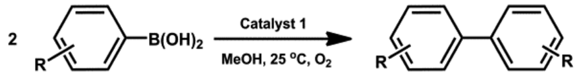


Fig. 2 DPVs in MeCN for $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ and **1–4**. Conditions: electrolyte, 0.1 M Bu_4NClO_4; working electrode, glassy carbon; scan rate, 100 mV s^{-1}. Potentials are *vs.* SCE. The inset shows the first one-electron quasi-reversible oxidation between 0.00 and 0.20 V *vs.* SCE.

Table 2 Substrate scope of arylboronic acid using catalyst **1**[a]



Entry	R	Cu (mol%)	Time (h)	Yield[b,c] (%)
1	*ortho*-Br	1.0	2	54
2	*meta*-Br	1.0	2	68
3	*para*-Br	1.0	2	88
4	*meta*-NO_2	1.0	24	97
5	*para*-NO_2	1.0	24	99[d]
6	*meta*-NO_2	0.5	38	98
7	*para*-OMe	1.0	2	70

[a] Reaction conditions: arylboronic acid (1.0 mmol), MeOH (3.0 mL), 25 °C, O_2 (1 atm, balloon). [b] Isolated yield as an average of three runs. [c] All reactions were monitored by TLC. [d] An addition–elimination side product 4-nitrophenol was isolated in 21% yield due to the presence of H_2O in the reaction and the major product 4,4′-dinitrobiphenyl was obtained in 78% yield. Therefore, the yield of 4,4′-dinitrobiphenyl was calculated as 99% (78%/79%).

nitro group gave the desired products in excellent yields (97%, entry 4; 99%, entry 5) which were higher than that (70%, entry 7) for phenylboronic acid with an electron-donating methoxy group or those (68%, entry 2; 88%, entry 3) with a weak electron-withdrawing bromo group. A Hammett plot[20,21] of $\log(K_{\mathrm{ArX}}/K_{\mathrm{ArBr}})$ (X = Br, NO_2, OMe) *versus* σ is shown in Fig. S7 (ESI†). The observed positive value (0.19) of ρ indicated that the reaction rate was accelerated by the electron-withdrawing substituents of arylboronic acid. Even when the Cu loading of catalyst **1** was decreased from 1.0 to 0.5 mol% in catalyzing 3-nitrophenylboronic acid, an excellent yield (98%, entry 6) was maintained with turnovers up to 196.

In conclusion, we have discovered a facile route to a new type of $TeFe_3(CO)_9$-incorporated mono- or bidentate-NHC Cu(I) complexes **1–4** which could effectively catalyze the homocoupling of arylboronic acids under an atmosphere of O_2 at room temperature with high turnovers per copper (54–196). These catalyst efficiencies were significantly enhanced by the participation of the electron-donating and bulky cluster anion $[TeFe_3(CO)_9]^{2-}$ as an inorganic ligand due to the ease of oxidation of the $TeFe_3Cu_2$ core. Further investigation will focus on the use of other modified anionic carbonyl chalcogenide clusters as inorganic ligands in order to fine-tune the electronic and steric factors of the resultant Cu catalysts for the efficient homocoupling of various arylboronic acids.

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Notes and references

1 (*a*) P. Braunstein and J. Rosé, in *Metal Clusters in Chemistry*, ed. P. Braunstein, L. A. Oro and P. R. Raithby, Wiley-VCH, Weinheim, 1999, vol. 2, ch. 2.2, pp. 616–677; (*b*) R. D. Adams, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 10; (*c*) *The Chemistry of Metal Cluster Complexes*, ed. D. F. Shriver, H. D. Kaesz and R. D. Adams, Wiley-VCH, New York, 1990.

2 (*a*) C. Mathonière, J.-P. Sutter and J. V. Yakhmi, in *Magnetism: molecules to materials*, ed. J. S. Miller and M. Drillon, Wiley-VCH, Weinheim, 2002, vol. 4, ch. 1; (*b*) C. Femoni, M. C. Iapalucci, F. Kaswalder, G. Longoni and S. Zacchini, *Coord. Chem. Rev.*, 2006, **250**, 1580–1604; (*c*) M. Shieh, C.-Y. Miu, Y.-Y. Chu and C.-N. Lin, *Coord. Chem. Rev.*, 2012, **256**, 637–694, and references therein.

3 (*a*) F. Dielmann, C. Heindl, F. Hastreiter, E. V. Peresypkina, A. V. Virovets, R. M. Gschwind and M. Scheer, *Angew. Chem., Int. Ed.*, 2014, **53**, 13605–13608; (*b*) A. C. Colson and K. H. Whitmire, *Chem. Mater.*, 2011, **23**, 3731–3739.

4 (*a*) *Metal Clusters in Catalysis, Studies in Surface Science and Catalysis Series*, ed. B. C. Gates, L. Guczi and H. Knözinger, Elsevier, Amsterdam, 1986, vol. 29; (*b*) S. Hermans, T. Khimyak, R. Raja, G. Sankar, J. M. Thomas and B. F. G. Johnson, in *Nanotechnology in Catalysis*, ed. B. Zhou, S. Hermans and G. A. Somorjai, Kluwer Academic, Plenum Publishers, New York, 2004; (*c*) R. D. Adams and B. Captain, *Acc. Chem. Res.*, 2009, **42**, 409–418.

5 (*a*) *N-Heterocyclic Carbenes in Transition Metal Catalysis*, ed. F. Glorius, Springer, Berlin, 2007; (*b*) *N-Heterocyclic Carbenes in Synthesis*, ed. S. P. Nolan, Wiley-VCH, Weinheim, Germany, 2006; (*c*) *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*, ed. C. S. J. Cazin, Springer, Heidelberg, 2011.

6 G. G. Melikyan, *Acc. Chem. Res.*, 2015, **48**, 1065–1079.

7 (*a*) J. A. Cabeza and P. García-Álvarez, *Chem. Soc. Rev.*, 2011, **40**, 5389–5405, and references therein; (*b*) J. Campos, L. S. Sharninghausen, R. H. Crabtree and D. Balcells, *Angew. Chem., Int. Ed.*, 2014, **53**, 12808–12811; (*c*) Y. Liu, R. Ganguly, H. V. Huynh and W. K. Leong, *Angew. Chem., Int. Ed.*, 2013, **52**, 12110–12113; (*d*) S. Saha and B. Captain, *Inorg. Chem.*, 2014, **53**, 1210–1216; (*e*) R. Della Pergola, A. Sironi, A. Rosehr, V. Colombo and A. Sironi, *Inorg. Chem. Commun.*, 2014, **49**, 27–29; (*f*) Y. Liu, R. Ganguly, H. V. Huynh and W. K. Leong, *Organometallics*, 2013, **32**, 7559–7563; (*g*) R. D. Adams, J. Tedder and Y. O. Wong, *J. Organomet. Chem.*, 2015, DOI: 10.1016/j.jorganchem.2015.03.024; (*h*) S. Banerjee, M. K. Karunananda, S. Bagherzadeh, U. Jayarathne, S. R. Parmelee, G. W. Waldhart and N. P. Mankad, *Inorg. Chem.*, 2014, **53**, 11307–11315.

8 (*a*) P. Puthiaraj, P. Suresh and K. Pitchumani, *Green Chem.*, 2014, **16**, 2865–2875, and references therein; (*b*) B. Kaboudin, Y. Abedi and T. Yokomatsu, *Eur. J. Org. Chem.*, 2011, 6656–6662, and references therein; (*c*) C. F. Nising, U. K. Schmid, M. Nieger and S. Bräse, *J. Org. Chem.*, 2004, **69**, 6830–6833; (*d*) B. Rao, W. Zhang, L. Hu and M. Luo, *Green Chem.*, 2012, **14**, 3436–3440.

9 R. N. Dhital and H. Sakurai, *Asian J. Org. Chem.*, 2014, **3**, 668–684, and references therein.

10 (*a*) A. R. Kapdi, G. Dhangar, J. L. Serrano, J. A. De Haro, P. Lozano and I. J. S. Fairlamb, *RSC Adv.*, 2014, **4**, 55305–55312, and references therein; (*b*) M. Guo, L. Qi, M. Lv, X. Zhou, H. Liang and S. Chen, *Lett. Org. Chem.*, 2015, **12**, 205–209; (*c*) J. Xia, M. Cheng, Q. Chen and M. Cai, *Appl. Organomet. Chem.*, 2015, **29**, 113–116.

11 T. Vogler and A. Studer, *Adv. Synth. Catal.*, 2008, **350**, 1963–1967, and references therein.

12 (*a*) K. Sharma, V. Bhalla and M. Kumar, *RSC Adv.*, 2014, **4**, 53795–53800, and reference therein; (*b*) A. Monopoli, A. Afzal, C. Di Franco, N. Ditaranto, N. Cioffi, A. Nacci, P. Cotugno and L. Torsi, *J. Mol. Catal. A: Chem.*, 2014, **386**, 101–107, and reference therein; (*c*) K. M. Parida, S. Singha, P. C. Sahoo and S. Sahu, *J. Mol. Catal. A: Chem.*, 2011, **342–343**, 11–17.

13 (*a*) A. S. Demir, Ö. Reis and M. Emrullahoglu, *J. Org. Chem.*, 2003, **68**, 10130–10134; (*b*) G. Cheng and M. Luo, *Eur. J. Org. Chem.*, 2011, 2519–2523; (*c*) B. Kaboudin, T. Haruki and T. Yokomatsu, *Synthesis*, 2011, 91–96;

(*d*) N. Kirai and Y. Yamamoto, *Eur. J. Org. Chem.*, 2009, 1864–1867; (*e*) S. A. R. Mulla, S. S. Chavan, M. Y. Pathan, S. M. Inamdar and T. M. Y. Shaikh, *RSC Adv.*, 2015, **5**, 24675–24680; (*f*) B. A. Dar, S. Singh, N. Pandey, A. P. Singh, P. Sharma, A. Lazar, M. Sharma, R. A. Vishwakarma and B. Singh, *Appl. Catal., A*, 2014, **470**, 232–238; (*g*) N. Hussain, P. Gogoi, V. K. Azhaganand, M. V. Shelke and M. R. Das, *Catal. Sci. Technol.*, 2015, **5**, 1251–1260.

14 R. E. Bachman and K. H. Whitmire, *Inorg. Chem.*, 1994, **33**, 2527–2533.

15 M. Shieh, C.-H. Ho, W.-S. Sheu, B.-G. Chen, Y.-Y. Chu, C.-Y. Miu, H.-L. Liu and C.-C. Shen, *J. Am. Chem. Soc.*, 2008, **130**, 14114–14116.

16 B. Liu, C. Chen, Y. Zhang, X. Liu and W. Chen, *Organometallics*, 2013, **32**, 5451–5460, and references therein.

17 F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 380–388.

18 C. Tubaro, A. Biffis, R. Gava, E. Scattolin, A. Volpe, M. Basato, M. M. Díaz-Requejo and P. J. Perez, *Eur. J. Org. Chem.*, 2012, 1367–1372.

19 G. J. Kubas, *Inorg. Synth.*, 1979, **19**, 90–92.

20 (*a*) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 1970; (*b*) H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191–261.

21 (*a*) K. Sun, S. Liu, P. M. Bec and T. G. Driver, *Angew. Chem., Int. Ed.*, 2011, **50**, 1702–1706; (*b*) T. M. Gregg, R. F. Algera, J. R. Frost, F. Hassan and R. J. Stewart, *Tetrahedron Lett.*, 2010, **51**, 6429–6432; (*c*) M. M. Díaz-Requejo, P. J. Pérez, M. Brookhart and J. L. Templeton, *Organometallics*, 1997, **16**, 4399–4402.