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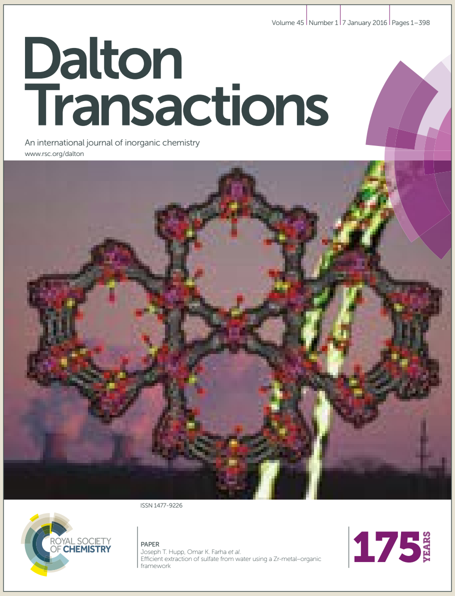

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Heteroleptic cobalt(III) acetylacetonato complexes with N-heterocyclic carbine-donating scorpionate ligands: synthesis, structural characterization and catalysis†

Toshiki Nishiura,[a] Asako Takabatake,[a] Mariko Okutsu,[a] Jun Nakazawa[a] and Shiro Hikichi *[a]

Exposure of O_2 to a reaction mixture containing bis(acac)cobalt(II), a facially capping tris(N-heterocyclic carbene)borate ligand and 1-methylimidazole yields a heteroleptic cobalt(III) complex with acac, 1-methylimidazole and tris(NHC)borate ligands. *meta*-Chloroperbenzoic acid is efficiently activated by this heteroleptic complex to catalytically oxidize cyclohexane at ambient temperature.

N-heterocyclic carbene (NHC) transition metal complexes have received significant attention because the strong σ-electron-donating nature of NHCs influences the degree of metal-based reactivity.[1] To date, various metallocomplex catalysts comprising NHC ligands have been explored. Particularly, NHC-containing chelating ligands have been employed extensively in the design of stable catalysts arising from the chelate effect.[2] Tris(1-R-imidazol-2-ylidene)borates ($[XB(RIm)_3]^-$; X = H or Ph, R denotes the substituent group at the first position on the imidazole), which have recently been classified into a new generation of scorpionate ligands, are unique NHC-containing chelators. These ligands are promising for applications in oxidation reaction catalysts on the basis of the characteristics of their complexes. First, upon coordination, these facially-capping tridentate ligands offer cis-orientated vacant sites for binding reactants. Second, the intramolecular charge separation created by the negatively charged borate with respect to cationic metal centers stabilizes complexes of high valent metals. The three strong σ-donors of these NHC ligands render metal centers relatively susceptible to oxidation.[3] Hitherto, however, $[XB(RIm)_3]^-$ ligands have not been designed into oxidation catalysts, although several metal complexes comprising NHC ligands other than $[XB(RIm)_3]^-$ are known to be active in the catalytic oxidation of organic compounds.[4] Catalytic oxygenations of hydrocarbons, such as arene hydroxylation and olefin epoxidation, have been achieved by iron and manganese complexes with planar tetradentate pyridine- or phenoxide-containing bis(NHC) ligands.[4(a)-(c)] No cobalt-NHC complex has been applied to oxidation catalysts so far, although a few cobalt-dioxygen adducts with NHC ligands have been reported.[5]

Metal complexes designed with hindered $[XB(RIm)_3]^-$ ligands, where R = *tert*-butyl and mesityl, have been explored extensively because the space restriction induced by the bulky R substituents can stabilize the coordinatively unsaturated metal centers of the complexes. Conversely, related less-hindered ligands have received less attention. Hitherto, there are multiple reports detailing the structural characterizations and reactivity of tetra-coordinated cobalt(II) and cobalt(III) species supported by the hindered $[PhB(RIm)_3]^-$ ligand,[6–9] whereas, to the best of our knowledge, there is only one report detailing the structural characterization of a hexa-coordinated cobalt(III) complex possessing the less-hindered imidazole-based ligand, hydrotris(1-ethyl-imidazol-2-ylidene)borate ($[HB(EtIm)_3]^-$)[10]. Our previous study revealed that highly-hindered scorpionate ligand complexes are not suitable as oxidation catalysts due to inaccessibility of substrates and/or intramolecular oxidation of substituent groups of the ligand.[11] Herein, the synthesis, structural characterization and alkane oxidation catalytic performance of cobalt complexes comprising tris(1-methylimidazol-2-ylidene)phenylborate, $[PhB(MeIm)_3]^-$, that possesses less-hindered methyl groups surrounding the metal center of the resulting complexes, $[Co^{III}([PhB(MeIm)_3])(acac)(MeImH)](OTf)$ (**1**[OTf]) and $[Co^{III}([PhB(MeIm)_3])_2](OTf)$ (**2**[OTf]), are investigated.

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† Electronic Supplementary Information (ESI) available: Experimental details, IR, ^1H NMR, electrospray ionization (ESI)-MS and UV-vis spectra, time course of catalytic reactions. See DOI: 10.1039/x0xx00000x

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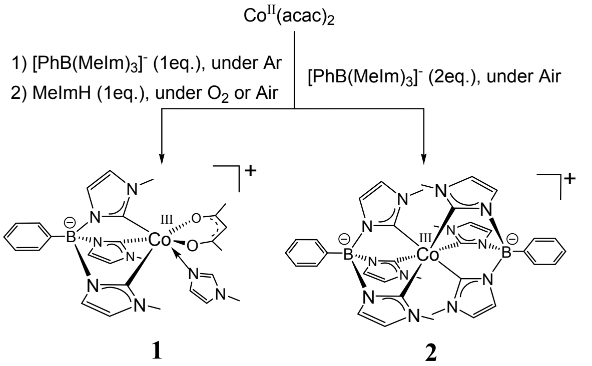

Scheme 1 Synthesis of cobalt(III) complexes with $[PhB(MeIm)_3]^-$.

The less-hindered $[PhB(MeIm)_3]^-$ ligand typically forms hexa-coordinated homoleptic $[M^n([PhB(MeIm)_3])_2]^{n-2}$ complexes (n = oxidation number of M); complexes of this general formula containing Mn(IV),[12] Mn(III),[13] Ru(III) and Os(III)[14] have been structurally characterized. However, only two heteroleptic $[M([PhB(MeIm)_3])L_x]^y$ complexes, where L, x, and y denote ligands other than $[PhB(MeIm)_3]^-$, the number of L ligands, and the charge of the resulting complex (depending on the charges of L and x), respectively, have been characterized by spectroscopic methods.[12,15] A tricarbonyl complex of d^6 manganese(I), $[Mn^I([PhB(MeIm)_3])(CO)_3]$, has been characterized by ^{1}H NMR and IR spectra, although its molecular structure has not been determined by X-ray crystallography.[12] In this work, the synthesis of a cobalt heteroleptic complex was studied. For this purpose, Co^{II}(acac)$_2$ was employed as a starting compound because the slow ligand exchanging behavior of acac, compared with other ligands, allows isolation of the desired heteroleptic complex, formed *via* the substitution of one acac ligand with $[PhB(MeIm)_3]^-$ chelated to the cobalt center. The reaction of Co^{II}(acac)$_2$ with an equivalent of the deprotonated $[PhB(MeIm)_3]^-$ ligand—generated *in situ* by treatment of $[PhB(MeImH)_3](OTf)_2$ with three equivalents of lithium diisopropylamide (LDA) under Ar—yielded an air-sensitive green species. Although the isolation and characterization of the green species were not successful, exposure of the green species solution to O$_2$ (or air) resulted in the formation of a brown species **1** (Scheme 1). It is noteworthy that **1** forms in low yield (~10%) even when 1-methylimidazole (MeImH) is not added; this trapped MeImH presumably forms via degradation of either $[PhB(MeIm)_3]^-$ or $[PhB(MeImH)_3](OTf)_2$. The yield of **1** increases to 45% when one equivalent of MeImH is added. The electrospray ionization-mass spectrometry (ESI-MS) spectra obtained from the brown species displayed ion peaks ascribed to $[Co([PhB(MeIm)_3])(acac)]^+$. Also, the cold-spray ionization mass spectra (CSI-MS; ionized at ambient temperature) exhibited ion peaks attributed to the same acac complex and its MeImH adduct **1** (Fig. S2). The IR spectrum exhibited bands at 1580 and 1513 cm^{-1} attributed to the νC=O and νC=C stretching vibrations of acac, respectively.[16,17] ^{1}H NMR signals appeared across the 0–10 ppm region supporting that the isolated brown species is a diamagnetic compound. The multiple signals suggested that the lower symmetric structure of **1** (a pseudo mirror symmetric structure consisting two equatorial and one axial MeIm in $[PhB(MeIm)_3]^-$ and neutral MeImH) and partial dissociation of the neutral MeImH ligand from **1** giving the mixture of cobalt(III) complexes. Recrystallization of the brown species yielded pale brown crystals of **1**[OTf] and X-ray crystallographic analysis revealed the molecular structure of **1** as the desired heteroleptic cobalt complex possessing a κ^3-capping $[PhB(MeIm)_3]^-$ ligand and a bidentate acac ligand (Fig. 1 (a)). The sixth coordination site is occupied by the 1-methylimidazole nitrogen donor. The Co-C bond lengths in **1** are calculated to be 1.908(2), 1.922(2) and 1.943(2) Å—close to the Co-C bond lengths of cobalt(III) complexes possessing related ligands. The Co-C bond lengths of previously reported pseudo-tetrahedral cobalt complexes comprising the bulky $[PhB(RIm)_3]^-$ ligand are reported to be between 2.01 and 2.13 Å for cobalt(II) species (Co-Cl,[6] Co-Me,[6] Co-amido,[7] Co-azido[8] and Co-OH[9]) and 1.89–1.99 Å for cobalt(III) complexes (imido,[7] hydroxo[9] and oxo[9] complexes). The distorted square-pyramidal di(azido) cobalt(III) complex of $[PhB(^tBuIm)_3]^-$ has Co-C bond lengths between 1.89 and 2.01 Å.[8] Additionally, the Co-C bond lengths of the homoleptic cobalt(III) complex $[Co^{III}(HB(EtIm)_3)_2]^+$ are in the range of 1.943–1.959 Å.[9] Furthermore, free OTf$^-$ exists as a counter anion in the crystal lattice of **1**. Therefore, the charge of the cobalt center in **1** is assigned as +3, as predicted from the diamagnetic nature. Notably, related scorpionate ligand complexes comprising cobalt(II) with acac, $[Co^{II}(Tp^*)(acac)(NCMe)]$ (**3**; Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate) and $[Co^{II}(To^M)(acac)]$ (**4**; To^M = tris(4,4-dimethyloxazol-2-yl)phenylborate), are inert toward O$_2$ and the formation of the corresponding cobalt(III)-acac complexes have, to the best of our knowledge, never been observed.[17] Hence, the observed differences in the oxidizing behaviors of the cobalt centers indicate that the electron-donating ability of $[PhB(MeIm)_3]^-$ is higher than the Tp* and To^M ligands.

A homoleptic complex **2**[OTf] could also be synthesized by the reaction of Co^{II}(acac)$_2$ and two equivalents of $[PhB(MeIm)_3]^-$ under air (Scheme 1). A diamagnetic ^{1}H NMR spectrum of **2**[OTf] exhibited only a single set of imidazolylidene signals indicating C_3 symmetric arrangement of $[PhB(MeIm)_3]^-$. X-ray analysis of almost colorless **2**[OTf] crystals revealed a pseudo-octahedral cobalt(III) center supported by two κ^3-$[PhB(MeIm)_3]$ ligands (Fig. 1 (b)). The Co-C bond lengths of **2**[OTf] are calculated to be 1.932(2), 1.946(2) and 1.952(2) Å (for molecule 1) and 1.931(2), 1.946(2) and 1.951(2) Å (for the crystallographically independent molecule 2 in the same lattice). An average Co-C length in **2**[OTf] (1.94 Å) is ca 0.02 Å longer than that in **1**[OTf].

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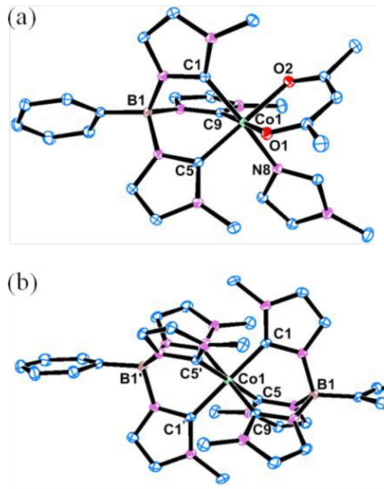
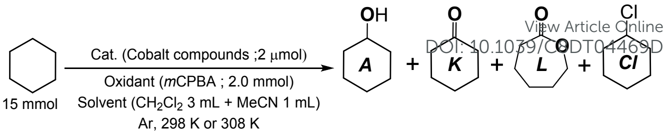


Fig. 1 Molecular structures of: (a) $[Co^{III}([PhB(MeIm)_3])(acac)(MeImH)]^+$ (**1**), and (b) $[Co^{III}([PhB(MeIm)_3])_2]^+$ (**2**). Thermal ellipsoids are set at 30% probability. All hydrogen atoms and trifluoromethanesulfonate counter anions for **1** and **2** are omitted for clarity.

There are reports of cobalt compounds, including those comprising scorpionate ligand complexes **3**, **4** and $[Co^{II}(To^M)(OAc)]$, that demonstrate activity toward the catalytic oxidation of alkanes with *meta*-chloroperbenzoic acid (*m*CPBA).[17–23] Hence, the catalytic performance of the synthesized cationic cobalt(III) complexes **1** and **2** toward the oxidation of cyclohexane with *m*CPBA was examined under the condition shown in Scheme 2 and their efficiencies compared with **3** and **4**. The catalytic performance of $Co(acac)_2$—the precursor to **1**–**4**—was examined as the control. At a reaction temperature of 25 °C, the order of alcohol yields was: **1** > $Co^{II}(acac)_2$ > **4** >> **3** >> **2** (Table 1). Although the total turnover numbers (TON; estimated based on the oxidizing equivalents of the products) of **1** is observed to be lower than that of $Co^{II}(acac)_2$, the alcohol selectivity (***A***/(***K*** + ***L***)) of **1** is enhanced by a factor of 1.3 relative that of $Co^{II}(acac)_2$. The initial turnover frequency (TOF, 369 h^{-1}) of **1** is observed to be higher than that of the cobalt(II)-acetato complex chelated to tris(2-pyridylmethyl)amine, $[Co^{II}(OAc)(TPA)]^+$ (300 h^{-1}), which is known to be an efficient hydroxylation catalyst.[19] Although the catalytic reaction in the presence of **1** reached saturation after 3 h, the addition of additional *m*CPBA (2 mmol) promoted the catalytic reaction to re-start without negatively impacting the oxidant utilization efficiency (*ca.* 53%; see Fig. S13). These observations suggest that the integrity of the catalyst structure (derived from **1**) was retained even in the presence of a large excess amount of the acidic *m*CPBA. Furthermore, the moderate oxidant utilization efficiency observed together with the moderate alcohol selectivity indicates that a putative reaction intermediate, such as metal-oxyl (M^{n+}–O·) or oxo ($M^{(n+1)+}$=O) species formed via O-O homolyses of the corresponding metal-acylperoxo complex,[24] may possess strong radical characteristics, concomitant to the non-productive consumption of *m*CPBA.



Scheme 2 Conditions of catalytic reactions.

Table 1 Oxidation of cyclohexane with *meta*-chloroperbenzoic acid (*m*CPBA) at 25 °C [a].

Cat.	Products / μmol				TON [b]	***A*** / (***K*** + ***L***)
	A	***K***	***L***	***Cl***		
Blank	3.9	4.1	0.2	3.6	–	0.9
1	704.7	80.7	82.4	56.7	543.8	4.3
2	18.0	11.7	0.3	4.7	23.3	1.5
3	146.3	43.8	3.6	14.2	127.6	3.1
4	547.0	124.4	37.9	36.3	453.9	3.4
$Co^{II}(acac)_2$	674.5	192.5	32.5	46.2	585.3	3.0

[a] Reaction time: 3 h.

[b] TON = {cyclohexanol (***A***) + chlorocyclohexane (***Cl***) + 2 × {cyclohexanone (***K***) + *ε*-caprolactone (***L***)}} / cobalt compound.

As noted above, the catalytic performance of the heteroleptic complex **1** was observed to be efficient, whereas the corresponding performance of the homoleptic complex **2** was almost inactive at 25 °C. The change in the UV-vis spectra during the reaction of *m*CPBA with **1** or **2,** without any substrate, at the same temperature supported the difference of the catalytic performance. Addition of excess *m*CPBA (ca. 10 equivalents) to a solution of **1** (dissolved in a 3:1 v:v mixture of CH_2Cl_2:MeCN) resulted in initially increasing the absorbance at 370 nm, but the intensity of this absorption band eventually decreased (Fig. S15). In contrast, addition of *m*CPBA to the homoleptic complex **2** under same condition led to increase the absorbance at 395 nm and this band remained intact on reaching the saturation of the spectral changing (Fig. S16). Although structures of the formed species are unclear at this moment, the thermal stabilities of the initially formed putative cobalt-*m*CPBA complexes are different and that is consistent with the catalytic performances. The lability of the MeImH and/or acac ligands likely facile permit *m*CPBA access to the cobalt center of **1**, and following activation of the cobalt-binding *m*CPBA seems to occur at ambient temperature. Even the homoleptic cobalt(III) complex **2** reacted with *m*CPBA at 25 °C to form something stable species. The pseudo-tetrahedral cobalt(II)-chlorido complexes possessing the hindered *tert*-butyl and mesityl-substituted ligands, $[Co^{II}([PhB(RIm)_3])Cl]$, react with HCl under ambient conditions, to form the carbene donor protonated complex $[Co^{II}(Cl)_2([PhB(RIm)_2(RImH)])]$.[6] Therefore, protonation of one carbene donor of $[PhB(MeIm)_3]^-$ in **2** would allow to access of *m*CPBA to the cobalt center. Further work is necessary to definitively explain the differences in activity of pre-catalysts **1** and **2**.

When increasing the reaction temperature to 35 °C, the homoleptic complex **2** also exhibited catalytic activity. Appearance of the catalytic activity of **2** was supported by changing the UV-vis spectra of the reaction of **2** with *m*CPBA. The stable intermediate formed at 25 °C changed to another

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species immediately at 35 °C (Fig. S16). The order of alcohol yields was **1** > **2** > **4** > **3** > Co^{II}(acac)$_2$. The initial TOF of the most active complex **1** reached ~1050 h^{-1}, although the catalytic reaction was terminated at 30 min and the oxidant utilization efficiency was 53%. When subjected to the same reaction conditions, an N4-donating ligand-supported cobalt complex, [Co^{II}(OAc)(L^{tBu})]$^+$ where L^{tBu} denotes *N*,*N*-bis(2-pyridylmethyl)-*N*-[(1-*R*-1*H*-1,2,3-triazol-4-yl)methyl]amine (Fig. S17), demonstrated higher oxidant utilization efficiency (83 %) and comparable alcohol selectivity (***A***/(***K*** + ***L***) = 5.4), however, the initial TOF (950 h^{-1}) was observed to be lower when compared with **1**.[20] The initial TOF of **2** was ~50% of that of **1**, although the final oxidant utilization efficiency was similar to that of **1**. The significantly higher TOF of **1** is considered to be attributed to the [PhB(MeIm)$_3$]$^-$ ligand having excellent electron-donating properties compared with other ligands, including N4-donating pyridylamines.[19–21] The catalytic reaction mediated by Co^{II}(acac)$_2$ at 35 °C was terminated after 30 min with an oxidant utilization efficiency of 40%. When increasing the reaction temperature to 35 °C, the catalyst derived from Co(acac)$_2$ was not sufficiently stable. Conversely, the scorpionate ligands [PhB(MeIm)$_3$]$^-$, Tp* and To^M appear to significantly enhance the thermal stabilities of their homogeneous cobalt catalysts relative that derived from Co^{II}(acac)$_2$.

Table 2 Catalytic reactions at 35 °C.

Cat.	Reaction time / min	Products / μmol				TON ^{a}	***A*** / (***K***+***L***)
		A	***K***	***L***	***Cl***		
Blank	180	69.4	0.5	2.1	3.8	–	26.6
1	30	731.7	88.8	36.6	70.0	526.0	5.8
2	60	675.0	116.7	43.1	57.0	525.8	4.2
3 ^{b}	180	587.2	104.1	52.4	36.2	468.1	3.8
4 ^{b}	60	653.9	149.3	32.8	47.9	533.0	3.6
Co^{II}(acac)$_2$ ^{b}	30	473.3	130.2	17.2	24.8	396.4	3.2

^{a} TON = {cyclohexanol (***A***) + chlorocyclohexane (***Cl***) + 2 × {cyclohexanone (***K***) + *ε*-caprolactone (***L***)}} / cobalt compound.
^{b} From ref. 17.

In summary, the synthesis of a heteroleptic cobalt(III) tris(carbene)borate complex with a low degree of hindrance, *via* aerobic oxidation of a cobalt(II) species, was successful. To the best of our knowledge, **1**[OTf] is the first heteroleptic complex of the less hindered [PhB(MeIm)$_3$]$^-$ to be characterized by X-ray crystallography. This heteroleptic complex was observed to be an efficient catalyst for the oxidation of alkanes with *m*CPBA, even at ambient temperatures. The homoleptic cobalt(III) bis([PhB(MeIm)$_3$]) complex also exhibited catalytic activity at elevated temperatures, but was inert at ambient temperatures. Both the formation of the cobalt(III) species by the oxidation of the cobalt(II) precursors, and the high catalytic performance of the [PhB(MeIm)$_3$]$^-$ ligand-containing complexes were attributed to the higher electron-donating ability of the carbene donors compared with the nitrogen donors of the related scorpionate ligands, Tp* and To^M. Additionally, the catalytic data presented, relating to the oxidation reaction in the presence of the Brønsted-acidic oxidant, will expand the use of tris(carbene)borate complexes to other catalyst designs.[25]

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There are no conflicts to declare.

Notes and references

1. (a) *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools: Edition 2 (RSC Catalysis Series No.27)*, ed. S. Diez-Gonzalez, The Royal Society of Chemistry, London, 2017; (b) *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis (Catalysis by Metal Complexes, vol.32)*, ed. C. S. J. Cazin, Springer Science+Business Media, Berlin, 2011; (c) *N-Heterocyclic Carbenes in Transition Metal Catalysis (Topics in Organometallic Chemistry, vol.21)*, ed. F. Glorius, Springer-Verlag, Berlin, Heidelberg, 2007.
2. V. Charraa, P. de Frémonta and P. Braunsteina, *Coord. Chem. Rev.*, 2017, **341**, 53-176.
3. (a) C. Santini, M. Marinelli and M. Pellei, *Eur. J. Inorg. Chem.* **2016**, 2312-2331; (b) A. Nasr, A. Winkler and M. Tamm, *Coord. Chem. Rev.*, 2016, **316**, 68-124; (c) J. M. Smith, *Comments. Inorg. Chem.*, 2008, **29**, 189-233; (d) J. Cheng, L. Wang, P. Wang and L. Deng, *Chem. Rev.*, 2018, **118**, 9930-9987.
4. (a) A. Raba, M. Cokoja, W. A. Herrmann and F. E. Kühn, *Chem. Commun.*, 2014, **50**, 11454-11457; (b) J. W. Kück, A. Raba, I. I. E. Markovits, M. Cokoja and F. E. Kühn, *ChemCatChem*, 2014, **6**, 1882-1886; (c) T. Yagyu, K. Yano,T. Kimata and K. Jitsukawa, *Organometallics*, 2009, **28**, 2342-2344; (d) M. J. Schultz, S. S. Hamilton, D. R. Jensen and M. S. Sigman, *J. Org. Chem.*, 2005, **70**, 3343-3352; (e) F. Hanasaka, K. Fujita and R. Yamaguchi, *Organometallics*, 2004, **23**, 1490-1492; (f) M. Poyatos, J. A. Mata, E. Falomir, R. H. Crabtree and E. Peris, *Organometallics*, 2003, **22**, 1110.
5. (a) X. Hu, I. Castro-Rodriguez and K. Meyer, *J. Am. Chem. Soc.*, 2004, **126**, 13464-13473; (b) A. A. Danopoulos, J. A. Wright, W. B. Motherwell and S. Ellwood, *Organometallics*, 2004, **23**, 4807-4810; (c) S. Dürr, B. Zarzycki, D. Ertler, I. Ivanović-Burmazović and U. Radius, *Organometallics*, 2012, **31**, 1730-1742.
6. R. E. Cowley, R. P. Bontchev, E. N. Duesler and J. M. Smith, *Inorg. Chem.*, 2006, **45**, 9771-9779.
7. R. E. Cowley, R. P. Bontchev, J. Sorrell, O. Sarracino, Y. Feng, H. Wang and J. M. Smith, *J. Am. Chem. Soc.*, 2007, **129**, 2424-2425.
8. J. J. Scepaniak, C. G. Margarit, R. P. Bontchev and J. M. Smith, *Acta Cryst.*, 2013, **C69**, 968-971.
9. M. K. Goetz, E. A. Hill, A. S. Filatov and J. S. Anderson, *J. Am. Chem. Soc.*, 2018, **140**, 13176−13180.
10. R. Fränkel, U. Kernbach, M. B. Christianopoulou, U. Plaia, M. Suter, W. Ponikwar, H. Nöth, C. Moinet and W. P. Fehlhammer. *J. Organomet. Chem.*, 2001, **617-618**, 530-545.
11. S. Hikichi, K. Hanaue, T. Fujimura, H. Okuda and J. Nakazawa, *Dalton Trans.*, 2013, **42**, 3346-3356.
12. A. P. Forshaw, R. P. Bontchev and J. M. Smith, *Inorg. Chem.*, 2007, **46**, 3792-3794.
13. (a) A. P. Forshaw, J. M. Smith, A. Ozarowski, J. Krzystek, D. Smimov, S. A. Zvyagin, T. D. Harris, H. I. Karunadasa, J. M. Zadrozny, A. Schnegg, K. Holldack, T. A. Jackson, A. Alamiri, D. M. Barnes and J. Telser, *Inorg. Chem.*, 2013, **52**, 144-159; (b) H. E. Colmer, C. G. Margarit, J. M. Smith, T. A. Jackson and J. Telser, *Eur. J. Inorg. Chem.*, 2016, 2413-2423.
14. F. Che, G.-F. Wang, Y.-Z. Li, X.-T. Chen and Z.-L. Xue, *Inorg, Chem. Commun.*, 2012, **21**, 88-91.

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Published on 29 January 2019. Downloaded by Gothenburg University Library on 1/29/2019 8:43:43 AM.

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15. I. Nieto, R. P. Bontchev, A. Ozarowski, D. Smirnov, J. Krzystek, J. Telser and J. M. Smith, *Inorg. Chim. Acta*, 2009, **362**, 4449-4460.
16. (a) S. Pasko, L. G. Hubert-Pfalzgraf, A. Abrutis and J. Vaissermann, *Polyhedron*, 2004, **23**, 735-741; (b) H. Lee, C. H. Lee., I. S. Oh, and I. M. Lee, *Bull. Korean Chem. Soc.*, 2010, **31**, 891-894; (c) M. Cortijo, C. Viala, T. Reynaldo, L. Favereau, I. Fabing, M. S. Hooper, J. Autschbach, N. R. Ramond, J. Crassous and J. Bonvoisin, *Inorg. Chem.*, 2017, **56**, 4555-4567.
17. T. Nishiura, T. Uramoto, Y. Takiyama, J. Nakazawa and S. Hikichi., *Molecules*, 2018, **23**, 1466.
18. R. R. Reinig, D. Mukherjee, Z. B. Weinstein, W. Xie, T. Albright, B. Baird, T. S. Gray, A. Ellern, G. J. Miller, A. H. Winter, S. L. Bud'ko and A. D. Sadow, *Eur. J. Inorg. Chem.* 2016, 2486-2494.
19. T. Nagataki, Y. Tachi and S. Itoh, *Chem. Commun.***,** 2006, 4016-4018.
20. (a) J. Nakazawa, A. Yata, T. Hori, T. D. P. Stack, Y. Naruta and S. Hikichi, *Chem. Lett.*, 2013, **42**, 1197-1199; (b) J. Nakazawa, Y. Doi and S. Hikichi, *Mol. Catal.*, 2017, **443**, 14–24.
21. E. Tordin, M. List, U. Monkowius, S. Schindler and G. Knör, *Inorg. Chim. Acta*, 2013, **402**, 90-96.
22. (a) W. Nam, I. Kim, Y. Kim and C. Kim, *Chem. Commun.*, 2001, **14**, 1262-1263; (b) W. Nam, J. Y. Ryu,; I. Kim and C. Kim, *Tetrahedron Lett.*, 2002, **43**, 5487-5490.
23. G. B. Shul'pin, D. A. Loginov, L. S. Shul'pina, N. S. Ikonnikov, V. O. Idrisov, M. M. Vinogradov, S. N. Osipov, Y. V. Nelyubina and P. M. Tyubaeva, *Molecules*, 2016, **21**, 1593.
24. Acylperoxo complexes of nickel(II) formed during alkane oxidation reaction have been characterized; ref. 11 and follows; J. Nakazawa, S. Terada, M. Yamada and S. Hikichi, *J. Am. Chem. Soc.*, 2013, **135**, 6010-6013.
25. (a) C. Tubaro, A. Biffis, E. Scattolin and M. Basato, *Tetrahedron*, 2008, **64**, 4187-4195; (b) A. Biffis, C. Tubaro, E. Scattolin, M. Basato, G. Papini, C. Santini, E. Alvarezc and S. Conejeroc, *Dalton Trans.*, 2009, 7223-7229.

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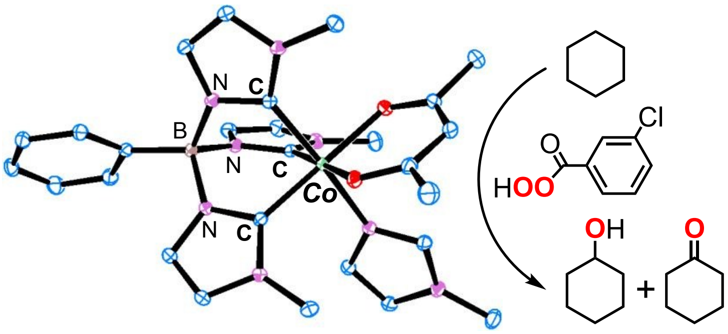

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