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N-Heterocyclic carbenes as supporting ligands in transition metal complexes of N_2

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Recent developments have substantially expanded the scope of N-heterocyclic carbenes (NHCs) as ancillary ligands in coordination chemistry and homogeneous catalysis. This review provides a short overview of the emerging field of NHC-supported transition metal complexes of N_2 and the possibilities to catalytically activate N_2 in these complexes.

(up to 50 words)

Introduction

N-Heterocyclic carbenes (NHCs) represent a class of nitrogen-containing heterocycles with a carbene moiety.[1] The rapid growth of NHC chemistry over the past quarter century was ignited by the seminal discovery of isolable imidazole-type carbenes,[2] the development of various other types of stable carbenes,[3] and the successful application of NHCs as supporting ligands in homogeneous catalysts.[4] One of the most prominent features of NHCs is the singlet state of their carbene moiety, which is stabilized by electron donation from the adjacent nitrogen atom(s) to the vacant p-orbital of the carbon atom (Figure 1).[5] The presence of both an electron pair and a vacant orbital at the carbene center renders a comparison between NHCs and phosphines regarding their interactions with transition metals pertinent, and the coordination chemistry of NHCs has been discussed in early studies.[6] Similar to phosphines, NHCs form robust bonds with transition metal ions (in particular with late transition metals) in various oxidation states, but relative to phosphines, NHCs are stronger σ-donors and weaker π-acceptors.[5b,7] Thus, the use of NHCs as alternatives to phosphines has become a standard method in the search of suitable ligands for transition metal complexes in catalytic applications.[4]

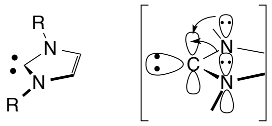
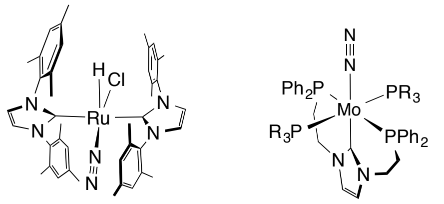


Fig. 1 Representative NHCs: 1,3-disubstituted imidazol-2-ylidenes.

The synthesis and reactivity of transition metal complexes that are able to coordinate and activate N_2[8] and/or generate reactive species via dissociation of the coordinated N_2, is currently receiving growing attention. Traditionally, phosphine-supported low-valent transition metal complexes have been employed for that purpose, but the use of NHCs in this area is rapidly expanding. The strong σ-donating properties of NHCs relative to phosphines are expected to facilitate a higher degree of N_2 activation through increased back-bonding from the d orbitals of the metals to the π* orbitals of N_2. This short review summarizes the role of NHCs as supporting ligands in such transition metal complexes of N_2. Although most of the complexes discussed herein contain N_2 as a labile ligand, we also present some examples that show an enhanced activation of N_2 within the transition metal-NHC scaffold.

Activation of N_2 and the influence of NHCs

The desirable electron-donating abilities of NHCs were demonstrated by Fogg *et al.* on the Ru(II) complex $RuHCl(IMes)_2(N_2)$ (IMes = 1,3-bis(mesityl)imidazol-2-ylidene) (Figure 2).[9] At room temperature, this complex resists substitution of N_2 by CO, thus reflecting a strong interaction between Ru and N_2. The theoretical analysis of this complex suggested a stronger bond between Ru and N_2 compared to Ru and IMes, which is consistent with the decrease of olefin binding rates in the presence of IMes. The weakening of N≡N bond is also supported by the ν_{NN} stretching frequency (2041 cm^{-1}) of this complex, which was observed at a lower wavenumber than those of the closely related phosphine complexes $RuHCl(PCy_3)(IMes)(N_2)$ (2048 cm^{-1}) and $RuHCl(PCy_3)_2(N_2)$ (2060 cm^{-1}). Similar effects of NHCs on (*mer*-PCP)$Mo(N_2)(PR_3)_2$ (PR_3 = PPh_2Me or $P(OMe)_3$, PCP = 1,3-bis(diphenylphosphinoethyl)imidazol-2-ylidene), i.e. Mo(0)-N_2 complexes with a mixed NHC/phosphine pincer ligand and a N_2 ligand located *trans* to the carbene moiety (Figure 2), have been reported by Tuczek and co-workers.[10] The ν_{NN} stretching frequency of the PPh_2Me complex was observed at 1876 cm^{-1}, which is significantly shifted relative to that of the pentaphosphine complex $Mo(N_2)(PMe_3)_5$ (1950 cm^{-1}).[11]

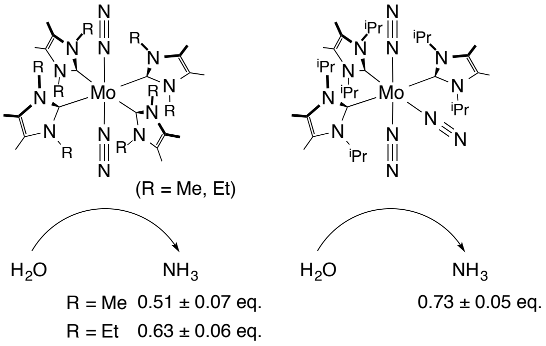


$RuHCl(IMes)_2(N_2)$

(*mer*-PCP)$Mo(N_2)(PR_3)_2$
$PR_3 = PPh_2Me, P(OMe)_3$

Fig. 2 Chemical structures of $RuHCl(IMes)_2(N_2)$ and (*mer*-PCP)$Mo(N_2)(PR_3)_2$.

The strong electron donation from the NHC ligands activates the N_2 ligand by making it more basic and thus susceptible to protonation. For example, NHC-supported Mo(0)-N_2 complexes developed in the group of Ohki undergo protonation of their N_2 ligands upon reaction with H_2O to release NH_3 (Scheme 1), which has not yet been accomplished with phosphine-stabilized Mo(0)-N_2 complexes.[12] Even though the yields of NH_3 obtained from the hydrolysis of the Mo(0) complexes *trans*-$Mo(N_2)_2(IRMe)_4$ (IRMe = 1,3-R_2-4,5-dimethylimidazol-2-ylidenes, R = Me, Et) and *mer*-$Mo(N_2)_3(I^iPrMe)$ (I^iPrMe = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) range from 0.51 ± 0.07 to 0.73 ± 0.05 equivalents per atom of molybdenum, truly catalytic applications still remain to be developed. Mo(0)-NHC complexes with *trans*-N_2 ligands exhibit asymmetric N_2 vibrations at significantly lower wavenumbers (ν_{NN} = 1838-1836 cm^{-1}) than those of the corresponding phosphine analogues *trans*-$Mo(N_2)_2(PR_3)_4$ ($\nu_{NN} > 1900$ cm^{-1}) (Figure 3). The significant weakening of N≡N bond is also supported by the larger J_{NN} coupling constants in the ^{15}N NMR spectra of these NHC complexes (7.4-7.7 Hz) relative to their phosphine analogues (3.6-5.8 Hz), as well as by the crystallographically determined shorter Mo-N and longer N-N bonds relative to the phosphine analogues.



Scheme 1 Protonation of N_2 complexes of Mo(0)-NHCs with H_2O.

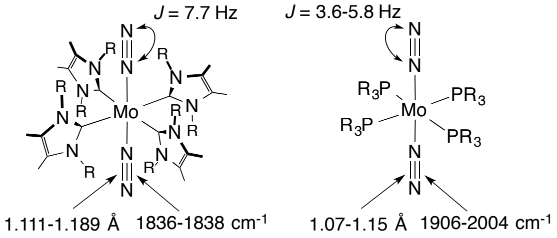
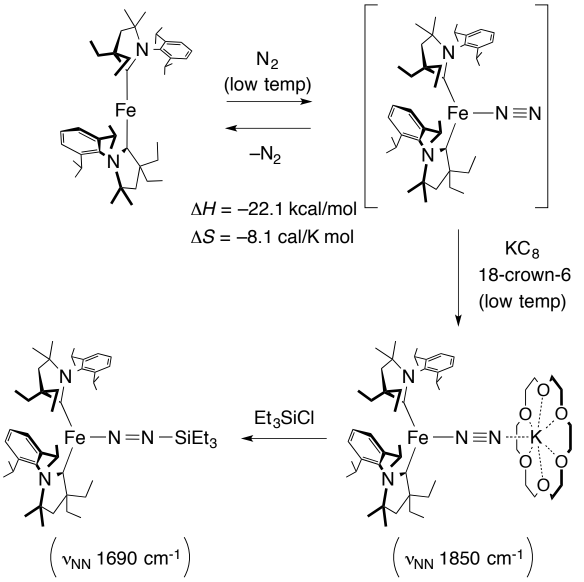
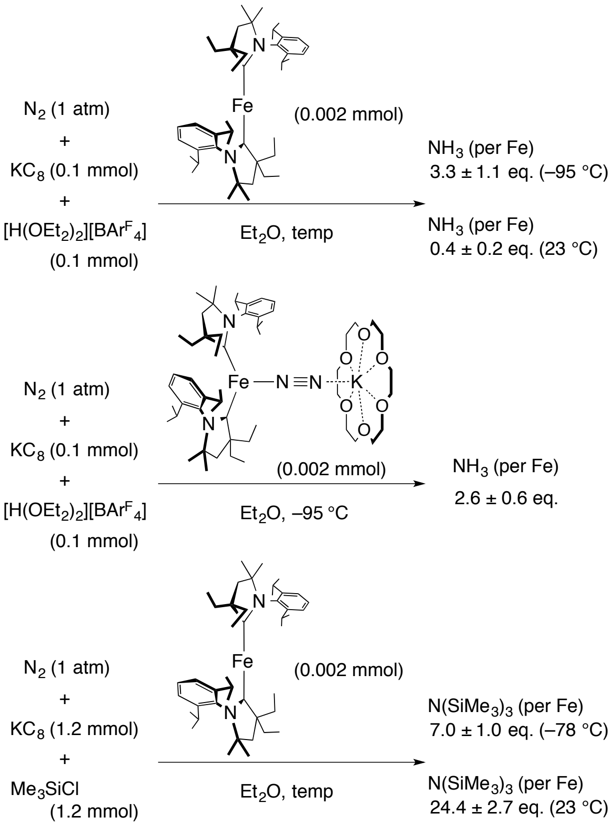


Fig. 3 Spectroscopic comparison between NHC- and phosphine-supported Mo(0) complexes of N_2.

Replacement of one of the two amino moieties in typical imidazole-type NHCs by an alkyl group furnishes cyclic (alkyl)(amino)carbenes (CAACs),[13] which have also been used as supporting ligands for homogeneous catalysts.[3b] Taking advantage of the strong bonding to transition metals and the steric hindrance of CAACs that efficiently stabilizes low-coordinate metal centers, Ung and Peters successfully accomplished the catalytic reduction of N_2 with an Fe-CAAC complex.[14] At room temperature, the coordination of N_2 to the two-coordinate Fe(0) complex $[(CAAC)_2Fe]$[15] is reversible (K_{eq} = 0.2), with thermodynamic parameters of ΔH = –22.1 kcal/mol and ΔS = –8.1 cal/K·mol (Scheme 2). Accordingly, binding of N_2 to the Fe(0) center is more favorable at low temperatures, and further reduction to the Fe(–I) complex $[(CAAC)_2Fe(N_2)]^{-1}$ was accomplished at –95 °C. All $[(CAAC)_2Fe]$ complexes of the redox series between Fe(+I) and Fe(–I) were found to reduce N_2 to NH_3 in the presence of KC_8 (reductant) and $[H(OEt_2)_2][BAr^F_4]$ (Ar^F = 3,5-$(CF_3)_2C_6H_3$) as the proton source. At –95 °C, yields of up to 3.3 ± 1.1 equivalents of NH_3 per atom of Fe were observed (Scheme 3). The higher yield of NH_3 at lower temperature relative to the room temperature reaction (0.4 ± 0.2 equivalents) is consistent with the less favorable binding of N_2 at higher temperature. At room temperature, [$(CAAC)_2Fe$] was also able to mediate the catalytic silylation of N_2 in the presence of KC_8 and Me_3SiCl, which furnished up to 24.4 ± 2.7 equivalents of $N(SiMe_3)_3$ per atom of Fe. At –78 °C, the yield decreased significantly (7.0 ± 1.0 equivalents per Fe), which was attributed to the insufficient generation of $Me_3Si\cdot$ radicals at this temperature. Although most of the mechanistic details for the conversion of N_2 to $NH_3/N(SiMe_3)_3$ still remain unclear, the initial protonation/silylation at the terminal nitrogen atom is supported by the successful synthesis of the diazenido complex [$(CAAC)_2Fe(N_2SiEt_3)$].



Scheme 2 Formation of Fe(0) and Fe(–I) N_2-complexes of the type [$(CAAC)_2Fe(N_2)$]$^{0/-1}$



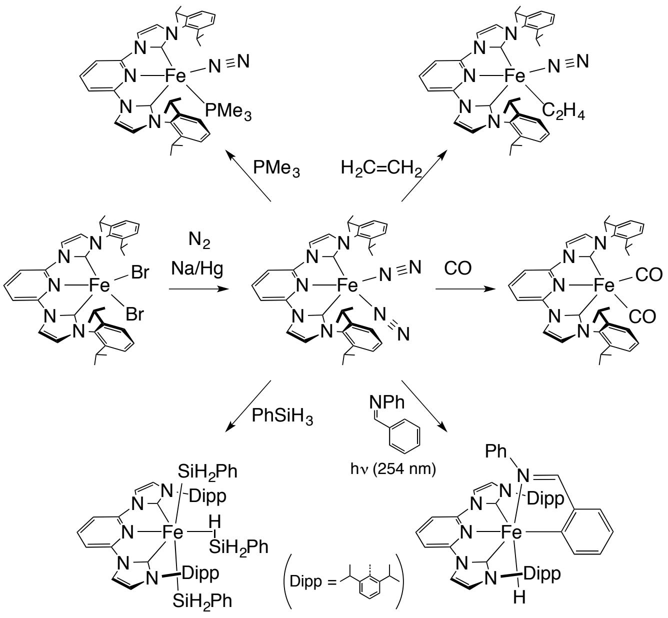
Scheme 3 Catalytic reduction of N_2 mediated by $[(CAAC)_2Fe(N_2)]^{0/-1}$

Transition metal-NHC complexes carrying labile N_2 ligands

Apart from those described in the previous section, the N_2 ligands in other transition metal-NHC complexes reported so far are labile. Interestingly, these complexes are still limited to transition metals from groups 8 and 9, indicating ample opportunity to investigate transition metal ions from other groups.

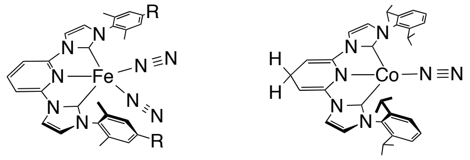
The first crystallographically analyzed N_2 complex of such a transition metal-NHC complex was $(IMes)_2Ru(H_2)(N_2)(H)_2$, which was reported by Leitner and co-workers. Even though this complex was not isolated, it was found to occupy *ca*. 20% of the crystal lattice of single crystals of $(IMes)_2Ru(H_2)_2(H)_2$.[16] Most likely, the adventitious N_2 ligand replaced one of the H_2 ligands of $(IMes)_2Ru(H_2)_2(H)_2$ during the preparation or mounting of the crystals for X-ray crystallography. The first isolation of an NHC-stabilized N_2 complex was accomplished by Danopoulos *et al*. in

2005 via the reduction of (^{iPr}C–N–C)FeBr$_2$ (^{iPr}C–N–C = 2,6-bis(2,6-^{i}Pr$_2$C$_6$H$_3$-imidazol-2-ylidene)pyridine) with Na/Hg under an atmosphere of N$_2$ (Scheme 4).[17] The resulting diamagnetic Fe(0)-N$_2$ complex (^{iPr}C–N–C)Fe(N$_2$)$_2$, supported by a mixed carbene/pyridine pincer ligand, exhibited N$_2$ vibrations (ν_{NN} = 2109 and 2031 cm^{-1}), which indicate an increased lability of the N$_2$ ligands relative to diphosphine-stabilized N$_2$ complexes of the type Fe(P^P)$_2$(N$_2$) (ν_{NN} = 1950-2068 cm^{-1}, P^P = diphosphines) or the tris(phosphine)borane-stabilized complex [Fe(TPB)(N$_2$)] (ν_{NN} = 2011 cm^{-1}, TPB = B(C$_6$H$_4$-2-P^{i}Pr$_2$)$_3$).[18] The lability of N$_2$ in (^{iPr}C–N–C)Fe(N$_2$)$_2$ renders this complex a convenient precursor for reactive (^{iPr}C–N–C)Fe^0 species. For example, replacement of one or two N$_2$ ligands occurs in the presence of 2e donor ligands (L) such as CO, CNxyl (xyl = 2,6-Me$_2$C$_6$H$_3$), ethylene, or phosphines to furnish (^{iPr}C–N–C)Fe(L)$_2$ (L = CO or CNxyl) or (^{iPr}C–N–C)Fe(N$_2$)(L) (L = C$_2$H$_4$ or phosphines).[17,19] The Fe(0) center in (^{iPr}C–N–C)Fe(N$_2$)$_2$ also promotes the oxidative addition of H-Si bonds of primary and secondary silanes at room temperature,[20] as well as the cyclometalation of *N*-benzylideneaniline under photo-irradiation conditions (λ = 254 nm).[19]



Scheme 4 Synthesis and reactivity of (^{iPr}C–N–C)Fe(N$_2$)$_2$.

The parallels between the $^{i\mathrm{Pr}}$C–N–C ligand and bis(imino)pyridines prompted Chirik *et al*. to extend their catalytic studies on bis(imino)pyridine complexes of Fe to ($^{i\mathrm{Pr}}$C–N–C)Fe$(N_2)_2$ and its analogues (Figure 4).[21, 22, 23] For ($^{\mathrm{R}}$C–N–C)Fe$(N_2)_2$ (R = ^{i}Pr, Me, Mes; $^{\mathrm{Me}}$C–N–C = 2,6-bis(2,6-$Me_2C_6H_3$-imidazol-2-ylidene)pyridine, $^{\mathrm{Mes}}$C–N–C = 2,6-bis(2,4,6-$Me_3C_6H_2$-imidazol-2-ylidene)pyridine), the catalytic hydrogenation of tri- or tetra-substituted alkenes was observed at high turnover frequencies, suggesting that the more electron-rich iron center in ($^{\mathrm{R}}$C–N–C)Fe^0 relative to bis(imino)pyridine-Fe^0 is more effective in such catalytic hydrogenations. Upon binding to Fe(0), the $^{i\mathrm{Pr}}$C–N–C ligand acts as a non-innocent ligand and functions as a π-acceptor, while it engages in ligand-centered reactions when bound to reduced Co. For instance, under an N_2 atmosphere, the hydride complex ($^{i\mathrm{Pr}}$C–N–C)CoH was found to transfer its Co-bound hydride to the 4-position of the pyridine ring to afford the N_2 complex (4-H_2-$^{i\mathrm{Pr}}$C–N–C)Co(N_2) (Figure 4). An analogous alkyl migration was observed upon treatment of ($^{i\mathrm{Pr}}$C–N–C)CoH with 1,1-diphenylehtylene in the presence of N_2.



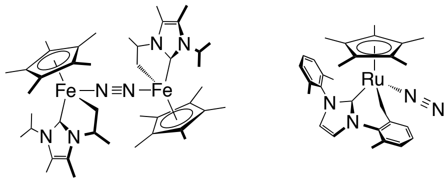
($^{\mathrm{Me}}$C-N-C)Fe$(N_2)_2$ (R = H)
($^{\mathrm{Mes}}$C-N-C)Fe$(N_2)_2$ (R = Me)

(4-H_2-$^{i\mathrm{Pr}}$C-N-C)Co(N_2)

Fig. 4 $^{\mathrm{R}}$C–N–C-supported N_2 complexes of Fe and Co

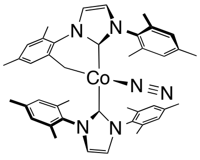
Some transition metal complexes of N_2 with cyclometalated NHC ligands were reported to act as precursors for C-H and Si-H bond activation reactions. For example, Ohki *et al*. synthesized the half-sandwich Fe complex Cp*Fe(I^{i}PrMe') (Cp* = η^5-C_5Me_5, I^{i}PrMe' = $CH_2CH(CH_3)$-3-isopropyl-4,5-dimethylimidazol-2-ylidene-1-yl) with a cyclometalated NHC ligand.

This complex is able to reversibly accommodate N_2 at the coordinatively unsaturated iron center to form the end-on N_2-bridged Fe dimer $Cp^*Fe(I^iPrMe')(\mu\text{-}N_2)Fe(I^iPrMe')Cp^*$ (Figure 5).[24] The unsaturated iron species $Cp^*Fe(I^iPrMe')$, generated upon dissociation of N_2, can activate the C-H bonds of various heteroarenes at room temperature, and further treatment with hydroboranes provides the corresponding borylated arenes and an Fe-borohydride complex. Subsequently, this reaction was developed into a catalytic C-H borylation of heteroarenes.[25] Tilley, Eisenstein, and co-workers reported the cyclometalated ruthenium complex Cp*Ru(IXy') (IXy' = $CH_2C_6H_3$-3-Me-2-(3-xylyl-imidazol-2-ylidene-1-yl)) that also reversibly binds N_2 (Figure 5). Upon loss of the N_2 ligand, the corresponding coordinatively unsaturated ruthenium species activates the Si-H bonds of primary and secondary silanes.[26] Coordination of N_2 onto cyclometalated NHC complexes is also known for cobalt: Deng and co-workers reported Co(IMes)(IMes')(N_2) (IMes' = $CH_2C_6H_2$-3,5-Me_2-2-(3-mesityl-imidazol-2-ylidene-1-yl)) (Figure 6) via cyclometalation of the transient Co(I) methyl complex $Co(IMes)_2Me$, followed by release of CH_4 and uptake of N_2.[27]



$Cp^*Fe(I^iPrMe')(\mu\text{-}N_2)Fe(I^iPrMe')Cp^*$ Cp*Ru(IXy')(N_2)

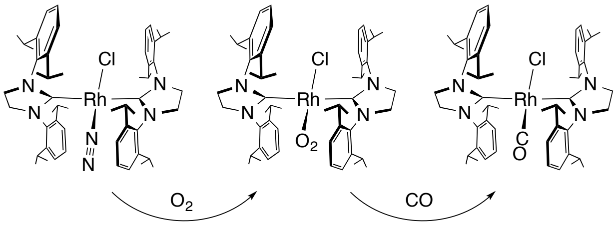
Fig. 5 Half-sandwich N_2 complexes of Fe and Ru with cyclometalated NHC ligands.



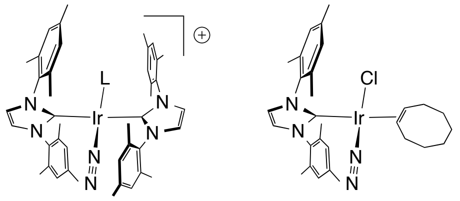
Co(IMes)(IMes')(N_2)

Fig. 6 Chemical structure of cyclometalated Co(IMes)(IMes')(N_2).

Coordination of N_2 has also been reported for some square-planar NHC complexes of rhodium and iridium, in which the transition metals have a d^8 electron configuration. For example, Crudden *et al*. found that N_2 is able to replace ethylene in the confined coordination space that is available on a square-planar Rh complex, which was obtained from the reaction of $[(C_2H_4)_2Rh]_2(\mu\text{-}Cl)_2$ with IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), to afford $(IPr)_2RhCl(N_2)$.[28] $(SIPr)_2RhCl(N_2)$ (SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene), i.e. the corresponding analogue with a saturated heterocycle backbone, was found to be susceptible to consecutive single-crystal to single-crystal ligand exchange from N_2 over O_2 to CO (Scheme 5).[29] Square-planar Ir(I) complexes containing bulky NHCs also represent suitable scaffolds for the accommodation of N_2: Aldridge *et al*. accomplished the incorporation of N_2 in $[(IMes)_2Ir(N_2)_2]^+$ and $[(IMes)_2Ir(N_2)(THF)]^+$ via replacement of two hydrides and a chloride in $[(IMes)_2Ir(H)_2Cl(Na)][BAr^F_4]$ (Figure 7).[30] Replacement of cyclooctene (coe) in $[Ir(coe)_2Cl]_2$ with IMes under an N_2 atmosphere also generates the N_2 adduct $Ir(coe)(IMes)(N_2)Cl$, in which N_2 can be exchanged with IMes to give $Ir(coe)(IMes)_2Cl$.[31]



Scheme 5 Single-crystal to single-crystal ligand exchange reactions of $(SIPr)_2RhCl(N_2)$ and $(SIPr)_2RhCl(O_2)$.



$[(IMes)_2Ir(N_2)(L)]^+$
(L = N_2, THF)

$Ir(coe)(IMes)(N_2)Cl$

Fig. 7 Square-planar Ir-N_2 complexes bearing NHCs.

Several methods have been reported for the generation of NHC-supported N_2 complexes of Ru(II). Gunnoe, Cundari, and co-workers, for example, reported $[(IMes)_2Ru(H)(CO)][BAr^F_4]$, which is a rare example of a tetra-coordinate Ru(II) complex with 14e. Even though the structural analysis in the solid state was hampered by disorder, this complex is able to reversibly bind N_2 to afford $[(IMes)_2Ru(H)(N_2)(CO)][BAr^F_4]$ in solution (Figure 8).[32] Macgregor, Pregosin, Whittlesey *et al.* reported the reversible binding of N_2 in the penta-coordinate Ru(II) hydrides $[Ru(IRMe)_4H][BAr^F_4]$ (R = Me, Et) with 16e to furnish $[Ru(IRMe)_4(N_2)H][BAr^F_4]$ (Scheme 6).[33] The back-donation from the metal center to the N_2 ligand in these complexes (ν_{NN} = 2100 cm^{-1}) is still stronger than that in the diphosphine-stabilized analogues $[Ru(P\text{^}P)_2H]^+$ (e.g. ν_{NN} = 2163 and 2184 cm^{-1} for P^P = depe and MeDuPHOS, respectively).[34] The binding ability of the ruthenium center is strongly influenced by the size of the substituent attached to the nitrogen atoms in the NHCs. For example, $[Ru(IMeMe)_4H]^+$ quantitatively affords an N_2 adduct at room temperature, while $[Ru(IEtMe)_4H]^+$ accommodates N_2 exclusively at low temperature, and even then only partially. Puetra, Valerga, and co-workers reported a ligand exchange between chloride and N_2 ligands in the presence of $NaBAr^F_4$ for the Ru(II) hydrotris(pyrazolyl)borate (Tp) complex $TpRu(^RC\text{^}N)Cl$, which contains the bidentate NHC-pyridine ligand ^RC^N (3-R-1-(2-picolyl)imidazol-2-ylidene, R = Me, ^{i}Pr, Ph) (Figure 8).[35] For R = Me or ^{i}Pr, the bridging N_2 ligand of the generated dimers does not dissociate under an argon atmosphere or under reduced pressure, even though it can be easily displaced with

CO and CH_3CN. An equilibrium mixture of the two diastereomers of these N_2-bridged dinuclear complexes and the mononuclear terminal N_2 complex is obtained for R = Ph. Severin *et al.* reported the activation of N_2O on the dinuclear Ru(II) complex (*p*-cymene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(IMes) to generate the Ru(II)/Ru(II)-N_2 complex (*p*-cymene)Ru(μ-Cl)$_3$RuCl(N_2)(IMes) and a mixed-valence Ru(II)/Ru(III) complex with a chelating and bridging alkoxy ligand (Scheme 7).[36] The Ru(II)/Ru(II)-N_2 complex can also be prepared by treatment of [(*p*-cymene)RuCl(μ-Cl)]$_2$ with IMes under an atmosphere of N_2 and converted into the bridging alkoxy Ru(II)/Ru(III) complex by reaction with N_2O.

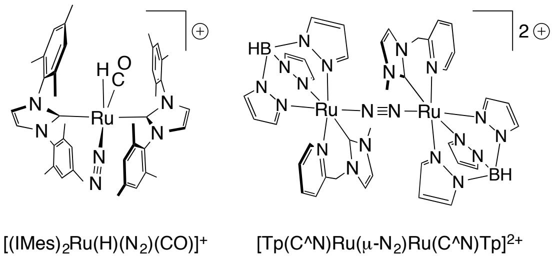
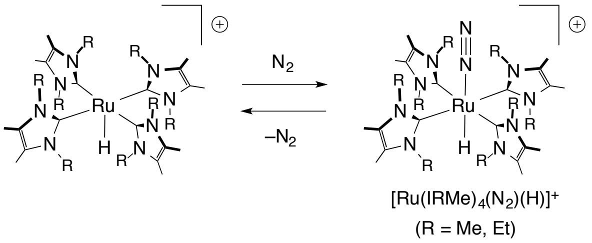
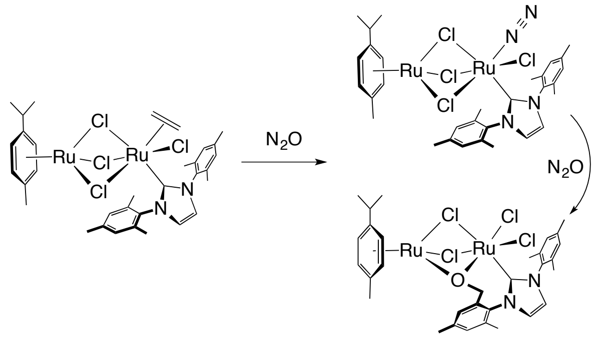


Fig. 8 Cationic N_2 complexes of Ru(II): [(IMes)$_2$Ru(H)(N_2)(CO)]$^+$ and [Tp(^{Me}C^N)Ru(μ-N_2)Ru(^{Me}C^N)Tp]$^{2+}$.



Scheme 6 Coordination of N_2 to afford the cationic complexes [Ru(IRMe)$_4$(N_2)H]$^+$.



Scheme 7 Consecutive formation of a dinuclear Ru(II)/Ru(II)-N_2 complex and a Ru(II)/Ru(III) complex via activation of N_2O.

Summary and outlook

Relative to phosphine-coordinated transition metal complexes, the strong σ-donating properties of NHCs lead to a higher electron density on the metal centers.[7c] Thus, the weakening of N≡N bond through extensive back-donation from the d-orbitals of the metal to the π*-orbital of N_2 is facilitated, as demonstrated by some examples discussed in this short review. The high reactivity of the carbene center should, however, still represent a major drawback of NHCs, as it may result in facile degradation through reactions with other ligands within the coordination sphere of the metals. Some of the examples include the migratory insertion of NHCs into metal-carbon bonds,[37] while others describe the insertion of nitride, alkyl, aryl, and alkynyl groups,[38,39] which is in some cases followed by the ring-opening of the NHC, or by the removal of N-bound substituents. From this perspective, transition metal-NHC complexes with a more robust ligand set would be preferable, even though the $(CAAC)_2Fe$ complex already represents a successful example for the catalytic reduction of N_2. One possibility to generate such ligand sets with increased robustness would be the use of relatively rigid, multi-dentate ligand scaffolds incorporating NHC moieties, e.g. pincer-type ^{R}C-N-C and P-C-P ligands. Another possibility is the use of the so-called scorpionate ligands, e.g. tris(carbene)borate and tris(carbene)amine ligands; these have been successfully applied to the isolation of Fe-nitride complexes,[40,41,42] which are relevant to intermediates in the N_2 fixation mediated by a single Fe center. In contrast to the expanding scope of NHC-based ligand sets, the variety of transition metals employed in NHC-supported N_2 complexes is still limited to elements from groups 8 and 9 and Mo. This should allow synthetic chemists to explore new avenues to activate N_2 with NHC complexes of transition metals, which have not yet been investigated in this context.

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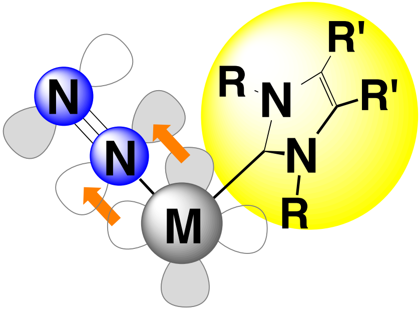

This review provides a short overview of the emerging field of NHC-supported transition metal complexes of N_2.

Author Profiles

Yasuhiro Ohki received a master's degree (1997) and a PhD (2002) from Tokyo Institute of Technology under the guidance of Prof. Hiroharu Suzuki. After working for one year at TOTO Co. Ltd., he rejoined the Suzuki group as a researcher assigned to a CREST project. In 2000, he was appointed Assistant Professor in the group of Prof. Kazuyuki Tatsumi at Nagoya University, where he was promoted to Associate Professor in 2008. In 2006, he spent a research sabbatical at the University of British Columbia, where he worked with Prof. Michael D. Fryzuk. He has been the recipient of the Japan Society of Coordination Chemistry Award for Young Chemists (2004), the Chemical Society of Japan Award for Young Chemists (2009), and the Young Scientists' Prize (Minister Award; 2009). His research interests include bioinorganic chemistry and organometallic chemistry with an emphasis on inorganic synthesis.

Hidetake Seino received his doctorate in 1997 from the University of Tokyo, where he studied the synthesis of organonitrogen compounds by using transition metal–dinitrogen complexes under the supervision of Professor M. Hidai. Subsequently, he joined the group of Professor Y. Mizobe at the Institute of Industrial Science (University of Tokyo), in order to investigate the chemistry of metal–sulfide clusters and the conversion of small molecules by using transition metal complexes. In 2013, he moved to Akita University, where he presently serves as an Associate Professor. His current research interests focus on the development of new catalytic systems that model mechanisms of metalloenzymes.

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