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Journal of Organometallic Chemistry 617–618 (2001) 65–69

Journal of Organometallic Chemistry

Mini Review

Coordination chemistry of CNH_2, the simplest aminocarbyne

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Received 17 July 2000; accepted 12 September 2000

Abstract

The coordination chemistry of the simplest aminocarbyne group, CNH_2, best described as a carbene (iminomethylenium or 2-azavinylidene), is presented, comprising the syntheses of its complexes, its electronic and structural features, and the chemical and electrochemical reactivity involving in particular deprotonation reactions (which are highly promoted by oxidation) with formation of CNH (hydrogen isocyanide) and CN (cyanide) complexes. The interconversion of the CNH_x ($x = 0$, 1 or 2) species is also analysed.

Keywords: Aminocarbyne; Carbene; Isocyanide; Cyanide; Electrochemistry; Protonation

1. Introduction

Within the well established chemistry of complexes with multiple metal–carbon bonds [1], that of aminocarbyne-type species, CNRR′ (R, R′ = alkyl, aryl or H), constitutes a less explored area than those of the much more common CR (R = alkyl or aryl) (carbyne) or CR_2 (carbene) complexes. In particular the primary and simplest aminocarbyne CNH_2 is still an extremely rare ligand, although the secondary and tertiary species, CNHR [2–5] and CNR_2 [6,7], respectively, are much more represented and in spite of the expected significance of CNH_2 in some natural processes. In fact, CNH_2 can be proposed as a conceivable intermediate in the known [8] biological reduction of aqueous cyanide (to metylamine, methane and ammonia) by nitrogenase, is believed [9] to exist in the interstellar space and to be a precursor therein for the synthesis of CNH and NCH, and the gas phase ion chemistry of such species has already received some attention. Moreover, there is a recent growth of interest [10] in the development of organometallic chemistry based on the related CN and CNH groups which, as shown below, can interconvert into CNH_2.

In this account, we describe the coordination chemistry of the aminocarbyne CNH_2 ligand, including the syntheses of its complexes, the structural and electronic features (which indicate that it can be viewed better as a carbene-type species $\bar{M}=C=\overset{+}{N}\!\!\swarrow$ rather than the carbyne one $M\equiv C\text{-}\dot{N}\!\!\swarrow$) and its reactivity, both chemical and electrochemical.

2. Syntheses and structural properties

A convenient starting material for the syntheses of the CNH_2 species has been shown [11,12] to be trimethylsilylisocyanide ($C\equiv NSiMe_3$) bound to an electron-rich metal centre (Scheme 1). It was obtained from an organosilane, trimethylsilyl cyanide, $N\equiv CSiMe_3$, which normally contains a smaller amount (ca. 5%) of the isocyanide isomer. Upon its reaction with the rhenium-dinitrogen complex *trans*-$[ReCl(N_2)(dppe)_2]$ (dppe=$Ph_2PCH_2CH_2PPh_2$) in THF, the isocyanide complex *trans*-$[ReCl(CNSiMe_3)(dppe)_2]$ (**1**) is formed (Eq. (1), Scheme 1). The preference of the $\{ReCl(dppe)_2\}$ centre to bind the isocyanide rather than the nitrile isomer, in spite of the predominance of the latter, is consistent with the stronger π-electron acceptor character of isocyanides relative to nitriles resulting in a more effective stabilization of the electron-rich Re(I) binding site.

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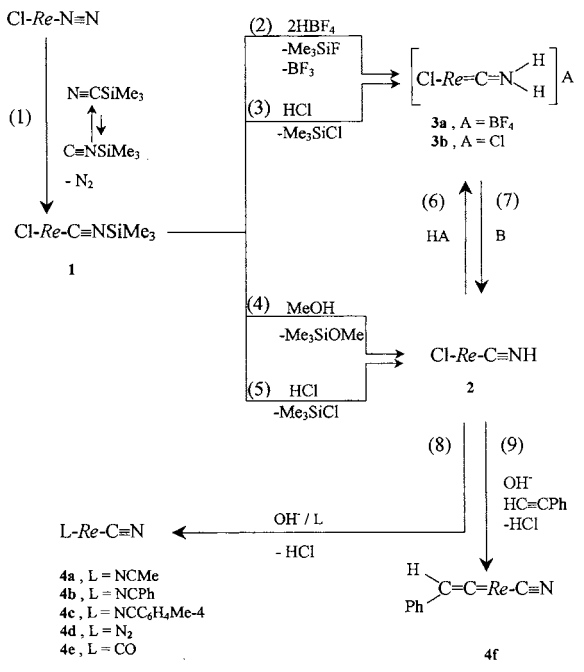
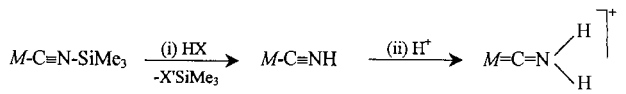
0022-328X/01/$ - see front matter
PII: S0022-328X(00)00641-0

The ligated $CNSiMe_3$ in complex **1** undergoes desilylation by HBF_4, HCl or MeOH to form the aminocarbyne *trans*-[ReCl(CNH$_2$)(dppe)$_2$]A (A = BF_4 **3a** or Cl **3b**) (treatment with an excess of acid) (Eqs. (2) and (3), Scheme 1) or the isocyanide complex *trans*-[ReCl(CNH)(dppe)$_2$] (**2**) (use of MeOH or a stoichiometric amount of HCl) (Eqs. (4) and (5), Scheme 1) [11,12]. These reactions are in accord with the high tendency of silicon to form stable Si–F, Si–Cl or Si–O bonds, and the other possible products comprise Me_3SiF (Eq. (2)), Me_3SiCl (Eqs. (3) and (5)) and Me_3SiOMe (Eq. (4)).

The formation of the CNH and CNH_2 complexes (**2** and **3)** involves protonation of the conceivable cyano-intermediate generated in situ by desilylation of the $CNSiMe_3$ ligand. Single protonation by MeOH or by a stoichiometric amount of acid (HCl) forms the CNH complex which undergoes further protonation in the presence of an excess of acid to yield the aminocarbyne CNH_2 product. In fact, the related iron(II) cyano-complex *trans*-[FeH(CN)(dppe)$_2$] is known [13,14] to give the corresponding isocyano-compound *trans*-[FeH(CNH)(dppe)$_2$][BF_4] on protonation by HBF_4, and the analogous rhenium(I) isocyanide compound *trans*-[ReCl(CNH)(dppe)$_2$] undergoes protonation (by HBF_4 or HCl) [11,12] to give the aminocarbyne complex *trans*-[ReCl(CNH$_2$)(dppe)$_2$]$^+$ (Eq. (6), Scheme 1), although CNH in the Fe(II) complex is no further protonated.



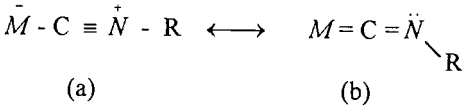
Scheme 1. *Re* = *trans*-{Re(dppe)$_2$}; (6) HA = HBF_4 or HCl; (7) B = NEt_3 or [NBu_4]OH; (8), (9) OH^- = [NBu_4]OH [11,12,25].



Scheme 2. *M* = *trans*-{ReCl(dppe)$_2$}; X = BF_4, Cl or MeO; X′ = F, Cl or MeO [11,12].

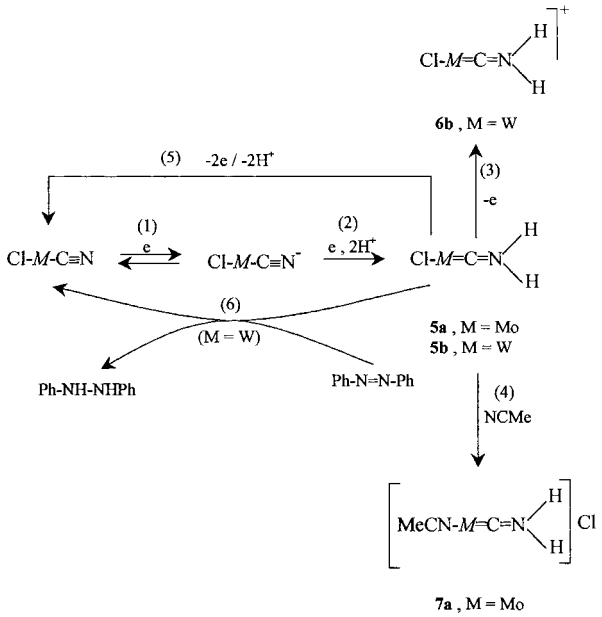
The formation of the aminocarbyne ligand at the rhenium site thus follows the overall Scheme 2 in which the desilylation step (i) is assisted by the propensity of Si to halogenation or alcoxidation, and the protonation step (ii) is promoted by the activation of the derived isocyanide (by a suitable metal binding site) towards protonation.

The susceptibility of CNH to protonation at the {ReCl(dppe)$_2$} centre is in agreement with the known [3] fast protic attack, e.g. by HBF_4, at the alkyl isocyanide complexes *trans*-[ReCl(CNR)(dppe)$_2$] (R = Me or Bu^t) to give the corresponding aminocarbyne products *trans*-[ReCl(CNHR)(dppe)$_2$][BF_4]. This can be accounted for by the extensive π-electron release from the electron-rich metal site to the isocyanide ligand [π* (C≡N) orbital], which results in a strengthening of the metal–carbon bond with a concomitant weakening of the unsaturated C–N bond and a localization of electronic charge at the N atom (rationalizations by extended Hückel calculations [15] and by some simplified π-MO schemes [16] have also been presented). Therefore, the isocyanide would display some carbene character as shown by a significant weight of the canonical form (b) in the VB representation:



Although the bending at the isocyanide N atom could not be confirmed by the X-ray structural analysis of *trans*-[ReCl(CNH)(dppe)$_2$] (**2**) (the hydrogen atom of CNH was not located), this analysis revealed a short Re–C bond length, 2.007(38) Å [11], which is shorter than the expected Re–C single bond length, 2.13 Å, being comparable with those found in the related alkyl isocyanide complexes *trans*-[ReCl(CNR)(dppe)$_2$], 1.950(22) and 1.833(23) Å (R = $SiMe_3$) [11], 1.861(12) Å (R = Me) [17] or 1.926(9) Å (R = Bu^t) [18]. Moreover, the methyl isocyanide ligand is extensively bent in *trans*-[ReX(CNMe)(dppe)$_2$] [C–N–C angle of 139.4(10)° (X = Cl) or 147.7(7)° (R = H)] [17], although the bending is hampered by steric hindrances in the isocyanides with bulky substituents, CNBu^t and $CNSiMe_3$.

The CNH_2 ligand is roughly planar with a dominant weighting of the canonical form (c) in the VB representation, as indicated by the X-ray diffraction analysis of *trans*-[ReCl(CNH$_2$)(dppe)$_2$][BF_4] (**3a**) [12] which shows that the C–N and the Re–C bond lengths, 1.309(5) and 1.802(4) Å, respectively, although much longer and shorter than the corresponding ones, 1.157(43) and 2.007(38) Å [11], for the isocyanide complex *trans*-[ReCl(CNH)(dppe)$_2$], are still shorter and longer, corre-



Scheme 3. $M = trans$-{M(dppe)$_2$} (M = Mo or W) [23,24].

spondingly, than those expected for a single C–N and a triple Re≡C bond (e.g. the latter one in the 1.72–1.75 Å range [3]). Accordingly, in the IR spectrum of **3a** or **3b**, ν(CN) is observed in the C=N double bond region, as a medium intensity band at 1585 cm^{-1} (KBr pellet) [11].

(c) (d)

Hence, the aminocarbyne ligand is best represented as a carbene-type (2-azavinylidene or iminomethylenium) species, with delocalized nitrogen lone pair electrons, conferring a positive charge at the ligand. It behaves as an effective π-electron acceptor, much stronger than isocyanides, as indicated (i) by the structural rearrangements of the complex resulting from the protonation, i.e. besides the above mentioned Re–C shortering and C–N elongation, also the lowering of the Re–Cl distance and the stretching of the Re–P bond lengths, and (ii) by the much higher oxidation potential ($E^{OX}_{p/2} = 0.90$ V vs. SCE) of the aminocarbyne complex **3** relatively to that ($E^{OX}_{1/2} = 0.45$ V vs. SCE) of the isocyanide compound **2** [11,19,20]. The CNH_2 ligand is even a stronger π-electron acceptor than CO as shown by the estimated value of the electrochemical P_L ligand parameter, P_L (CNH_2) = 0.09 V [20], which is higher than that ($P_L = 0$ V) of CO (an increase of P_L corresponds [21] to an increase of the net π-electron acceptance minus σ-donor character of the ligand). However, the aminocarbyne is not such a stronger π-electron acceptor as the carbynes ≡C–CH_2R (P_L ca. 0.27 V [22]).

These structural and electronic features of CNH_2 are comparable to those displayed by organoaminocarbynes (CNHR or CNH_2), namely in the related complexes *trans*-[ReCl(CNHR)(dppe)$_2$][BF_4] (R = Me or Bu^t) [3] obtained by protonation of the corresponding organoisocyanide compounds.

An electrochemical approach to the generation of the CNH_2 ligand has also been achieved by cathodically induced protonation of a cyanide ligand. Hence, *trans*-[MCl(CNH_2)(dppe)$_2$] (M = Mo (**5a**) [23] or W (**5b**) [24]) were electrosynthesized by cathodic reduction of the corresponding cyano-complexes *trans*-[MCl(CN)-(dppe)$_2$] in the presence of phenol, according to an overall 2e/2H$^+$ process (reactions 1 and 2, Scheme 3). The reduction of the cyano-complexes activates the coordinated cyanide towards protonation to give the aminocarbyne product conceivably via an isocyanide (CNH) intermediate. Single-electron oxidation (chemical or electrochemical) of the W complex *trans*-[WCl(CNH_2)(dppe)$_2$] (**5b**) yields the paramagnetic cationic species *trans*-[WCl(CNH_2)(dppe)$_2$]$^+$ (**6b**) (reaction 3, Scheme 3) and, as shown by X-rays [24], in both complexes the ligated CNH_2 exhibits a C–N bond length, 1.200(12) or 1.156(24) Å, that is shorter than that in *trans*-[ReCl(CNH_2)(dppe)$_2$][BF_4] (**3a**), 1.309(5) Å (see above) [12], suggesting an even greater contribution of the carbene (iminomethylenium) form (c) relative to the aminocarbyne (d). This is believed [23] to account for the labilising effect of CNH_2 on the Cl ligand in the *trans* position as a result of the localization of electron density at the metal in the canonical form (c), allowing the ready ionization of the molybdenum complex **5a** in NCMe to yield *trans*-[Mo(CNH_2)-(NCMe)(dppe)$_2$]Cl (**7a**) (reaction 4, Scheme 3).

3. Reactivity

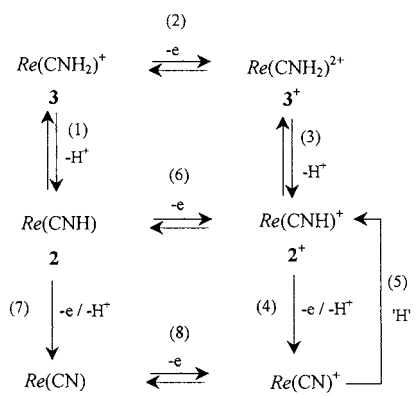
The CNH_2 ligand exhibits some acidic character and treatment of *trans*-[ReCl(CNH_2)(dppe)$_2$][BF_4] (**3a**) with NEt_3 or [NBu_4]OH (stoichiometric amount) gives the corresponding isocyanide complex *trans*-[ReCl(CNH)(dppe)$_2$] (**2**) (Eq. (7), Scheme 1) [11,12,25]. Moreover, a slight H$^+$ dissociation from CNH_2 to form the ligated isocyanide CNH was detected by cyclic voltammetry in a NCMe–[NBu_4][BF_4] solution of **3a** [19] (Eq. (1), Scheme 4). The acidity constant (6.3×10^{-9} mmol cm^{-3}) increases dramatically (by a factor over 10^9) on oxidation (Eq. (2), Scheme 4) of the complex, as estimated by an electrochemical study which also indicates that the rate constant of H$^+$ liberation from the ligated CNH_2 is enhanced, also on oxidation of the complex, by a factor over 10^2 [19].

Therefore, the single-electron oxidation of the CNH_2 complex **3a** induces (on both thermodynamic and ki-

netic grounds) H^+ releasing (Eq. (2) and (3), Scheme 4) to give the cationic isocyanide complex *trans*-[ReCl(CNH)(dppe)$_2$]$^+$ (**2**$^+$). The latter undergoes a similar anodically-induced deprotonation to yield the cyano-complex *trans*-[ReCl(CN)(dppe)$_2$]$^+$ (Eq. (4), Scheme 4), and the mechanisms of both redox processes were established [19] by digital simulation of cyclic voltammetry. This cyano-complex, upon hydrogen abstraction from the electrolytic medium (Eq. (5), Scheme 4), converts into the isocyanide species *trans*-[ReCl(CNH)(dppe)$_2$]$^+$ **2**$^+$ and both of them can alternatively be obtained by anodic oxidation of the neutral isocyanide complex *trans*-[ReCl(CNH)(dppe)$_2$] (**2**) (Eq. (6) to give **2**$^+$, or Eqs. (7) and (8) to form the cyano-product) [11,19].

The anodic deprotonation of the ligated CNH_2 was also recognized [23,24] in the Mo or W complexes *trans*-[MCl(CNH_2)(dppe)$_2$] (**5a**) or (**5b**) which, upon oxidation via an overall $-2e/-2H^+$ process (Eq. (5), Scheme 3), regenerate (in the presence of a base such as NEt_3 or PhO^- in the case of the W compound) the parent cyanide. A curious hydrogen-transfer reaction from the CNH_2 ligand was reported [24] for the tungsten aminocarbyne complex **5b** which converts azobenzene (Ph–N=N–Ph) into hydrazobenzene (PhNHNHPh) (reaction 6, Scheme 3).

The acidity of the ligated aminocarbyne and of the derived isocyanide (CNH) at the above rhenium centre has been explored towards the syntheses of a variety of derived cyano-complexes, in particular the nitrile, dinitrogen, carbonyl and vinylidene complexes *trans*-[Re(CN)L(dppe)$_2$] (L = NCMe (**4a**), NCPh (**4b**), NCC_6H_4Me-4 (**4c**), N_2 (**4d**), CO (**4e**) or C=CHPh (**4f**)) obtained via the CNH complex **2** on treatment with [NBu_4]OH in the presence of the appropriate substrate [reactions (7)–(9), Scheme 1] [25]. These reactions involve dehydrochlorination of the isocyanide complex, conceivably occuring via the anionic unstable intermediate [ReCl(CN)(dppe)$_2$]$^-$ with a labilized chloride ligand that is easily replaced by a π-electron-rich acceptor



Scheme 4. *Re* = *trans*-{ReCl(dppe)$_2$} [11,12,19,25].

(L) with ability to stabilize the electron-rich d^6 Re centre. In the reaction of **2** with phenylacetylene (PhC≡CH) (Eq. (9), Scheme 1) to give the vinylidene product **4f** [25], a 1,2-hydrogen migration also occurred, as observed [22] in reactions of 1-alkynes (RC≡CH) with *trans*-[ReCl(N_2)(dppe)$_2$] to yield *trans*-[ReCl(=C=CHR)(dppe)$_2$]. The H-migration can be rationalized [22,26,27] by considering the destabilizing interaction between the filled $\pi_\perp$ orbital of a ligated alkyne (in the intermediate complex) and a filled metal d_π orbital of the electron-rich Re d^6 site, which promotes the conversion of the alkyne into a derived ligand (vinylidene) without this destabilizing interaction.

4. Final comments

Both chemical and electrochemical methods have already been devised to the synthesis of the simplest aminocarbyne (CNH_2) ligand at electron-rich metal centres, such as {M(dppe)$_2$} (M = Mo^0, W^0 or Re^I), based on the generation of ligated hydrogen isocyanide (CNH) or cyanide (CN^-) which, on activation by such metal sites towards β-protonation, convert into CNH_2. However, methods for the preparation of CNH_2 complexes with less electron-rich metal centres are yet to be reported.

The structural and electronic features of the CNH_2 ligand have been elucidated by a variety of techniques (in particular X-ray diffraction, spectroscopic and electrochemical ones) indicating that it exhibits a cationic iminocarbene character represented by the iminomethylenium (or 2-azavinylidene) form $\bar{M}\text{=}C\text{=}\overset{+}{N}H_2$, and behaves as a very strong π-electron acceptor.

The chemical property that has been most explored is its acidity which has been applied to the generation of various CNH and CN complexes, following either a stepwise deprotonation by base (chemical route) to yield lower oxidation state metal complexes or the anodically induced stepwise deprotonation that is drastically enhanced by oxidation of the complex (electrochemical route) leading to higher metal oxidation state compounds.

The redox induced interconversion of the CNH_x ($x = 2$, 1 or 0) species involves an increase of the acidity, promoted by oxidation, of the more protonated forms with resulting conversion into the less protonated ones, and, conversely, the generation of the former from the latter as a result of reduction of the oxidized forms which thus become activated, towards protonation, by the reduced electron-rich binding metal centres. Such CNH_x species represent conceivable sequencial stages in the reduction of cyanide by nitrogenase, but the conversion of CNH_2 into the final enzymatic products has not yet been achieved.

The possibility of CNH_2 to act also as a 2H-atom transfer reagent to a suitable unsaturated substrate was demonstrated, but the generality of this type of reaction (observed in a single case) has not yet been established.

Therefore, the coordination chemistry of the aminocarbyne CNH_2 group appears to be a promising and emerging topic of research which deserves further exploration.

Acknowledgements

Our work has been partially supported by the Foundation for Science and Technology (FCT) and the PRAXIS Programme (Portugal) and, formerly, by the Junta Nacional de Investigação Científica e Tecnológica (JNICT). The authors also gratefully acknowledge Professor R.L. Richards (University Sussex) and Dr C.J. Pickett (John Innes Centre, Norwich) for high valuable discussions and cooperation in the early stages of the chemical work, Dr M.A.N.D.A. Lemos (Centro de Química Estrutural) for cooperation in electrochemical studies, and Professor J.J.R. Fraústo da Silva (Centro de Química Estrutural) for general support and facilities.

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