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Preliminary communication

Synthesis of transition-metal Lewis acid adducts of *trans*-[ReCl(CNR)($Ph_2PCH_2CH_2PPh_2$)$_2$] (R = alkyl). A chemical and a quantum-chemical study of electrophilic β-addition to ligating isocyanide

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Abstract

Treatment of *trans*-[ReCl(CNR)(dppe)$_2$] (R = Me or Bu^t, dppe = $Ph_2PCH_2CH_2PPh_2$) with $CoCl_2(THF)_{1.5}$, [$ReOCl_3(PPh_3)_2$] or [WCl_4L_2] (L = PPh_3 or $PEtPh_2$) affords the dinuclear adducts [ReCl(CN(M)R)(dppe)$_2$] (M = $CoCl_2$(THF), $ReOCl_3(PPh_3)$ or WCl_4L, respectively) (formed via electrophilic β-addition of the electron-acceptor molecules to the isocyanide ligands), which undergo dissociation upon anodic oxidation (for M = $CoCl_2$(THF) or $ReOCl_3(PPh_3)$). These reactions are considered in the light of results of extended Hückel calculations.

Electrophilic β-addition to an unsaturated C-bonded ligand, such as an isocyanide or an alkyne-derived species, provides an increasingly important route to compounds with metal–carbon multiple bonds [1]. However, relevant theoretical studies have been performed in only a few cases [2,3], in spite of the success of the application of MO calculations to the understanding of the reactions of metal–carbon multiple bonds [4], particularly towards nucleophilic additions. We now report a development of the electrophilic β-addition reaction and extended Hückel calculations on electron-rich isocyanide complexes that are known to behave as suitable precursors for aminocarbyne-type species.

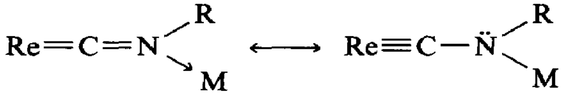
When bonding to an electron-rich transition metal centre with a high π-electron releasing ability, such as in species of the type {ReCl(dppe)$_2$} (dppe = $Ph_2PCH_2CH_2PPh_2$) [5] or {M(dppe)$_2$} (M = Mo or W) [6], isocyanides behave as strong π-acceptors and the resulting complexes have low IR ν(CN) values, and short metal–carbon distances [7,8] corresponding to considerable double bond character. Bending at N of the isocyanide ligand may also occur [8]. Moreover, in the complexes the isocyanides are activated towards electrophilic attack by H^+ [9,10], a carbocation (Me^+ or Et^+) [11], or Al_2Et_6 [10], and such attack has been shown to occur at the β-position (N atom) to give the aminocarbyne-type species CNHR, CNMeR, CNEtR or $CN(AlEt_3)R$.

Thus, e.g., *trans*-$[ReCl(CNR)(dppe)_2]$ (**1**, R = H, alkyl or aryl) react with protic acid to give, in high yields, *trans*-$[ReCl(CNHR)(dppe)_2]^+$ (**2**) [9]. The molecular structures of **1** (R = Bu^t) [7] and **2** (R = H [12] or Me [9]) have been determined by X-ray diffraction studies, and show that protonation results in a shortening of the Re–C bond and an elongation of the unsaturated C–N bond; the aminocarbyne ligand can be represented as a hybrid of the two valence bond forms $\overset{+}{M}{\equiv}C{-}\ddot{N}HR \leftrightarrow M{=}C{=}\overset{+}{N}HR$. No protonation at any atom other then the isocyanide nitrogen was observed.

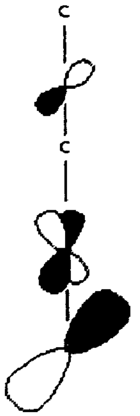
We have examined the behaviour of a different type of electrophile, viz. transition metal Lewis acids towards ligating isocyanides in *trans*-$[ReCl(CNR)(dppe)_2]$ (**1**, R = Me or Bu^t). Furthermore, we have investigated by extended Hückel calculations the site of electrophilic attack and the resulting electronic changes at the complexes.

Compounds **1**, in THF, react with a stoichiometric amount of an electron-acceptor transition metal species such as $CoCl_2(THF)_{1.5}$, $[ReOCl_3(PPh_3)_2]$ or $[WCl_4L_2]$ (L = PPh_3 or $PEtPh_2$), to give dinuclear adducts of the type $[ReCl\{CN(M)R\}(dppe)_2]$ (**3**, M = $CoCl_2(THF)$, $ReOCl_3(PPh_3)$ or WCl_4L, respectively). Related reactions have been reported [13] for the dinitrogen complex *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$, which undergoes addition of the electron-acceptor centre to the terminal nitrogen atom of the ligating dinitrogen to give dinuclear adducts with a bridging N_2, $Re{-}N{\equiv}N \rightarrow M$.

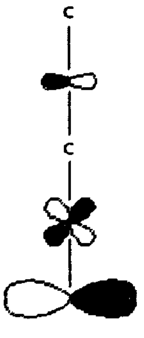
Complexes **3** were isolated as green (M = $CoCl_2(THF)$), yellow (M = $ReOCl_3(PPh_3)$) or greenish-yellow (M = WCl_4L) solids. Their IR spectra exhibit strong bands in the 1600–1550 cm^{-1} range; this is well below the range observed for ν(CN) in the parent isocyanide compounds **1** (ca. 1800 or 1920 cm^{-1}, for R = Me or Bu^t, respectively), but is similar to that quoted for the related aminocarbyne compounds **2**, and by analogy with the latter those bands are assigned to ν(C=N) of the novel aminocarbyne-type ligands CN(M)R represented by the following valence bond forms:



Complexes **3** dissociate with liberation of the Lewis acid as a result of an overall two-electron irreversible anodic oxidation (at ca. 1.0 V vs. SCE), at a Pt electrode, in 0.2 *M* $[Bu_4N][BF_4]$/THF, by cyclic voltammetry, in the cases where the Lewis acid is harder to oxidize than **3** (M = $CoCl_2(THF)$ or $ReOCl_3(PPh_3)$). This is consistent (see below) with the expected decrease of basicity of the nitrogen atom upon the oxidation of the Re centre. Moreover, the adducts **3** are much harder to oxidize than the parent isocyanide complexes **1** [5], in accord with a stronger net electron acceptor character of the aminocarbyne relative to the isocyanide ligand [14].



(1)

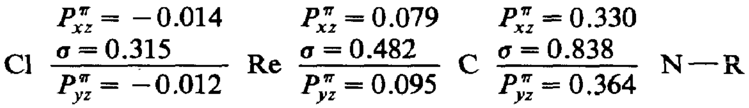


(2)

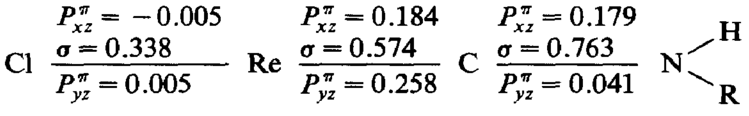
The electronic factors governing the electrophilic addition to the isocyanide Re complexes **1**, were investigated by means of extended Hückel calculations [15,16]. The most relevant MO's, responsible for the nucleophilic behaviour of the complexes are the HOMO, **1**, and NHOMO, **2**. All other occupied MO's are energetically far below from these two MO's and therefore have no chemical significance.

It is clear that both these MO's (separated by only 0.03 eV) are mostly delocalized over the Cl–Re–C–N nuclear framework, their corresponding charge-partitioning being 72, 16, 0 and 5%, respectively. Moreover, based upon the frontier electron density values [17] ($P_r^{(HO)}$ and $P_r^{(NHO)}$ indices) and net atomic charges, q, of the most relevant atoms, the electrophilic attack should preferentially occur at the Cl($P^{(HO)} \simeq P^{(NHO)} \simeq 0.81$; $q = -0.31$) and/or N ($P^{(HO)} \simeq P^{(NHO)} \simeq 0.04$; $q = -0.11$) atoms, and not at the metal, the latter possessing a positive charge ($P^{(HO)} \simeq P^{(NHO)} \simeq 0.13$; $q = +0.06$). However, although the P_r values of these atoms do not vary significantly upon bending of the CNR moiety, the net charge on the N atom increases ($q = -0.33$), becoming larger than that of the Cl atom ($q = -0.30$) at a CNBu^t bending angle of 120°. Therefore, these two nucleophilic centers of the complex might compete each other for the acceptance of the electrophile. However, the experimental observation of electrophilic attack at the N atom (β-electrophilic addition) strongly suggests that the interactions between the two reactants must be predominantly charge- rather than frontier-controlled. Thus, the electrophile must be orientated towards the atom possessing the higher negative charge (nitrogen) and certainly far away from the positively-charged metal atom. Furthermore, although the Cl atom still has the higher P_r values, electrophilic attack there was excluded on the basis of electronic criteria by performing calculations on the two isoelectronic *trans*-$[ReCl(CNHBu^t)(dppe)_2]^+$ and *trans*-$[Re(ClH)(CNBu^t)(dppe)_2]^+$ complexes; it was found that the former is energy-favored by about 246 kcal mol^{-1} over the latter (H–Cl = H–N = 0.96 Å).

Conclusion about the natures of the isocyanide and the derived aminocarbyne bonding modes could be drawn through comparison of the σ- and π-overlap populations of the axial bonds of the corresponding complexes, schematically depicted as in **3** and **4**. Thus, the protonation of the isocyanide complex results in a significant strengthening of the two π-type Re–$C_{lig.}$ bonds, followed by a concomitant weakening of the two π-type $C_{lig.}$–N ones. The σ-population value of the former bond increases, whereas that for of the latter decreases. These results are in



(3)



(4)

agreement with the abovementioned IR and X-ray data.

Moreover, the lowering of the eigenvalues of the HOMO and NHOMO's, and the increase of the effective charge of the Re atom resulting from electrophilic attack on the isocyanide ligand account well for the harder oxidation of the aminocarbyne complex. Furthermore, any two-electron oxidation of the latter compound results in the appearance of a positive charge (+0.14) on the nitrogen atom, and this could be responsible for the observed experimentally dissociation of the complex (see above). Finally, in view of the positive net charge on the nitrogen atom of the oxidized dissociation product, the irreversibility of this reaction can be understood.

Acknowledgement

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16 Calculations were performed on the well characterized *trans*-[ReCl(CNBu^t)(dppe)$_2$] and *trans*-[ReCl(CNHMe)(dppe)$_2$]$^+$ complexes. (see refs. 7 and 9, respectively). For the sake of simplicity, as well as to avoid the use of very large basis sets, all phenyl groups of the dppe ligands and the Me groups of the Bu^t moiety were replaced by hydrogen atoms (P–H and C–H bond lengths 1.42 and 1.08 Å, respectively). In all calculations a right-hand Cartesian coordinate system was used, with the z axis pointing towards the ligating carbon atom. This facilitates examination of the axial coordination bonds, puts the two dppe ligands of the metal into the xy plane and the metal at the origin. The parameters were from: A. Dedieu, T.A. Albright and R. Hoffmann, J. Am. Chem. Soc., 101 (1979) 3141, and E.G. Bakalbassis, G.A. Katsoulos and C.A. Tsipis, Inorg. Chem., 26 (1987) 3151.

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