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CHEMICAL REDUCTION OF SOME MONOSUBSTITUTED DERIVATIVES OF (1–3-η-ALLYL)DICARBONYLNITROSYLIRON

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Summary

The chemical reduction of the complexes $[(1\text{–}3\text{-}\eta\text{-}C_3H_5)Fe(CO)(NO)L]$ ($L = PPh_3$, $P(OPh)_3$, $P(OMe)_3$, $P(OEt)_3$, $PEtPh_2$, $P(OCH_2)_3CEt$, $P(OCH_2)_3CMe$) and $[(1\text{–}3\text{-}\eta\text{-}C_3H_4X)Fe(CO)(NO)L]$ ($X = 2\text{-Me}$, 2-Cl; $L = PPh_3$) with $NaBH_4$ has been investigated. The reaction products are $[Fe(NO)_2L_2]$ and the salts $[Fe(CO)_2(NO)L]^- Na^+$ and $[Fe(CO)(NO)L_2]^- Na^+$. A reaction mechanism is proposed.

Introduction

The electrochemical or chemical reduction of some η^3-allylcarbonyl complexes with $NaBH_4$ in acetonitrile gives propene and anionic complexes [1]. The reaction products correspond with a reducing attachment to the allyl ligands; this behaviour is also observed with η^3-allyl complexes containing easily reduced ligands, such as nitrosyl [2,3]. These results are in agreement with increase in the electrophilic character of the allyl ligand upon the coordination to metals [4].

The results of the reduction of the allylic complexes of cobalt and iron $[(1\text{–}3\text{-}\eta\text{-}C_3H_5)Co(CO)_3]$ [1], $[(1\text{–}3\text{-}\eta\text{-}C_3H_5)Co(CO)_2L]$ [1] and $[(1\text{–}3\text{-}\eta\text{-}C_3H_4X)Fe(CO)_2NO]$ [2] indicate that the reaction mechanism and the end products are very sensitive to the electronic structure of the complexes; a slight variation in the nature of the ligands suffices to direct the reaction to a completely different path.

To provide further information on the influence of the electronic structure on the reaction, the reduction of the monosubstituted complexes $[(1\text{–}3\text{-}\eta\text{-}C_3H_5)Fe(CO)(NO)L]$ ($L = PPh_3$, $P(OPh)_3$, $P(OMe)_3$, $P(OEt)_3$, $PEtPh_2$, $P(OCH_2)_3CEt$, $P(OCH_2)_3CMe$) and $[(1\text{–}3\text{-}\eta\text{-}C_3H_4X)Fe(CO)(NO)L]$ ($L = PPh_3$; $X = 2Me$, $2Cl$) has been studied.

Experimental

All the reductions were carried out in acetonitrile purified as described in ref. 5 and carefully deareated. The IR spectra were recorded on a 257 Perkin–Elmer

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spectrophotometer. The mulls of the salts in Nujol and Fluorolube were prepared in a dry-box under argon to avoid decomposition. The complexes $[(\sigma\text{-}CH_2CH{=}CH_2)Fe(CO)_2(NO)PPh_3]$ and $[(1\text{–}3\text{-}\eta\text{-}C_3H_4X)Fe(CO)(NO)L]$ were prepared by the method described in ref. 6.

Reduction of $[(\sigma\text{-}CH_2CH{=}CH_2)Fe(CO)_2(NO)PPh_3]$. A solution of 0.5 g of $[(\sigma\text{-}CH_2CH{=}CH_2)Fe(CO)_2(NO)PPh_3]$, in acetonitrile ($c$ 5×10^{-2} M) was treated with an excess of $NaBH_4$ for 5 h at room temperature. The IR analysis of the gas phase showed the presence of propene. The solution was evaporated to dryness, and the residue was dissolved in the smallest possible volume of diethyl ether. The solution was kept at −15°C and gave yellow crystals of $[Fe(CO)_2NOPPh_3]^- Na^+$ (yield: 60%). Analysis: found: C, 55.8; H, 3.7; N, 3.1. $C_{20}H_{15}NNaO_3P$ calcd.: C, 56.24; M, 3.54; N, 3.28%. The CO and NO IR frequencies are given in Table 1 and agreed with those of an authentic sample prepared as described in the literature [7,8].

Reduction of $[(1\text{–}3\text{-}\eta\text{-}C_3H_4X)Fe(CO)(NO)L]$ *(*$L = PPh_3$*,* $X = H$*, Me;* $L = PPh_2Et$*,* $X = H$*).* These complexes reacted very slowly (~ 15 days) with $NaBH_4$ at room temperature in acetonitrile. The reaction was slower for X = Me. The products were mainly the salts $[Fe(CO)_2NOL]^- Na^+$ (yield ~ 30%) and the propene derivatives C_3H_4X. The formation of $[Fe(NO)_2L_2]$ (yield 5–10%) was also observed. The products were separated and identified as follows. The solution of products was evaporated to dryness and the residual solid was extracted with benzene. The benzene solution, which contained $[Fe(NO)_2L_2]$, was worked up as described in the literature [9] to give $[Fe(NO)_2L_2]$, which was identified by comparison with an authentic sample. The residue from the benzene extraction was dissolved with the smallest volume of diethyl ether, and crystallisation at −15°C gave yellow crystals of $[Fe(CO)_2NOL]^- Na^+$, which were identified by analysis: $[Fe(CO)_2NOPPh_2Et]^- Na^+$: found: C, 51.1; H, 4.03; N, 3.41. $C_{16}H_{15}FeNNaO_3P$ calcd.: C, 50.69; H, 3.99; N, 3.72%.

The molar ratio $[Fe(CO)_2NOL]^-/[Fe(NO)_2L_2]$ did not change on varying the concentration of the free ligand L in the range 5×10^{-1}–5×10^{-2} M.

Reduction of $[(1\text{–}3\text{-}\eta\text{-}2\text{-}Cl\text{-}C_3H_4)Fe(CO)(NO)PPh_3]$. This complex was reduced with $NaBH_4$ in acetonitrile at room temperature for 10 days. The products were $[Fe(NO)_2L_2]$ (yield 30–35%) and $[Fe(CO)_2(NO)PPh_3]^- Na^+$ (yield 5%); the separa-

TABLE 1

CO AND NO IR STRETCHING FREQUENCIES IN CH_3CN

Complex	ν(CO) (cm^{-1})	ν(NO) (cm^{-1})
$[Fe(CO)_2(NO)PPh_3]^- Na^+$	1894, 1822	1639
$[Fe(CO)_2(NO)PPh_2Et]^- Na^+$	1892, 1823	1630
$[Fe(CO)(NO)(P(OCH_2)_3CEt)_2]^- Na^+$	1859	1590
$[Fe(CO)(NO)(P(OEt)_3)_2]^- Na^+$	1836	1580
$[Fe(CO)(NO)(P(OPh)_3)_2]^- Na^+$	1849	1585
$[Fe(CO)(NO)(P(OMe)_3)_2]^- Na^+$	1831	1576
$[Fe(CO)(NO)(P(OCH_2)_3CMe)_2]^- Na^+$	1852	1592
$[Fe(NO)_2(P(OEt)_3)_2]$		1735, 1683
$[Fe(NO)_2(PPh_3)_2]$		1715, 1672
$[Fe(NO)_2(PPh_2Et)_2]$		1705, 1665

tion and identification of the products were as described in the previous experiment.

Reduction of $[(1\text{-}3\text{-}\eta\text{-}C_3H_4X)Fe(CO)(NO)L]$ *(X = H, L =* $P(OCH_2)_3CEt$, $P(OCH_2)_3CMe$, $P(OEt)_3$, $P(OPh)_3$; *X = 2Cl, L =* $P(OMe)_3$, $P(OEt)_3$*).* The complexes $[(1\text{-}3\text{-}\eta\text{-}C_3H_5)Fe(CO)(NO)L]$ (L = $P(OCH_2)_3CEt$, $P(OCH_2)_3CMe$, $P(OPh)_3$) were reduced with a saturated solution of $NaBH_4$ in acetonitrile at room temperature during 4–5 days. The red solutions obtained were cooled to 0°C and the precipitated $NaBH_4$ was filtered off. The solution was dried and the solid residue crystallized from diethyl ether. Yellow crystals (yield 30%) were obtained by cooling on −20°C. They analysed as disubstituted $[Fe(CO)(NO)L_2]^- Na^+$ salts. $[Fe(CO)(NO)\text{-}(P(OCH_2)_3CMe)_2]^- Na^+$: found: C, 31.0; H, 4.2; N, 3.1. $C_{11}H_{18}FeNNaO_8P_2$ calcd.: C, 30.51; H, 4.19; N, 3.23%. $[Fe(CO)(NO)\text{-}(P(OCH_2)_3CEt)_2]^- Na^+$: found; C, 34.2; H, 5.1; N, 2.9. $C_{13}H_{22}FeNNaO_8P_2$ calcd.: C, 33.86; H, 4.81; N, 3.04%. $[Fe(CO)(NO)(P(OPh)_3)_2]^- Na^+$: found; C, 59.00; H, 4.2; N, 1.8. $C_{37}H_{30}FeNNaO_8P_2$ calcd.: C, 58.67; H, 3.99; N, 1.85%.

The other phosphite allyl complexes also gave $[Fe(CO)(NO)L_2]^- Na^+$ salts, but they could not be purified. They were identified by their IR spectra. With X = 2Cl the formation of small quantities of $[Fe(NO)_2L_2]$ was also observed [9].

Results and discussion

The reductive cleavage of the σ-allyl complex $[(\sigma\text{-}CH_2CH{=}CH_2)\text{-}Fe(CO)_2(NO)PPh_3]$ gives the salt $[Fe(CO)_2(NO)PPh_3]^- Na^+$ and propene. The salt was identified by comparison with a specimen prepared by reduction of the complex $[Hg(Fe(CO)_2(NO)PPh_3)_2]$ [10] with sodium amalgam as described in the literature [7]. The propene was identified in the gas phase by its IR spectrum.

The reductive cleavage can proceed via an H^- attachment to the iron promoted by the nitrosyl ligand, which can act as a mono- or tri-electron donor [11], to form the intermediate hydride, which gives the observed products by reductive coupling [12].

The reduction of the complexes $[(1\text{-}3\text{-}\sigma\text{-}C_3H_4X)Fe(CO)(NO)L]$ gives different products depending on the properties of X and L. Thus there is: (a) Predominant formation of the monosubstituted salts $[Fe(CO)_2(NO)L]^- Na^+$, small quantities of $[Fe(NO)_2L_2]$ and decomposition products, when X = H, Me and L = phosphine.

(b) Predominant formation of $[Fe(NO)_2L_2]$, small quantities of the salts $[Fe(CO)_2(NO)L]^- Na^+$, and decomposition products, when X = 2Cl and L = phosphine.

(c) Predominant formation of $[Fe(CO)(NO)L_2]^- Na^+$ and decomposition product when L = phosphite.

In none of the above reactions was a single product formed; several reaction products were present in each case but the relative amounts were different. This suggests that the reaction mechanism is the same in all cases and the different amounts of the products are due to different kinetic parameters of the various steps of the reaction.

The overall reaction rate depends on the rate of the initial attachment of $NaBH_4$ to the $[(1\text{-}3\text{-}\eta\text{-}C_3H_4X)Fe(CO)(NO)L]$ complexes. With X = CH_3, H and L = phosphine the rate is slower than with X = 2Cl and L = phosphite; this is due to the increase in the electronic density on the electrophilic reaction center (allyl ligand or iron atom) owing to the donor power of CH_3 and phosphine. The electron-withdrawing power of Cl and the π-acceptor effect of the phosphite ligands decrease the ease of reaction with the nucleophile [2].

On the basis of the results obtained in the study of the reaction of $[(1-3-\eta-C_3H_5)Fe(CO)_2NO]$ with stabilized carbanions [13] and with neutral strong Lewis bases [14] (trialkylphosphine), it seems that the reduction with $NaBH_4$ can proceed via a nucleophilic attachment of H^- to the allylic ligand of the complexes $[(1-3-\eta-C_3H_4X)Fe(CO)(NO)L]$, to give an olefinic anionic complex $[(\eta-CH_2{=}CXCH_3)Fe(CO)(NO)L]^-$. While this anionic intermediate is observed spectrophotometrically in the reaction of $[(1-3-\eta-C_3H_5)Fe(CO)_2NO]$ with $NaBH_4$ [2], it is not observed, with $[(1-3-\eta-C_3H_4X)Fe(CO)(NO)L]$ although the Fe–L bond should stabilize the η^2-olefinic bond [15]. This is probably due to the very slow rate of the first step of the reaction, which hinders the accumulation of the olefinic intermediate. The olefinic intermediates are very reactive, either via dissociation of the olefinic ligand or via hydrogen extraction by the iron atom [14,16].

The decomposition can give anionic unsaturated intermediates, which form dinuclear or polynuclear anionic carbonyl nitrosyl complexes. These species are common with Co [17], Ni [18] and in particular with Fe [19]. In these complexes the formation of CO [20] and NO [21] bridge bonds is very common and can account for the transfer of the CO and NO ligand necessary to explain the formation of $[Fe(CO)_2NOL]Na^+$ and $[Fe(NO)_2L_2]$. The explanation of the formation of $[Fe(CO)(NO)L_2]^-$ Na^+ and $[Fe(NO)_2L_2]$ for which the transfer of the L ligand is necessary, is more difficult; their formation does not occur by an intermolecular reaction with the free ligand L, since the $[Fe(CO)_2NOL]^-/[Fe(NO)_2L_2]$ ratio is not influenced by the concentration of the free ligand.

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