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Preliminary communication

ISOCYANIDE COMPLEXES OF MOLYBDENUM NITROSYL

W.G. KITA, J.A. McCLEVERTY*, B. PATEL and J. WILLIAMS
Chemistry Department, The University, Sheffield. S3 7HF (Great Britain)
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Summary

Reaction of π-cyclopentadienylmolybdenum nitrosyl halide with CNR (R = alkyl) gives $[(\pi\text{-}C_5H_5)Mo(NO)X_2(CNR)]$ (X = Br or I), $[Mo(NO)(CNR)_5]X$ (X = I or PF_6) and $[Mo(NO)(CNR)_4I]$; treatment of $[Mo(NO)(CNR)_5]I$ with $R'NH_2$ gives $[Mo(NO)(CNR)_4\{C(NHR)(NHR')\}]I$ or $[Mo(NO)(CNR)_4(NH_2R')]I$ (R' = alkyl) depending on temperature.

Cleavage of the halogen bridges in $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ by Lewis bases L (phosphines, arsines, pyridines, etc.) affords [1] the monomeric $[(\pi\text{-}C_5H_5)Mo(NO)X_2L]$. In attempting to prepare related isocyanide complexes we have found that reaction of CNR (R = alkyl) with π-cyclopentadienylmolybdenum nitrosyl halides results in partial dehalogenation and in ready elimination of the cyclopentadienyl ring. The products of these reactions are octahedral isocyanide nitrosyl complexes.

Addition of CNR (R = Me, Et, i-Pr, t-Bu, C_6H_{11}) to $[(\pi\text{-}C_5H_5)Mo(NO)I_2]_2$ at room temperature in acetone gave $Mo(NO)(CNR)_5I$. In refluxing acetone, however, a mixture of $Mo(NO)(CNR)_5I$ and $Mo(NO)(CNR)_4I$ was formed, and these products were also obtained from $[(C_5H_5)_2Mo(NO)I]$ in cold acetone. However, reaction of $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ with CNR at 0° in acetone gave the Lewis base adducts $[(\pi\text{-}C_5H_5)Mo(NO)X_2(CNR)]$ (X = Br, R = Me, Et, i-Pr, t-Bu, p-ClC_6H_4 naphthyl; X = I, R = naphthyl).

The carmine-pink pentaisocyanide species were 1/1 electrolytes in nitromethane, and treatment with KPF_6 readily afforded the pink $[Mo(NO)(CNR)_5][PF_6]$. The latter could be prepared independently from $[Mo(NO)_2(NCMe)_4][PF_6]_2$ [2] and CNR, in a denitrosylation reaction analogous to the formation of $[Cr(NO)(CNR)_5][PF_6]$ [3]. By heating the iodide salt in acetone, quantitative conversion to the yellow $[Mo(NO)(CNR)_4I]$ occurred, Addition to this non-electrolyte of CNR caused regeneration of the pink salt. The ^{13}C NMR spectrum of $[Mo(NO)(CNEt)_5][PF_6]$ in $CDCl_3$ (room temperature)

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*Author to whom correspondence should be addressed.

consisted of two resonances (intensity 4) due to the ethyl groups of the *cis*-coordinated isocyanides, and two signals (intensity 1) due to the *trans*-CNEt; isocyanide carbon atom resonances were not resolved.

Treatment of $[Mo(NO)(CNR)_5]I$ with primary amines ($R'NH_2$) at room temperature gave $[Mo(NO)(CNR)_4\{C(NHR')(NHR)\}]I$ (R' = Me, Et, n-Pr) in which the carbene ligand is presumed to be *trans* to the NO group. In refluxing amine, however, only $[Mo(NO)(CNR)_4(NH_2R')]I$ was formed. These reactions did not occur with the PF_6^- salt.

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References

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