Reactivity of Functionalised Isonitriles in Molybdenum Carbonyl Complexes

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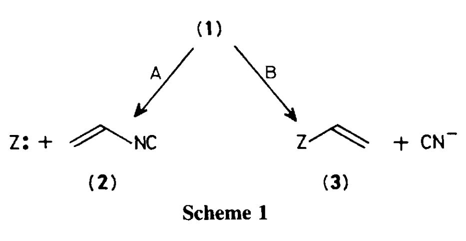
Elimination–addition reactions of β-phenoxy- and β-thiophenoxy-ethylisonitrile complexes of molybdenum have been examined; elimination pathways are accelerated by factors of between 20 and 50, while complexation renders vinylisonitrile strongly electrophilic.

Preliminary work has shown[1] that isonitriles (**1**), on treatment with bases, undergo elimination in two directions: the leaving group Z and vinylisonitrile (**2**) are formed in pathway A, while cyanide ion and alkene (**3**) are formed in pathway B (Scheme 1).

These results show the isonitrile group to be a moderate activator of elimination and also a moderately ranked leaving group.[1,2]

The incorporation of polyfunctional organic ligands in metal complexes is known, from the work of Sargeson and his collaborators, to increase the reactivity of certain functions.[3]



Scheme 1

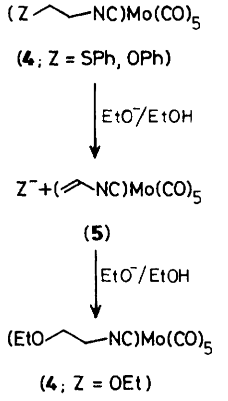
Isonitriles as ligands in metal complexes are well known,[4] but no studies of the behaviour of functionalised isonitriles in metal complexes has been reported.

We now report quantitative results on elimination reactions of β-functionalised isonitriles, of the type we investigated earlier, when incorporated as ligands in molybdenum carbonyl complexes (**4**).

$$(ZCH_2CH_2NC)Mo(CO)_5$$
(**4**)

Crystalline complexes (**4**; Z = SPh, OPh) have been obtained by treatment of molybdenum hexacarbonyl with the isonitrile (**1**; Z = SPh, OPh) and trimethylamine *N*-oxide in acetonitrile, according to the procedure described for bis-(diphenylphosphinomethane) (ddpm) and carbonyl complexes of molybdenum and tungsten.[5]

In contrast to the behaviour shown by the simple isonitriles (**1**), in which both pathways A and B were followed, treatment of the complexes (**4**; Z = SPh, OPh) with ethanolic sodium ethoxide gave only the vinyl isonitrile complex (**5**) (Scheme 2),



Scheme 2

Table 1. Elimination in isonitriles.

	$k(Z^-)^a$/mol^{-1} s^{-1} dm^3		Products (%) from (4)		
Z	(1)	(4)	Z^-	(5)	(4; Z = OEt)
SPh	3.18×10^{-6}	6.07×10^{-5}	70^b	63^c	37^c
OPh	2.20×10^{-6}	1.01×10^{-4}	96^{b,c}	80^c	14^c

[a] In EtO$^-$/EtOH at 25 °C. [b] Determined spectroscopically at 50 °C for Z = SPh and 45 °C for Z = OPh. [c] Determined by h.p.l.c. at the same temperatures as in b.

together with the ethoxyethylisonitrile complex (**4**; Z = OEt), whose proportions were measured by h.p.l.c. (column: Partisil PXS 10/25 PAC; solvent: 90% hexane, 10% dichloromethane), in comparison with authentic specimens.

The authentic crystalline vinylisonitrile complex (**5**) was obtained from the crystalline tosylate isonitrile complex (**4**; Z = OTs, Ts = toluene-*p*-sulphonate) on treatment with an equimolar quantity of ethanolic sodium ethoxide, and the semi-solid ethoxyethylisonitrile complex (**4**; Z = OEt) was obtained when an excess of ethanolic sodium ethoxide was used.

The kinetics of the elimination reactions of the complexed isonitriles were followed both spectroscopically, in the range 270—290 nm, and by h.p.l.c. In the spectrophotometric determinations, appearance of phenoxide or thiophenoxide ion was accompanied by photo-decomposition of the complexes,[5] so that the absorbances of the reacting solutions rose and then fell eventually to the level of the stoicheiometric phenoxide or thiophenoxide concentrations. Estimated infinity values were therefore employed and the good agreement between rate constants obtained by each technique showed that photo-decomposition of the complexes does not affect the conclusions drawn. Photo-decomposition also occurs with molybdenum hexacarbonyl itself under the conditions of the spectrometric analyses and is base independent.

The rates of appearance of leaving group (Z = OPh) and disappearance of starting complexes, followed by h.p.l.c., are in good agreement. The rate of addition of ethoxide ion to the vinylisonitrile complex (**5**) was also obtained in runs with thiophenoxyisonitrile (**4**; Z = SPh) by subsequent disappearance of vinylisonitrile complex (**5**) and appearance of ethoxyethylisonitrile complex (**4**; Z = OEt). The rate constant obtained was $k = 8.8 \times 10^{-5}$ mol^{-1} s^{-1} dm^3 at 50 °C.

The product analyses and the results of Table 1 show a number of striking features. First, elimination with cleavage of the carbon–nitrogen bond of the isonitrile (pathway B) is not observed in the complexes. No vinyl derivatives (**3**) were detected in any reactions, under conditions under which they would have been detectable in trace amounts by h.p.l.c. Second, elimination of the leaving group Z is accelerated by a factor of twenty for the thiophenoxy complex (**4**; Z = SPh) and fifty for the phenoxy complex (**4**; Z = OPh). These accelerations are presumably due to enhancement of the kinetic and thermodynamic acidity of the β-protons, as a result of co-ordination of the isonitrile group which is thereby rendered electron deficient. At present we have no explanation for the different degree of acceleration between the phenoxy and thiophenoxy complexes and the accelerations, while substantial, are modest by comparison with those observed by Sargeson for the elimination of leaving groups in amino-acids co-ordinated to Co^{III}.[3a]

We established in the earlier work[1] that all eliminations occurred by an $(E_1cB)_R$ mechanism (loss of leaving group from the intermediate carbanion, rate determining); we plan labelling studies on the complexes to determine the mechanism.

Co-ordination of the isonitrile group of vinylisonitrile (**5**) renders the alkenyl group very much more electrophilic than in the simple isonitrile (**2**). We have been unable to detect addition of ethoxide ion to (**2**) and substantial polymerisation occurs. Addition to the vinylisonitrile complex (**5**) occurs smoothly and comparison of the rate constant obtained for (**5**) with an estimated value (allowing for a maximum of 5% addition) for (**2**) gives an approximate minimum ratio for (**5**) : (**2**) of 56. Again, it is clear that co-ordination to the metal stabilises the β-carbanion intermediate; the effect is smaller than that observed by Sargeson (10^4) for nucleophilic addition to acrylonitrile co-ordinated to Co^{III}.[3b] No nucleophilic additions to vinylisonitrile (**2**), other than that of thiophenoxide (which could be homolytic) have ever been reported.[7,8]

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References

1 B. A. Jones, M. Varma, and C. J. M. Stirling, *J. Am. Chem. Soc.*, 1986, **108**, 3153.
2 C. J. M. Stirling, *Acc. Chem. Res.*, 1979, **12**, 198.
3 (a) E. K. Chong, J. M. Harrowfield, W. G. Jackson, A. M. Sargeson, and J. Springborg, *J. Am. Chem. Soc.*, 1985, **107**, 2015; (b) I. I. Creaser and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.*, 1975, 974.
4 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, New York, 1982, vol. 3.
5 T. S. A. Hor and S.-M. Chee, *J. Organomet. Chem.*, 1987, **331**, 23.
6 'Organometallic Photochemistry,' G. L. Geoffroy and M. S. Wrighton, Academic Press, New York, 1979.
7 'Isonitrile Chemistry,' I. Ugi, Academic Press, New York and London, 1971.
8 D. S. Matteson and R. A. Bailey, *Chem. Ind.* (*London*), 1967, 191.