Modelling the Ammoxidation of Propylene to Acrylonitrile: Preparation and Structure of the First Molybdenum Allylimido Complex

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The preparation and structure of a molybdenum allylimido complex, which serves as an entry point for homogeneous model studies of the ammoxidation reaction, are reported.

The heterogeneous oxidation of propylene by O_2 in the presence of ammonia to yield acrylonitrile (*i.e.*, the 'ammoxidation' of propylene) now accounts for virtually all of the *ca.* four million tons of annual worldwide acrylonitrile production, and thus constitutes the largest volume example of an allylic oxidation process in industrial practice.[1] The reaction, equation (1), is commonly carried out at temperatures of 400—500 °C using a catalyst of the minimal composition ($Bi_2O_3{\cdot}nMoO_3$); under these conditions the yield of acrylonitrile is *ca.* 65%. Similar reactions employing methylbenzenes are used in the manufacture of benzonitriles and terephthalonitriles. Allylimido molybdenum species [$Mo{\equiv}N{-}CH_2{-}CH{=}CH_2$] are postulated as key surface intermediates in propylene ammoxidation, yet such systems have hitherto remained unknown as discrete complexes. We report herein that allyl azide[2] serves as a convenient reagent for the introduction of the allylimido ligand into soluble molybdenum complexes, thus opening the way for an examination of the chemistry of molybdenum allylimido systems.

$$CH_2{=}CH{-}CH_3 + NH_3 + 3/2\ O_2 \rightarrow CH_2{=}CH{-}C{\equiv}N + 3\ H_2O \qquad (1)$$

Allyl azide (1.1 equiv.) was reacted with $MoCl_4(thf)_2$ (thf = tetrahydrofuran) in CH_2Cl_2 under nitrogen (25 °C, 2 h); PPh_3

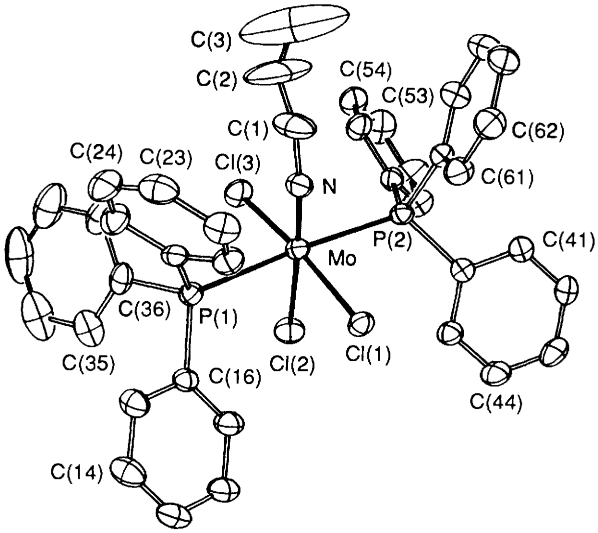

Figure 1. Structure of $Mo(NAll)Cl_3(PPh_3)_2$. Important dimensions: Mo–N 1.712(4), Mo–Cl(1) 2.424(1), Mo–Cl(2) 2.475(1), Mo–Cl(3) 2.383(1), Mo–P(1) 2.602(2), Mo–P(2) 2.612(2), N–C(1) 1.427(7), C(1)–C(2) 1.40(1) Å; Mo–N–C(1) 173.8(4), N–C(1)–C(2) 112.0(7), C(1)–C(2)–C(3), 137(2)°.

(2 equiv.) was then added and after an additional 2 h, bright red crystalline cubes of the Mo^V allylimido complex $Mo(NAll)Cl_3(PPh_3)_2{\cdot}CH_2Cl_2$ (**1**; All = $CH_2{-}CH{=}CH_2$) were obtained by slow evaporation of solvent.† An identical procedure employing benzyl azide in place of allyl azide yields the Mo^V benzylimido complex $Mo(NBz)Cl_3(PPh_3)_2$ (**2**) as orange microcrystals.† The formation of (**1**) and (**2**) likely proceeds *via* the intermediate Mo^{VI} allyl and benzylimido species $Mo(NR)Cl_4(thf)$;[3] an allylimido tungsten analogue, $W(NAll)Cl_4(thf)$, has recently been described.[4]

The structure of (**1**) was determined by *X*-ray crystallography and is shown in Figure 1.‡ The short Mo–N bond length [1.712(4) Å] and nearly linear Mo–N–C bond angle [173.8(4)°] are consonant with the presence of a $Mo{\equiv}N$ triple bond, leading to a seventeen-electron configuration for the complex with the allylimido ligand serving as a four-electron donor. As previously observed in seventeen-electron pseudo-octahedral arylimido complexes, the allylimido ligand exerts a modest *trans*-influence (0.07 Å).

Preliminary studies suggest that molybdenum allylimido complexes will serve as both structural and reactivity models for ammoxidation chemistry: we have observed ready base-induced H-abstraction within the α-CH_2 group in molybdenum allylimido complexes leading to the formation of molybdenum allylideneamido ($Mo{=}N{=}CH{-}CH{=}CH_2$) systems. The results of these studies will be reported in due course.

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† For (**1**): ESR spectroscopy (C_6H_6, 296 K) principal triplet [*g* 1.958; $A(^{31}P)$ 27.4 G]. 68% yield based on $MoCl_4(thf)_2$. Satisfactory elemental analyses were obtained for (**1**) and (**2**).

‡ *Crystal data* for (**1**): triclinic, $P\bar{1}$, $a = 10.247(3)$, $b = 12.384(4)$, $c = 17.610(6)$ Å; $\alpha = 82.18(3)$, $\beta = 81.21(3)$, $\gamma = 81.98(3)°$; $V = 2172.1(14)$ Å^3, $Z = 2$, $D_c = 1.325$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 7.04$ cm^{-1}. Of 7934 data collected (Nicolet R3m diffractometer, $4 \leqslant 2\theta \leqslant 50°$, $T = 293$ K), 7662 were independent, and 5184 with $F_o \geq 5\sigma F_o$ were used in refinement. The three allylic carbon atoms, C(1), C(2), and C(3), show a high thermal activity which is likely the result of an unresolved disorder. The C(2)–C(3) distance, 1.05(3) Å, is an artifact of this disorder. A multisite-disordered molecule of CH_2Cl_2 was located in the lattice; the atoms CS(1), CS(2), and Cl(4)–Cl(7′) represent the best model drawn from difference electron maps. With all non-hydrogen atoms anisotropic [except for CS(2)], hydrogen atoms idealized isotropic contributions, and phenyl rings constrained to rigid, planar hexagons: $R = 4.79\%$, $R_w = 5.21\%$, GOF = 1.369. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.