η-Cyclopentadienyl Molybdenum Imido Compounds; Halo, Alkene, Alkyne, Allyl and Tertiary Phosphine Derivatives

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The new imido compounds $[M(\eta\text{-}C_5H_4R)Cl_2(NR')]$* ($M$ = Mo, R = H, R′ = Bu^t, Pr^n or Ph; M = Mo, R = Me, R′ = Bu^t or Ph; M = W, R = H, R′ = Bu^t), $[Mo(\eta\text{-}C_5H_4R)Cl(L)(NR')]$ (R = H, R′ = Bu^t, L = η-C_2H_4, or η-C_2Me_2; R = Me, R′ = Bu^t, L = C_2H_4*; R = H, R′ = Ph, L = η-C_2Me_2), $[\{Mo(\eta\text{-}C_5H_4R)(\eta\text{-}C_2H_4)(NBu^t)\}_2Hg]$* (R = H, Me), $[Mo(NBu^t)Cl_2(PMe_3)_3]$, $[Mo(\eta\text{-}C_5H_5)Cl_3(NBu^t)]$ and the π-allyl complex $[Mo(\eta\text{-}C_5H_4Me)(\eta\text{-}C_3H_5)(NBu^t)]$ are synthesised; *indicates that the crystal structure has been determined.

Much interest has been shown recently in organometallic imido complexes,[1] due in part to their suspected involvement in alkene metathesis and ammoxidation catalysis, in which imido allyl species have been implicated.[2] Here we report the straightforward syntheses of mononuclear η-cyclopentadienylimidodichloro-molybdenum compounds and some tungsten analogues. Preliminary reactivity studies indicate they have a rich and diverse chemistry (see Scheme 1).

Treatment of the tetrachlorides $[Mo(\eta\text{-}C_5H_4R)Cl_4]$ **1** [M = Mo, R = H (**1a**) or Me (**1b**); M = W, R = H (**1c**) or Me (**1d**)] with 3 equiv. of $R'NH_2$ ($R' = Bu^t$, Pr^n or Ph) in toluene affords the corresponding η-cyclopentadienylimidodichloro compounds $[Mo(\eta\text{-}C_5H_4R)Cl_2(NR')]$ [M = Mo, R = H, $R' = Bu^t$ (**2a**), Pr^n (**2c**) or Ph (**2d**); M = Mo, R = Me, $R' = Bu^t$ (**2b**) or Ph (**2e**); M = W, R = H, $R' = Bu^t$ (**2f**)] in *ca.* 50% yield.† The crystal structure‡ of the compound **2a** has been determined and the molecular structure is shown in Fig. 1.

Reduction of the compounds **2a**, **b** with sodium amalgam under ethene yields a mixture of the imido-η-ethene compounds $[Mo(\eta\text{-}C_5H_4R)(\eta\text{-}C_2H_4)Cl(NBu^t)]$ [R = H (**3a**) or Me (**3b**)] and the binuclear mercury-bridged compounds $[\{Mo(\eta\text{-}C_5H_4R)(\eta\text{-}C_2H_4)(NBu^t)\}_2Hg]$, [R = H (**4a**) or Me (**4b**)]. The relative yields of the compounds **3a**, **b** and **4a**, **b** are variable; however, selective formation of pure compounds **3a**, **b** is achieved by using C_8K as the reductant.

The crystal structures of the compounds **3b** and **4a** have been determined‡ and the molecular structures are shown in Figs. 2 and 3, respectively. The C–C vectors of the η-ethene ligands in **3b** and **4a** do not lie parallel to the plane of the cyclopentadienyl ring, but are skewed at angles of *ca.* 30 and *ca.* 12°, respectively.

Analogous reduction of the compounds **2a** and **2d** in the presence of but-2-yne affords the imido-alkyne-halo compounds $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_2Me_2)Cl(NR)]$ [R = Ph (**5a**) or Bu^t (**5b**)]. The IR spectrum of **5b** shows a band assignable to ν(C≡C) at 1855 cm^{-1}.

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† Satisfactory analyses have been obtained for all the new compounds described, except for **4b**, **5b**, **8** and **9** which have been spectroscopically characterised.

Selected spectroscopic data: NMR data recorded at 300 MHz (^1H) or 75.5 MHz ($^{13}C\text{-}\{^1H\}$) and given as δ relative to $SiMe_4$, relative intensity, multiplicity, coupling constant (in Hz) and assignment; *J* refers to $^1H\text{-}^1H$ coupling constant unless stated otherwise. [a] In $[^2H_6]$benzene, [b] in $[^2H_2]$dichloromethane, [c] in $[^2H_8]$toluene. DEPT = distortionless enhancement by polarisation transfer. IR data given as cm^{-1} with spectra recorded as CsI disks.

2a: ν(Mo=N) 1362, ν(Mo–Cl) 300, 330, 380. **2b**: ν(Mo=N) 1362, ν(Mo–Cl) 300, 330, 380. **2c**: ν(Mo=N) 1358, ν(Mo–Cl) 300, 330, 350. **2d**: ν(Mo=N) 1312, ν(Mo–Cl) 310, 340, 360. **2e**: ν(Mo=N) 1313, ν(Mo–Cl) 310, 340, 360.

3a: ^1H:[a] 5.30 (5H, s, C_5H_5), 2.78–2.89 (1H, m, C_2H_4), 2.52–2.62 (1H, m, C_2H_4), 2.17–2.26 (1H, m, C_2H_4), 1.95–2.04 (1H, m, C_2H_4), 0.87 (9H, s, Bu^t). $^{13}C\text{-}\{^1H\}$ DEPT NMR:[a] 102.5 (C_5H_5), 49.1, 38.5 (2 × C_2H_4), 28.9 (CMe_3). IR: ν(Mo=N) 1355, ν(Mo–Cl) 340, 370.

3b: ^1H:[c] 5.43, 5.36, 5.25, 4.49 [4 × 1H, 4 × virtual q (*J* = 3), C_5H_4Me], 2.55–2.75 (2H, m, C_2H_4), 2.13–2.21 (1H, m, C_2H_4), 1.75 (3H, s, C_5H_4Me), 1.65–1.73 (1H, m, C_2H_4), 0.92 (9H, s, Bu^t). $^{13}C\text{-}\{^1H\}$:[c] 105, 101, 97.6, 97.1 (4 × *C*H of C_5H_4Me), 71 (CMe_3), 49, 39 (2 × C_2H_4), 29 (CMe_3), 14 (C_5H_4Me). IR: ν(Mo=N) 1360, ν(Mo–Cl) 310, 340, 380.

4a: ^1H;[a] 5.20, 5.19 (2 × 5H, 2 × s, C_5H_5), 1.99 (4H, m, C_2H_4), 1.64, 1.45 (2 × 2H, 2 × m, C_2H_4), 1.07 (18H, s, Bu^t). $^{13}C\text{-}\{^1H\}$ DEPT NMR:[a] 92.2 (C_5H_5), 31.5 (CMe_3), 19.8, 13.9 (2 × C_2H_4). IR: ν(Mo=N) 1355.

4b: ^1H:[a] 5.36, 5.24 (2 × 2H, 2 × m, C_5H_4Me), 5.17 (4H, m, C_5H_4Me), 2.10 (4H, m, C_2H_4), 1.64 (6H, s, C_5H_4Me), 1.49 (2H, m, C_2H_4), 1.13 (2H, partially obscured m, C_2H_4), 1.09 (18H, s, Bu^t).

5a: ^1H:[a] 6.9–6.7 (5H, m, C_6H_5), 5.51 (5H, s, C_5H_5), 2.74, 2.36 (2 × 3H, 2 × s, C_2Me_2).

5b: ^1H:[a] 5.60 (5H, s, C_5H_5), 2.61, 2.38 (2 × 3H, 2 × s, C_2Me_2), 0.92 (9H, s, Bu^t). $^{13}C\text{-}\{^1H\}$ NMR:[a] 104.8 (C_5H_5), 29.4 (CMe_3), 18.3, 10.7 (2 × C_2Me_2). IR: ν(Mo=N) 1357, ν(C≡C) 1855, ν(Mo–Cl) 280.

6: ^1H:[a] 1.43 [18H, virtual t (*J* = 3.6), *trans*-PMe_3], 1.25 [9H, d (*J* = 7.6), PMe_3], 1.01 (9H, s, Bu^t). $^{13}C\text{-}\{^1H\}$ DEPT NMR:[a] 30.9 [CMe_3], 23.6 [d, (*J* = 23.4), PMe_3], 18.1 [virtual t (*J* = 11.0), *trans*-PMe_3]. $^{31}P\text{-}\{^1H\}$:[a] 3.2 [t (*J* = 17), *cis*-PMe_3], −9.9 [d (*J* = 17), *trans*-PMe_3]. IR: ν(Mo=N) 1360, ν(Mo–Cl) 300.

7: ^1H:[b] 6.80 (5H, s, C_5H_5), 1.56 (9H, s, Bu^t). $^{13}C\text{-}\{^1H\}$ DEPT NMR:[b] 118.3 (C_5H_5), 27.4 (CMe_3). IR: ν(Mo=N) 1363, ν(Mo–Cl) 280, 330, 380.

8: ^1H:[a] 5.67, 4.64 [2 × 2H, 2 × virtual t (*J* = 2.2 Hz), C_5H_4Me], 4.07 [2H, m, $(CH_2)_2CH$], 2.96 [1H, m, $(CH_2)_2CH$], 1.68 [3H, s, C_5H_4Me], 0.92 [9H, s, Bu^t], 0.36 [2H, m, $(CH_2)_2CH$]. $^{13}C\text{-}\{^1H\}$ NMR (assignments confirmed by a $^{13}C\text{-}^1H$ correlation spectrum):[a] 94, 89 [2 × *C*H of C_5H_4Me], 78 [$(CH_2)_2CH$], 45 [$(CH_2)_2CH$], 31 [CMe_3], 15 [C_5H_4Me]. Mass spectrum (EI): *m/z* 289 (M^+).

9: ^1H:[a] 6.72 (1H, m, $CH_2CH{=}CH_2$), 5.29, 5.17, 5.05, 4.61 [4 × 1H, 4 × virtual q (*J* = 2.2 Hz), C_5H_4Me], 5.07 (1H, m, $CH_2CH{=}CH_2$), 5.01 (1H, m, $CH_2CH{=}CH_2$), 3.19 (1H, m, $CH_2CH{=}CH_2$), 2.65 (1H, m, $CH_2CH{=}CH_2$), 2.30, 1.95, 1.84 (3 × 1H, 3 × m, C_2H_4), 1.39 (3H, s, C_5H_4Me), 0.98 (1H, m, C_2H_4), 0.88 (9H, s, Bu^t). $^{13}C\text{-}\{^1H\}$ NMR (assignments confirmed by a $^{13}C\text{-}^1H$ correlation spectrum):[a] 152 ($CH_2CH{=}CH_2$), 105 ($CH_2CH{=}CH_2$), 24 ($CH_2CH{=}CH_2$), 107, 98, 97, 96 (4 × *C*H of C_5H_4Me), 41 (C_2H_4), 29.8 (Bu^t), 28.6 (C_2H_4), 13 (C_5H_4Me).

‡ *Crystal data* for **2a**: $C_9H_{14}Cl_2MoN$, *M* = 303.1, crystal size = *ca.* 0.55 × 0.35 × 0.30 mm, monoclinic, space group $P2_1/c$, $a = 12.528(5)$, $b = 16.317(5)$, $c = 12.697(5)$ Å, $\beta = 112.32(3)°$, $V = 2401.0$ Å^3, $Z = 8$ (2 independent molecules in the asymmetric unit), $D_c = 1.68$ g cm^{-3}, μ(Mo-Kα) = 14.76 cm^{-1}, $F(000) = 1208$, scan type ω, $T = 231$ K, $3 < 2\theta < 60°$, total unique data 6991, number of observations $[I > 3\sigma(I)]$ 5766, number of variables 253, observations/variables 24.5, $R_{merge} = 0.063$, $R = 0.041$, $R_W = 0.056$ $\{w = [\sigma^2(F) + 0.0009F^2]^{-1}\}$, maximum peak in final Fourier difference synthesis 1.80 eÅ^{-3}.

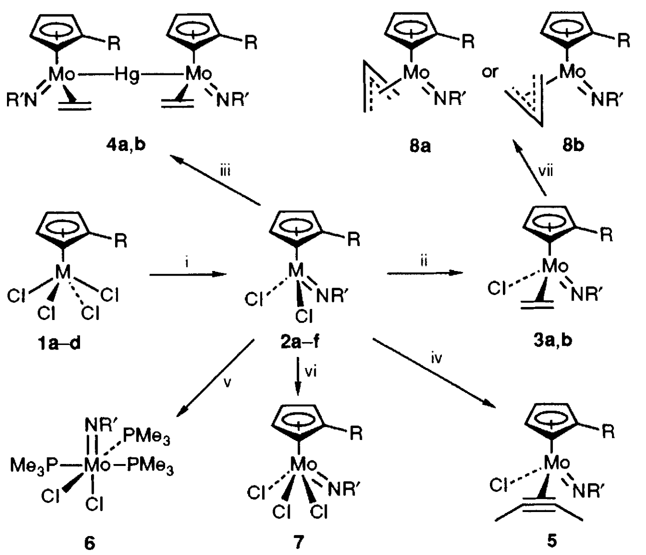
4a: $C_{22}H_{36}HgMo_2N_2$, *M* = 721.01, crystal size = *ca.* 0.20 × 0.40 × 0.35 mm, monoclinic, space group $P2_1/c$, $a = 11.234(3)$, $b = 13.388(6)$, $c = 16.982(3)$ Å, $\beta = 91.59(2)°$, $V = 2553.1$ Å^3, $Z = 4$, $D_c = 1.88$ g cm^{-3}, μ(Mo-Kα) = 69.53 cm^{-1}, $F(000) = 1384$, scan type ω–2θ, $T = 293$ K, $3 < 2\theta < 46°$, total unique data 3551, number of observations $[I > 3\sigma(I)]$ 1776, number of variables 204, observations/variables 8.8, $R_{merge} = 0.028$ (after applying a DIFABS[4] correction based on an isotropic model of **4a**), $R = 0.065$, $R_w = 0.069$ (Chebyshev; parameters 6.21, −2.69, 3.67), maximum peak in final Fourier difference synthesis 3.3 eÅ^{-3} {located 0.49 Å from the lower occupancy Hg atom [Hg(101), not shown in Fig. 4]}.

3b: $C_{12}H_{20}ClMoN$, *M* = 309.69, crystal size = *ca.* 0.20 × 0.35 × 0.45 mm, monoclinic, space group $P2_1/n$, $a = 6.608(3)$, $b = 14.120(7)$, $c = 15.132(6)$ Å, $\beta = 92.22(3)°$, $V = 1410.9$ Å^3, $Z = 4$, $D_c = 1.46$ g cm^{-3}, μ(Mo-Kα) = 10.72 cm^{-1}, $F(000) = 632$, scan type ω–2θ, $T = 293$ K, $3 < 2\theta < 48°$, total unique data 2213, number of observations $[I > 3\sigma(I)]$ 1215, number of variables 149, observations/variables 8.2, $R_{merge} = 0.032$, $R = 0.036$, $R_w = 0.035$ (Chebyshev; parameters 4.94, −7.60, 3.58, −2.45), maximum peak in final Fourier difference synthesis 0.6 eÅ^{-3}.

Data were collected on a Nicolet R3m/V diffractometer (for **2a**) or on an Enraf-Nonius CAD4-F diffractometer. For **2a** and **3b** an empirical absorption correction based on azimuthal scans was applied. For **4a** a DIFABS[4] correction was applied during data reduction before merging equivalent reflections. The heavy atom positions were determined using a Patterson synthesis (**2a** and **3b**) or the SIR88[5] package (**4a**); subsequent Fourier difference syntheses revealed the remaining non-hydrogen atoms. The structures were refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms with the exception of the cyclopentadienyl carbon atoms of **4a** which were unstable to anisotropic refinement. Hydrogen atoms attached to C were placed in calculated positions and refined with fixed isotropic thermal parameters riding on their supporting carbon atoms with the exception of the ethene ligand of **3b** for which the hydrogen atoms could be located from a difference synthesis and their fractional atomic coordinates were refined. A SIR88[5] analysis of the reflection data for **4a** showed pseudotranslational symmetry in the $h = 4n$ class of reflections. After the initial model had refined to convergence ($R = 0.096$) a large peak remained in the difference map located roughly halfway between Mo(1) of one molecule and Mo(2) of the neighbouring molecule at ($x + 1$), y, z. This was interpreted as a fractional pseudotranslational disorder and the residual density treated as a second (minor) Hg site [Hg(101)]. After setting the isotropic thermal parameters of Hg(1) and Hg(101) to be equal, their occupancies were refined to be 0.1 and 0.9 for Hg(101) and Hg(1) respectively; both Hg(101) and Hg(1) were then refined with fixed occupancies and anisotropic thermal parameters. The Mo positions in both the major and the minor molecules are apparently coincident; no other atoms could be reliably located for the 10% occupancy molecule.

Crystallographic calculations were carried out using SHELXTL PLUS[6] on a MicroVAX II (for **2a**) or using the CRYSTALS[7] suite of programs on a MicroVAX 3800 computer.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1 *Reagents and conditions*: i, 3 $R'NH_2$, toluene, (50%); ii, C_8K or Na–Hg, C_2H_4, tetrahydrofuran (thf), (up to 50%); iii, Na–Hg, C_2H_4, thf, (up to 30%); iv, Na–Hg, C_2Me_2, thf, (60%); v, Na–Hg, PMe_3, thf, (50%); vi, Cl_2, CH_2Cl_2, (60%); vii, $CH_2{=}CHCH_2MgCl$, thf, *hν*, (*ca.* 70%)

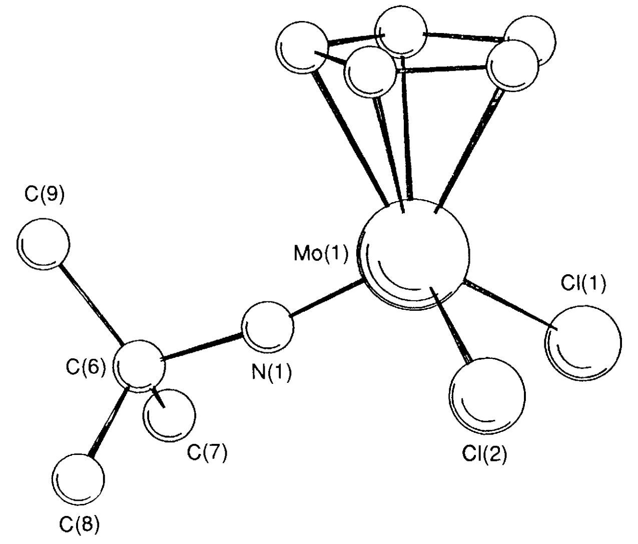


Fig. 1 Molecular structure of one of the two crystallographically independent molecules of $[Mo(\eta\text{-}C_5H_5)Cl_2(NBu^t)]$ **2a**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) as follows: Mo(1)–Cl(1) 2.367(1), Mo(1)–Cl(2) 2.361(1), Mo(1)–N(1) 1.712(2), Mo–Cp_{cent} 2.052, N(1)–C(6) 1.450(4), Cl(1)–Mo(1)–Cl(2) 91.9(1), Cl(1)–Mo(1)–N(1) 102.3(1), Mo(1)–N(1)–C(6) 170.1(2) where Cp_{cent} refers to the computed $\eta\text{-}C_5H_5$ centroid.

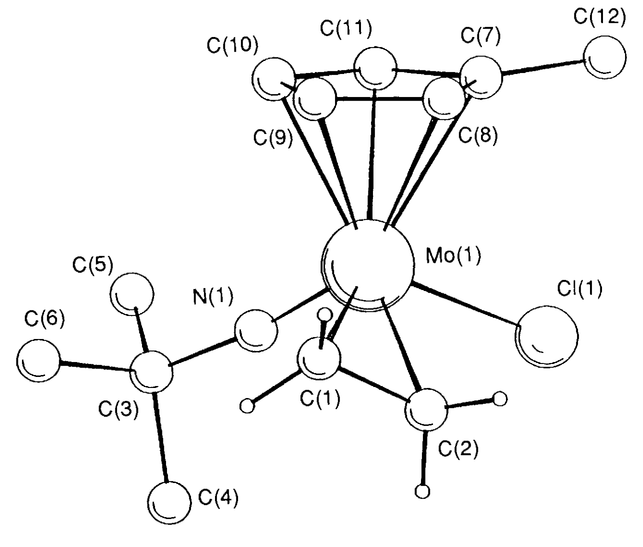


Fig. 2 Molecular structure of $[Mo(\eta\text{-}C_5H_4Me)(\eta\text{-}C_2H_4)Cl(NBu^t)]$ **3b**. Only hydrogens bonded to the $\eta\text{-}C_2H_4$ ligand are shown for clarity. Selected bond lengths (Å) and angles (°) as follows: Mo(1)–N(1) 1.704(6), Mo(1)–C(1) 2.215(8), Mo(1)–C(2) 2.190(9), C(1)–C(2) 1.40(1), Mo(1)–Cp_{cent} 2.07, Mo(1)–N–C(3) 172.3(5) where Cp_{cent} refers to the computed $\eta\text{-}C_5H_4Me$ centroid.

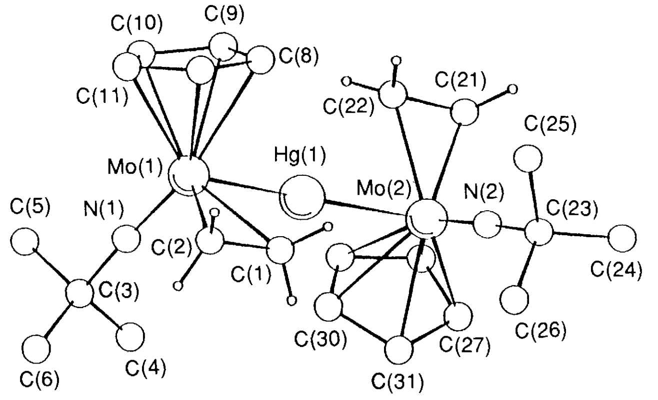


Fig. 3 Molecular structure of $[\{Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_2H_4)(NBu^t)\}_2Hg]$ **4a**. Only hydrogens bonded to the $\eta\text{-}C_2H_4$ ligand are shown for clarity. Selected bond lengths (Å) and angles (°) as follows: Mo(1)–N(1) 1.75(2), Mo(2)–N(2) 1.72(3), Mo(1)–C(1) 2.28(3), Mo(2)–C(21) 2.17(3), Mo(1)–C(2) 2.18(3), Mo(2)–C(22) 2.26(2), Mo(1)–$Cp_{cent(1)}$ 2.05, Mo(2)–$Cp_{cent(2)}$ 2.01, Mo(1)–Hg(1) 2.692(2), Mo(2)–Hg(1) 2.773(2), C(1)–C(2) 1.427(5), C(21)–C(22) 1.426(5), N(1)–C(3) 1.44(3), N(2)–C(23) 1.40(3), Mo(1)–N(1)–C(3) 175.9(20), Mo(2)–N(2)–C(23) 177.0(18), N(1)–Mo(1)–Hg(1) 90.7(6), N(2)–Mo(2)–Hg(1) 87.6(6), Mo(1)–Hg(1)–Mo(2) 175.8(1) where $Cp_{cent(1)}$ and $Cp_{cent(2)}$ refer to the computed $\eta\text{-}C_5H_5$ centroids for Mo(1) and Mo(2), respectively.

Reduction of the compound **2b** with sodium amalgam in the presence of trimethylphosphine causes displacement of the η-cyclopentadienyl ring to form the compound $[Mo(NBu^t)Cl_2(PMe_3)_3]$ **6** which is presumably isostructural with the congener $[W(NPh)Cl_2(PMe_3)_3]$.[3] Oxidation of the compound **2a** with chlorine gas affords the d^0 imidotrichloro compound $[Mo(\eta\text{-}C_5H_5)Cl_3(NBu^t)]$ **7** in *ca.* 60% yield.

Photolysis of the imido alkene chloro complex **3b** in the presence of allylmagnesium chloride yields the π-allyl compound $[Mo(\eta\text{-}C_5H_4Me)(NBu^t)(\eta^3\text{-}C_3H_5)]$ **8** as indicated by ^1H, ^{13}C and ^{13}C–^1H correlation NMR spectroscopy. The data are compatible with either of the structures **8a** or **8b** shown in Scheme 1. To our knowledge, compound **8** is the first isolated example of an imido-π-allyl compound.

Such species have been implicated as intermediates in the ammoxidation of propene.[2] Preliminary NMR data indicate that formation of the compounds **8** proceeds *via* the intermediate σ-allyl imido alkene complex $[Mo(\eta\text{-}C_5H_4Me)(\sigma\text{-}CH_2CH{=}CH_2)(\eta\text{-}C_2H_4)(NBu^t)]$ **9** which, upon photolysis, gives the π-allyl compounds **8**.

The reactions and the structures proposed for the new compounds **2–8** are shown in Scheme 1.

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