η^2-Iminoethyl-*C,N* *vs.* η^3-Aminoethylene-*C,C′,N* Formation† in the Thermally Induced Rearrangement of Isocyanide Alkyl Complexes of Molybdenum

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Thermal rearrangement of the isocyanide alkyl complexes $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5R_5})(\mathrm{Me})(\mathrm{CO})_2(\mathrm{CNBu^t})]$ **1**, ($\mathrm{R_5} = \mathrm{H_5}$, **1a**; $\mathrm{H_4Me}$, **1b**; $\mathrm{Me_5}$, **1c**) yields η^2-iminoethyl-*C,N* complexes $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5R_5})\{\eta^2\text{-}\mathrm{C({=}NBu^t)Me_3}\}(\mathrm{CO})_2]$ **2**, and/or η^3-aminoethylene-*C,C′,N* complexes $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5R_5})\{\eta^3\text{-}\mathrm{H_2CC(H)NBu^t}\}(\mathrm{CO})_2]$ **3**, in reactions whose course is dramatically solvent dependent.

Insertion reactions, particularly those of carbon monoxide and isocyanides into transition metal–carbon bonds, are of fundamental importance in organometallic chemistry.[1] We report here the outcome of our recent studies with methyl derivatives of molybdenum containing the sterically demanding *tert*-butyl isocyanide group. These have resulted in the first observation of competitive coupling reactions between an alkyl and an isocyanide ligand, to afford either an η^2-iminoethyl-*C,N*, or an isomeric η^3-aminoethylene-*C, C′,N* functionality. Although the ubiquitous η^3-allyl group has become a standard organometallic ligand,[1] and transition metal complexes of η^3-oxa,[2] -phospha[3] and other allyls containing heteroatoms[4] have recently been reported, little is known about related complexes containing the aza-analogue, the η^3-aminoethylene group.[5]

When a thermodynamic mixture of the fast equilibrating isomeric species‡ *cis*- and *trans*-$[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{Me})(\mathrm{CO})_2(\mathrm{CNBu^t})]$ **1a** {prepared by treating $\mathrm{Na}[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{CNBu^t})]$ with MeI} was heated in tetrahydrofuran (thf), a smooth insertion reaction ensued with formation of the expected[6] η^2-iminoethyl complex $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})\{\eta^2\text{-}\mathrm{C({=}NBu^t)Me}\}(\mathrm{CO})_2]$ **2a**. No intermediates were detected, but monitoring of the reaction by NMR spectroscopy clearly showed concomitant formation of a second product **3a**, in low yield (see Scheme 1). The latter compound was unambiguously characterized by spectroscopy§ as the η^3-aminoethylene

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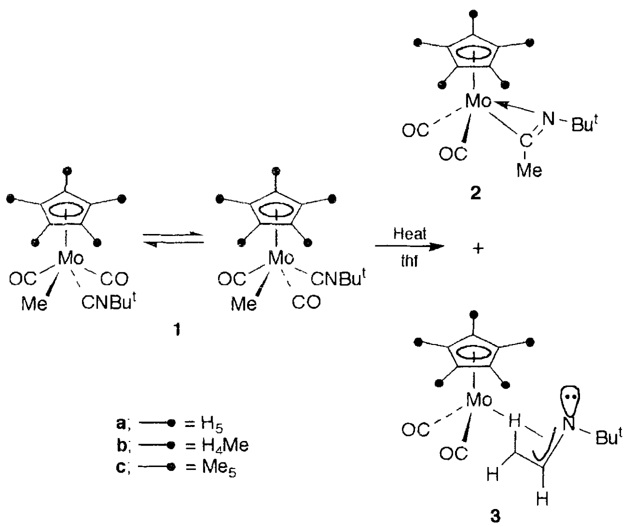
† The terms η^2-iminoacyl and η^3-1-azaallyl respectively have also been used to name these ligands.

‡ Satisfactory elemental analyses have been obtained for all new compounds.

§ Selected spectroscopic data for **3a** are as follows: ^{1}H NMR (200 MHz; $\mathrm{C_6D_6}$; J values in Hz; S = *syn*, A = *anti* with respect to $\mathrm{H_C}$; C = central): δ 1.05 (s, 9H, $\mathrm{NBu^t}$), 2.16 (d, J_{SC} 7.4, 1H, $\mathrm{C}H_{\mathrm{S}}\mathrm{H}$), 2.52 (d, J_{AC} 4.1, 1H, $\mathrm{CH}H_{\mathrm{A}}$), 4.78 (dd, 1H, $\mathrm{C}H_{\mathrm{C}}$), 4.89 (s, 5H, $\mathrm{C_5H_5}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50 MHz; $\mathrm{C_6D_6}$; J values in Hz): δ 27.2 ($^1J_{\mathrm{CH}}$ 158, $\mathrm{CH_2}$), 30.7 ($\mathrm{C}Me_3$), 56.6 ($C\mathrm{Me_3}$), 94.7 ($\mathrm{C_5H_5}$), 115.0 ($^1J_{\mathrm{CH}}$ 163, CH), 247.4 (CO), 247.7 (CO).



Scheme 1

derivative $[Mo(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}H_2CC(H)NBu^t\}(CO)_2]$. Competitive formation of isomeric η^2-iminoethyl and η^3-aminoethylene derivatives was also observed for the ring-substituted complexes **1b** and **1c**. Compounds **2** and **3** are thermally stable; spectroscopically pure samples of each showed no signs of interconversion, even during prolonged heating at 60–80 °C. This would suggest that they are formed from **1** as the result of different mechanistic pathways.

Compounds **3** are unusual examples of transition metal complexes containing the η^3-aminoethylene functionality. Although alkali metal aminoethylene species[7] and a molybdenum complex of a protonated aminoethylene ligand[8a] have been reported recently, to our knowledge the only fully characterized transition metal η^3-aminoethylene derivatives are those prepared by Green and coworkers by the low-yield reaction of 2-substituted azirines with the unsaturated molybdenum dimer $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$.[5] After submission of this manuscript a report on other related Mo–aminoethylene complexes has appeared.[8b]

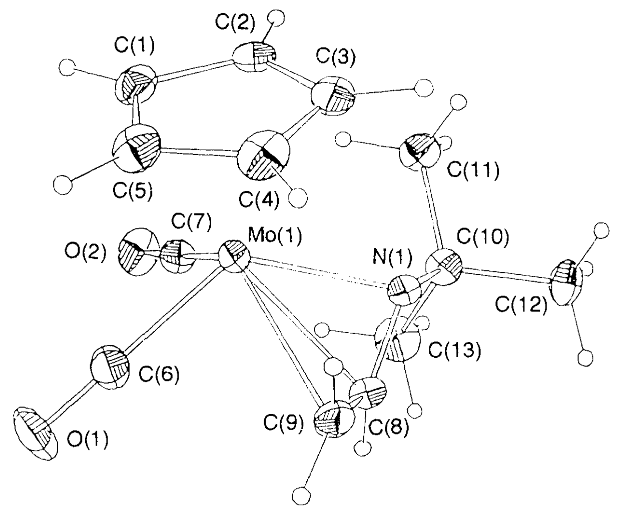


Fig. 1 ORTEP plot of the structure of complex **3a**. Selected bond lengths (Å) and angles (°): Mo(1)–C(6) 1.948(4), Mo(1)–C(7) 1.940(3), Mo(1)–C(8) 2.317(3), Mo(1)–C(9) 2.288(4), Mo(1)–N(1) 2.227(3), C(6)–Mo(1)–C(7) 76.4(1), Mo(1)–N(1)–C(10) 131.3(2), Mo(1)–N(1)–C(8) 76.9(2), Mo(1)–C(8)–N(1) 69.4(2), Mo(1)–C(8)–C(9) 71.3(2), Mo(1)–C(9)–C(8) 73.7(2), C(8)–N(1)–C(10) 120.0(3).

Table 1 Relative ratio (%) of aminoethylene **3c** to iminoethyl **2c** formation[a] in a range of solvents

Solvent	**3c** : **2c**
Benzene	100 : 0
Diethyl ether	100 : 0
thf	20 : 80
2-Methf	80 : 20
2,5-Me$_2$thf	>90 : <10
2,2,5,5-Me$_4$thf	100 : 0
Acetone	0 : 100
Acetonitrile	0 : 100
Pyridine	0 : 100
2,6-Dimethylpyridine	100 : 0

[a] Samples of **1c** were thermally transformed (80 °C) and the respective ratios of products obtained by ^{1}H NMR spectroscopy (C_6D_6). The reactions are quantitative by NMR spectroscopy and isolated yields of pure materials range from 50 to 80%.

To confirm unequivocally the proposed formulation for compounds **3**, an X-ray diffraction study of complex **3a** was undertaken.¶ Fig. 1 shows an ORTEP diagram of the molecule, illustrating its distorted 'four-legged piano-stool' structure. As in Green's $[Mo(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}H_2CC(p\text{-}C_6H_4Me)NH\}]$, the aminoethylene ligand of complex **3a** adopts an *endo*-conformation with respect to C_5H_5, in accord with the solution structure indicated by NOE experiments. In view of the thermal stability displayed by compounds **3** (*vide supra*) the *endo*-isomer seems to be thermodynamically favoured over the *exo*-alternative. The *tert*-butyl group bonded to nitrogen has a *syn* orientation, minimizing adverse steric interactions with the cyclopentadienyl ligand. The value of 120.0(3)° observed for the C(8)–N(1)–C(10) angle is clear evidence of sp^2 hybridization at nitrogen. Further proof of the η^3-bonding mode of the aminoethylene entity is provided by the short contacts of the nitrogen atom to molybdenum [2.227(3) Å] and to the central allylic carbon [1.323(4) Å], the latter distance being intermediate between those of single and double C–N bonds.

Although this study has unambiguously established the structure of compounds **3**, both in the solid state and in solution, the precise mechanism of the reaction leading to **3** remains to be clarified. Remarkably, the nature of the products resulting from the thermal activation of **1** depends dramatically upon the choice of solvent (Table 1). Thus, the use of polar, coordinating solvents like thf or Me$_2$CO yields predominantly the η^2-iminoethyls **2**, whereas poor-donor solvents such as aromatic hydrocarbons, diethyl ether and 2,2,5,5-tetramethyltetrahydrofuran provide exclusively the aminoethylene complexes **3**. Work aimed at ascertaining the role of the solvent and other mechanistic aspects of this interesting transformation is presently under way. At this

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¶ *Crystal data* for $C_{13}H_{17}NO_2Mo$: $M = 314.9$, monoclinic, $C2/c$, $a = 31.388(3)$, $b = 7.3980(7)$, $c = 12.175(2)$ Å, $\beta = 106.00(1)°$, $U = 2717.6(6)$ Å^3, $D_c = 1.54$ g cm^{-3}, $Z = 8$, $F(000) = 1280$, $\mu(\text{Mo-K}\alpha) = 9.32$ cm^{-1}. A prismatic brown crystal of dimensions 0.2 × 0.2 × 0.3 mm was used for measurements at 295 K on a Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) using a $\omega/2\theta$ scan technique. A total of 2814 reflections were collected, of which 2367 were independent, and 2230 had $I > 2\,\sigma(I)$ ($1° < \theta < 25°$). The cell dimensions were refined by least-squares fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo were taken from the International Tables. The structure was solved by Patterson and Fourier methods. An empirical absorption correction was applied at the end of the isotropic refinement (N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158). The final R value was 0.020 ($R_w = 0.028$). A final refinement was undertaken with fixed isotropic factors and coordinates for H atoms. 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.

preliminary stage we merely note that the effect of coordinating solvents on the formation of **2** and related iminoethyls[6] may be similar to that recently demonstrated for nucleophilic catalysis of the migratory CO insertion.[9,10] As for the formation of the aminoethylene complexes **3**, the reaction involves formally a 1,2-hydrogen shift within an iminoethyl ligand.[11] A similar transformation has been observed recently by Rothwell[12] in the isomerization of η^2-iminoethyl ligands to vinylamido groups through the putative intermediacy of an intramolecularly stabilized η^1-iminoethyl species. In the present case the η^2-iminoethyls **2** are clearly not intermediates in the reaction leading to the η^3-aminoethylene complexes **3**. In view of this, and taking into consideration the recent isolation of agostic acyl complexes of molybdenum,[13] it is tempting to speculate upon the possible existence of an agostic iminoethyl aminoethylene precursor, although other reaction pathways cannot be discarded.‖

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‖ *Note added in proof*: In recent contributions, Filippou and coworkers have independently observed the formation of similar isomeric η^2-iminoalkyl-*C,N* and η^3-aminoethylene-*C,C′,N* complexes in closely related systems (*J. Organomet. Chem.*, 1991, **410**, 175 and 1991, **413**, 181). They have further demonstrated that the latter are the thermodynamically more stable isomers.