

Formation of a Highly Asymmetric Tridentate New Ligand upon Addition of Acetone to a Co-ordinated 1,4-Diazabuta-1,3-diene

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The new ligand $\text{Bu}^t\text{-N}=\text{CH}-\text{CH}(\text{CH}_2\text{COMe})-\text{N}(\text{H})-\text{Bu}^t$ has been formed on intramolecular addition of acetone to an imine group of the co-ordinated diazabutadiene in $\text{fac}[\text{Mn}(\text{CO})_3(\text{Bu}^t\text{-N}=\text{CH}-\text{CH}=\text{N}-\text{Bu}^t)(\text{MeCOMe})][\text{ClO}_4]$, (1); the structures of $\text{cis}[\text{Mn}(\text{CO})_2(\text{CN}-\text{Bu}^t)\{\text{Bu}^t\text{-N}=\text{CH}-\text{CH}(\text{CH}_2\text{COMe})-\text{N}(\text{H})-\text{Bu}^t\}][\text{ClO}_4]$, (4), and $\text{cis}, \text{trans}[\text{Mn}(\text{CO})_2(\text{CN}-\text{Bu}^t)_2\{\text{Bu}^t\text{-N}=\text{CH}-\text{CH}(\text{CH}_2\text{COMe})-\text{N}(\text{H})-\text{Bu}^t\}][\text{ClO}_4]$, (5), where the ligand acts in a tridentate and a bidentate fashion respectively, have been established by X-ray diffraction methods.

Although the acetone hydrogen atoms are acidic in character, intramolecular condensation of the enolate form under mild conditions has rarely been observed in transition metal complexes.¹

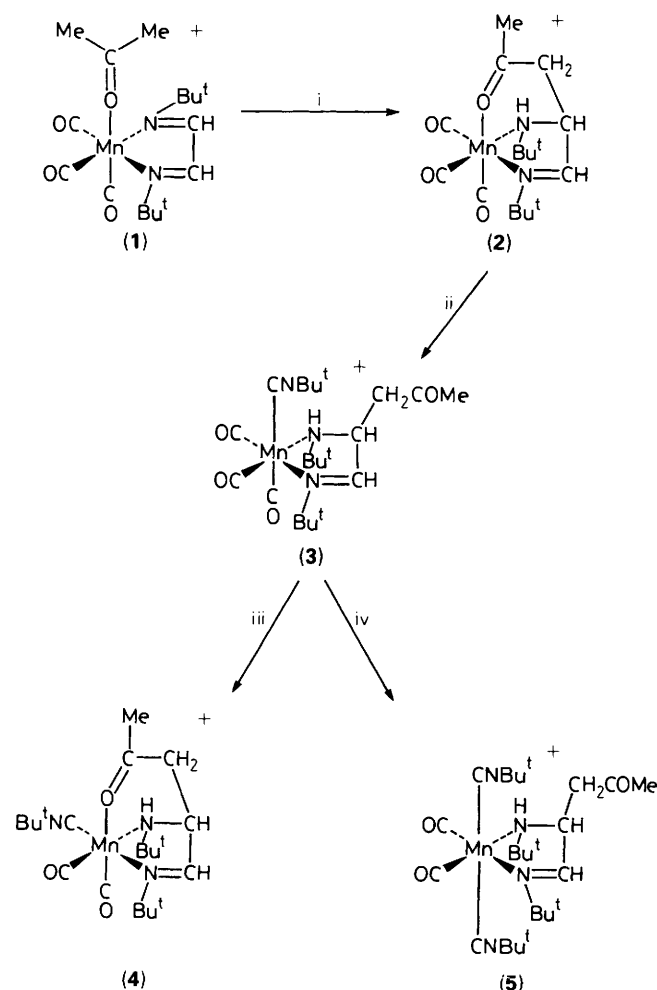
Examples of intramolecular C-C bond formation, including aldol condensations, are known in co-ordination chemistry.² Moreover, the reactivity of co-ordinated diazabutadienes towards organic substrates leads to an unusually rich chemistry involving C-C, C-H, N-C, and N-H coupling reactions.³ However, to the best of our knowledge, there are no

precedents of simultaneous C-C and N-H bond formation starting from σ, σ' - N, N' -co-ordinated diazabutadienes.

We report the addition of acetone to an imine group of a σ, σ' - N, N' -co-ordinated diazabutadiene, giving new C-C and N-H bonds. In fact, after stirring $\text{fac}[\text{Mn}(\text{CO})_3(\text{Bu}^t\text{-N}=\text{CH}-\text{CH}=\text{N}-\text{Bu}^t)(\text{MeCOMe})][\text{ClO}_4]$, (1),[†] in acetone at room temperature for 3 days, the compound $\text{fac}[\text{Mn}(\text{CO})_3\{\text{Bu}^t\text{-N}=\text{CH}-\text{CH}(\text{CH}_2\text{COMe})-\text{N}(\text{H})-\text{Bu}^t\}][\text{ClO}_4]$, (2), was isolated from the solution in good yield (93%) (Scheme 1). The acetone moiety which adds to the imine group should be metal co-ordinated rather than a solvent molecule, since $\text{fac}[\text{Mn}(\text{CO})_3(\text{Bu}^t\text{-N}=\text{CH}-\text{CH}=\text{N}-\text{Bu}^t)\text{Br}^4]$ remains unaltered after 10 days in acetone at room temperature.

Elemental analyses and spectroscopic data[‡] are in accordance with the proposed structure. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (2) shows two close peaks for the ketone (δ 223.63 and 223.56) and also for the imine (δ 174.56 and 174.14) carbon atoms, with some of the other signals being unexpectedly broad. This may be due to the existence of two or more conformers, arising from the non-planarity of the rings in the molecule.

The formation of (2) provides further support for some of the proposed mechanisms for acetone activation,^{1a, 1b} which suggest that this activation is the result of co-operation between the metal centre, to which the acetone is oxygen-bonded, and an oxygen or nitrogen atom; the former would enhance the acidity of the methyl protons, while the latter would act as a base. In our case, the proton seems to be removed from the co-ordinated acetone by an imine nitrogen, but unlike in the above mechanisms, the transferred proton remains bonded to the nitrogen atom, the acetone remains



Scheme 1. Reagents and conditions: i, room temp., 3 days; ii, Bu^tNC , room temp., 12 h; iii, refluxing CHCl_3 , 2 h; iv, Bu^tNC , refluxing acetone, 3 h.

[†] Complex (1) is the resulting species when $\text{fac}[\text{Mn}(\text{CO})_3(\text{Bu}^t\text{-N}=\text{CH}-\text{CH}=\text{N}-\text{Bu}^t)\text{O}(\text{ClO}_3)]$, {which is obtained by treating $\text{fac}[\text{Mn}(\text{CO})_3(\text{Bu}^t\text{-N}=\text{CH}-\text{CH}=\text{N}-\text{Bu}^t)\text{Br}^4]$ with AgClO_4 } is solvated in acetone.

[‡] Selected spectroscopic data for (2): $\nu(\text{NH})$ (KBr) 3218w, $\nu(\text{CO})$ (MeCN) 2042s, 1949s, 1929s, $\nu(\text{CO})$ (KBr) 1666m cm^{-1} ; $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN) δ 223.63, 223.56 (CH_2COMe), 174.56, 174.14 ($\text{HC}=\text{N}$), 56.8 ($\text{HC}-\text{N}$), 42.1 (CH_2COMe), 31.6 (CH_2COCH_3). For (3): $\nu(\text{NH})$ (KBr) 3229w, $\nu(\text{CN})$ (CH_2Cl_2) 2182m, $\nu(\text{CO})$ (CH_2Cl_2) 2051s, 1975s, 1942s, $\nu(\text{CO})$ (KBr) 1720m cm^{-1} ; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 206.8 (CH_2COMe), 173.2 ($\text{HC}=\text{N}$), 59.4 ($\text{HC}-\text{N}$), 44.5 (CH_2COMe), 30.5 (CH_2COCH_3). For (4) $\nu(\text{NH})$ (KBr) 3245m, $\nu(\text{CN})$ (CH_2Cl_2) 2156m, $\nu(\text{CO})$ 1950s, 1873s, $\nu(\text{CO})$ (KBr) 1667m cm^{-1} ; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 219.2 (CH_2COMe), 169.9 ($\text{HC}=\text{N}$), 55.6 ($\text{HC}-\text{N}$), 41.5 (CH_2COMe), 30.5 (CH_2COCH_3). For (5): $\nu(\text{NH})$ (KBr) 3251w, $\nu(\text{CN})$ (CH_2Cl_2) 2135m, $\nu(\text{CO})$ (CH_2Cl_2) 1975s, 1903s, $\nu(\text{CO})$ (KBr) 1725m cm^{-1} ; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 206.8 (CH_2COMe), 170.6 ($\text{HC}=\text{N}$), 59.1 ($\text{HC}-\text{N}$), 45.9 (CH_2COMe), 30.4 (CH_2COCH_3).

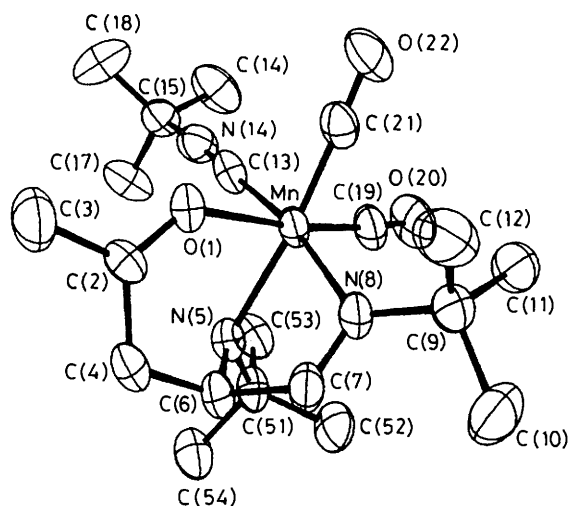


Figure 1. Structure of compound (4). Selected bond distances (Å) and dihedral angles (°): O(1)–Mn 2.099(3), N(5)–Mn 2.160(4), N(8)–Mn 2.084(4), C(6)–N(5) 1.506(6), C(7)–N(8) 1.263(6); N(5)–C(6)–C(7)–N(8) 25.52, Mn–N(5)–C(6)–C(7) –38.65, C(51)–N(5)–C(6)–C(4) –138.72.

O-bonded to the manganese, and the resulting acetyl group, MeCOCH₂, does not attack the metal but the imine carbon atom.

The ketone CO group of the tridentate ligand is smoothly replaced (12 h, room temp.) by Bu^tNC in complex (2) to afford *fac*-[Mn(CO)₃(CN–Bu^t){Bu^t–N=CH–CH(CH₂COMe)–N(H)–Bu^t}] [ClO₄], (3), where the new ligand acts in a bidentate mode. In refluxing chloroform, (3) loses a CO ligand and the ketone CO group becomes co-ordinated again, giving *cis*-[Mn(CO)₂(CN–Bu^t){Bu^t–N=CH–CH(CH₂COMe)–N(H)–Bu^t}] [ClO₄], (4). However, in the presence of Bu^tNC the reaction leads to *cis*, *trans*-[Mn(CO)₂(CN–Bu^t)₂{Bu^t–N=CH–CH(CH₂COMe)–N(H)–Bu^t}] [ClO₄], (5).

The structures of (4) and (5) have been established by X-ray diffraction methods,[§] and are shown in Figures 1 and 2

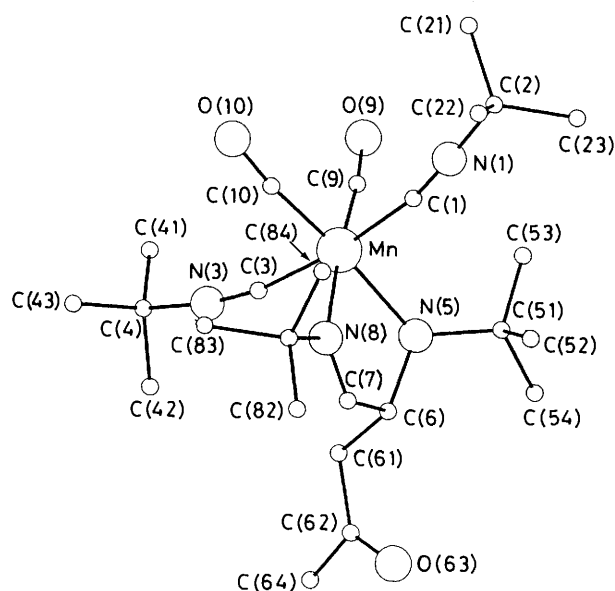


Figure 2. Structure of compound (5). Selected bond distances (Å) and dihedral angles (°): N(5)–Mn 2.188(2), N(8)–Mn 2.109(2), C(6)–N(5) 1.536(15), C(7)–N(8) 1.233(16); N(5)–C(6)–C(7)–N(8) 14.75, Mn–N(5)–C(6)–C(7) –25.72, C(51)–N(5)–C(6)–C(61) –124.78.

respectively. They confirm that the acetyl group is actually bonded to the carbon atom next to the amine nitrogen, and that the new ligand, Bu^t–N=CH–CH(CH₂COMe)–N(H)–Bu^t, acts in a tridentate [in (4)] or a bidentate [in (5)] fashion. As expected, the nitrogen and carbon atoms of the starting α -di-imine skeleton, N–C–C–N, are not in the same plane and the observed N–C distances are shorter in the imine fragments than in the amine groups. Moreover, the acetyl and the adjacent *t*-butyl groups point to opposite directions [in both (4) and (5)].

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[§] *Crystal data* for (4): C₂₀H₃₅N₃O₇ClMn, *M* = 519.91, monoclinic, space group *P*2₁/*a*, *a* = 14.618(4), *b* = 13.005(3), *c* = 13.967(4) Å, β = 94.43(3)°, *U* = 2647(2) Å³, *Z* = 4, *D*_c = 1.304 g cm⁻³, *F*(000) = 1096.0, (Mo–K α) = 0.71069 Å, μ (Mo–K α) = 6.67 cm⁻¹, 298 K. *R* = 0.066, *R*_w = 0.075. 3786 Reflections were measured in the range 2 ≤ θ ≤ 25°; 2900 with *I* ≥ 2.5 σ (*I*) were assumed observed. For (5): C₂₅H₄₄N₄O₇ClMn, *M* = 603.0, orthorhombic, space group *P*2₁2₁2₁, *a* = 16.299(3), *b* = 14.029(2), *c* = 14.321(2) Å, *U* = 3275(2) Å³, *Z* = 4, *D*_c = 1.223 g cm⁻³, *F*(000) = 1280.0 (Mo–K α) = 0.71069 Å, μ (Mo–K α) = 5.50 cm⁻¹, 298 K. *R* = 0.052, *R*_w = 0.058. 1834 Reflections were measured in the range 2 ≤ θ ≤ 25°; 1298 with *I* ≥ 2.5 σ (*I*) were assumed observed. For the determination of both structures, intensities were collected on a Philips PW-1100 four-circle diffractometer using the ω -scan technique, with scan width 0.8° and scan speed 0.03° s⁻¹. The structures were solved by direct methods using the MULTAN system, with refinement by the full-matrix least-squares method using the SHELX-76 computer program. 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.

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