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 But–N=CH–CH(CH₂COMe)–N(H)–But has been formed on intramolecular addition of acetone to an imine group of the co-ordinated diazabutadiene in fac-[Mn(CO)₃(But–N=CH–CH=N–But)(MeCOMe)][ClO₄], (1); the structures of cis-[Mn(CO)₂(CN–But){But–N=CH–CH(CH₂COMe)–N(H)–But}][ClO₄], (4), and cis, trans-[Mn(CO)₂(CN–But)₂{But–N=CH–CH(CH₂COMe)–N(H)–But}][ClO₄], (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 fac-[Mn(CO)₃(But–N=CH–CH=N–But)(MeCOMe)][ClO₄], (1),† in acetone at room temperature for 3 days, the compound fac-[Mn(CO)₃{But–N=CH–CH(CH₂COMe)–N(H)–But}][ClO₄], (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 fac-[Mn(CO)₃(But–N=CH–CH=N–But)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 ¹³C{¹H} 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

(1)   (2)

(3)

(4)   (5)
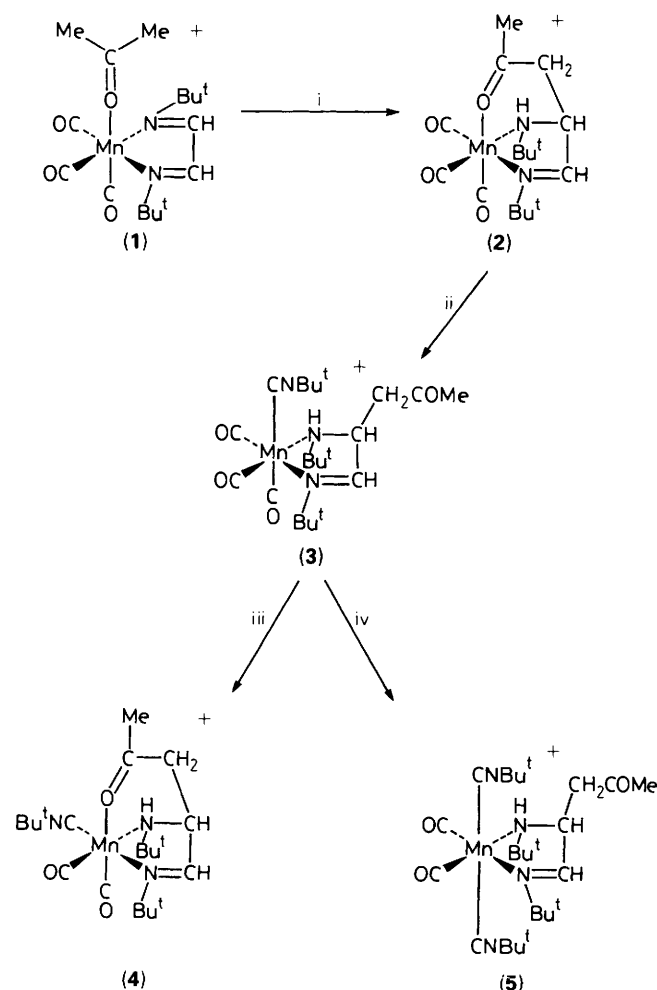
Scheme 1. Reagents and conditions: i, room temp., 3 days; ii, ButNC, room temp., 12 h; iii, refluxing CHCl₃, 2 h; iv, ButNC, refluxing acetone, 3 h.
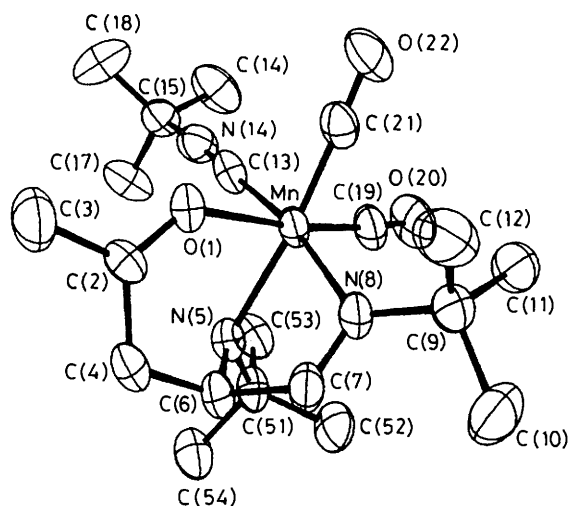
Figure 1. Structure of compound (4). Selected bond distances (Å) and dihedral angles (°): O(1)–Mn 2.099(3), N(5)–Mn 2.160(4), N(8)–Mn 2.084(4), C(6)–N(5) 1.506(6), C(7)–N(8) 1.263(6); N(5)–C(6)–C(7)–N(8) 25.52, Mn–N(5)–C(6)–C(7) −38.65, C(51)–N(5)–C(6)–C(4) −138.72.

O-bonded to the manganese, and the resulting acetonyl group, MeCOCH$_2$, 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^{t}NC in complex (2) to afford *fac*-[Mn(CO)$_3$(CN-Bu^t){Bu^t-N=CH-CH(CH$_2$-COMe)-N(H)-Bu^t}][ClO$_4$], (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(CH$_2$COMe)-N(H)-Bu^t}][ClO$_4$], (4). However, in the presence of Bu^{t}NC the reaction leads to *cis, trans*-[Mn(CO)$_2$(CN-Bu^t)$_2${Bu^t-N=CH-CH(CH$_2$COMe)-N(H)-Bu^t}][ClO$_4$], (5).

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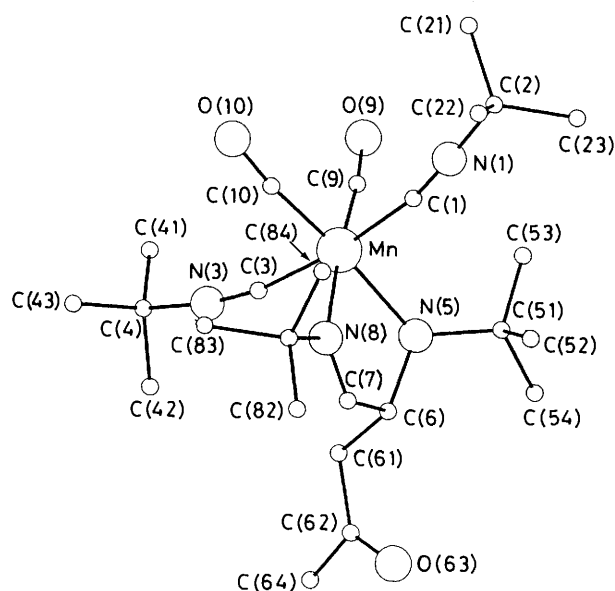

Figure 2. Structure of compound (5). Selected bond distances (Å) and dihedral angles (°): N(5)–Mn 2.188(2), N(8)–Mn 2.109(2), C(6)–N(5) 1.536(15), C(7)–N(8) 1.233(16); N(5)–C(6)–C(7)–N(8) 14.75, Mn–N(5)–C(6)–C(7) −25.72, C(51)–N(5)–C(6)–C(61) −124.78.

respectively. They confirm that the acetonyl group is actually bonded to the carbon atom next to the amine nitrogen, and that the new ligand, Bu^t-N=CH-CH(CH$_2$COMe)-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 acetonyl and the adjacent t-butyl groups point to opposite directions [in both (4) and (5)].

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