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Partial and Total Deprotonation of the Methyl Group of Acetone under Mild Conditions with Concomitant C−C and N−H Bond Formations

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Acetone adds intramolecularly to a coordinated diazabutadiene in *fac*-[Mn(CO)$_3$(^{t}BuN=CH-CH=N^{t}Bu)(CH$_3$COCH$_3$)]ClO$_4$, **2**, to yield *fac*-[Mn(CO)$_3${^{t}BuN=CHCH(CH$_2$COCH$_3$)N(H)^{t}Bu}]-ClO$_4$, **3**, a [3.2.1] bicyclic complex containing a ketone−amino−imino ligand. Compound **3** is deprotonated by KOH to give the enolate derivative *fac*-[Mn(CO)$_3${^{t}BuN=CHCH(CH=C-{O}CH$_3$)N(H)^{t}Bu}], **4**, which reacts with CN^{t}Bu to afford a [2.2.1] bicyclic complex, *fac*-[Mn-(CO)$_3${^{t}BuN=CHCH(C{=CN(H)^{t}Bu}COCH$_3$)N(H)^{t}Bu}], **5**. In each of these three reactions, an acetone methyl group loses a hydrogen and results overall in fully deprotonated **5**. On the other hand, the coordinated ketone carbonyl group in the *fac*-tricarbonyl complex **3** is smoothly replaced by CN^{t}Bu to generate another tricarbonyl derivative, *fac*-[Mn(CO)$_3$(CN-^{t}Bu){^{t}BuN=CHCH(CH$_2$COCH$_3$)N(H)^{t}Bu}]ClO$_4$, **6**, which reacts with a second isocyanide to give the dicarbonyl compound *cis,trans*-[Mn(CO)$_2$(CN^{t}Bu)$_2${^{t}BuN=CHCH(CH$_2$COCH$_3$)N(H)-^{t}Bu}]ClO$_4$, **7**. Upon heating, **6** loses a carbonyl CO ligand and rearranges to yield a [3.2.1] bicyclic dicarbonyl complex *cis*-[Mn(CO)$_2$(CN^{t}Bu){^{t}BuN=CHCH(CH$_2$COCH$_3$)N(H)^{t}Bu}]ClO$_4$, **8**. In complexes **6** and **7**, the acetone−amino−imino ligand acts in a N,N′-bidentate fashion, while in **8**, it acts again as a tridentate ligand. The structure of **5** has been determined by X-ray diffraction methods: $M = 446.44$, monoclinic, space group $P2_1/n$, $a = 8.530(2)$ Å, $b = 18.47(1)$ Å, $c = 15.375(8)$ Å, $\beta = 103.04(2)°$, $V = 2361(2)$ Å^3, $Z = 4$, $D_x = 1.25$ g cm^{-3}, Mo Kα radiation (graphite crystal monochromator, $\lambda = 0.710\ 73$ Å), $\mu = 5.63$ cm^{-1}, $F(000) = 948$, $T = 200$ K; final conventional R factor 0.028 for 3155 "observed" reflections and 365 parameters.

Introduction

The reactivity of coordinated ligands is a central issue of coordination and organometallic chemistry.[1] In particular, coordinated α-diimines show a rich chemistry, as they can undergo C−C, C−H, C−N, and N−H coupling reactions with a wide variety of organic substrates.[2] On the other hand, substitution reactions at the α-position of a carbonyl group such as aldol condensation with C−C bond formation are well-known in coordination chemistry.[3] However, carbon−hydrogen activation of acetone by intramolecular cooperation between a metal center and a ligand attached to it is very unusual.[4]

We wish to report here an intramolecular addition of acetone to an imine group of a coordinated diazabutadiene to form a highly asymmetric tridentate ligand and the subsequent studies carried out to explore its reactivity, specifically, its deprotonation by KOH, and the later C−H activation of the resulting enolate moiety which leads to a fully deprotonated acetone methyl group. Part of this work, showing the ability of the asymmetric ketone−amino−imino ligand to act in a bidentate and tridentate fashion, has been published previously.[5]

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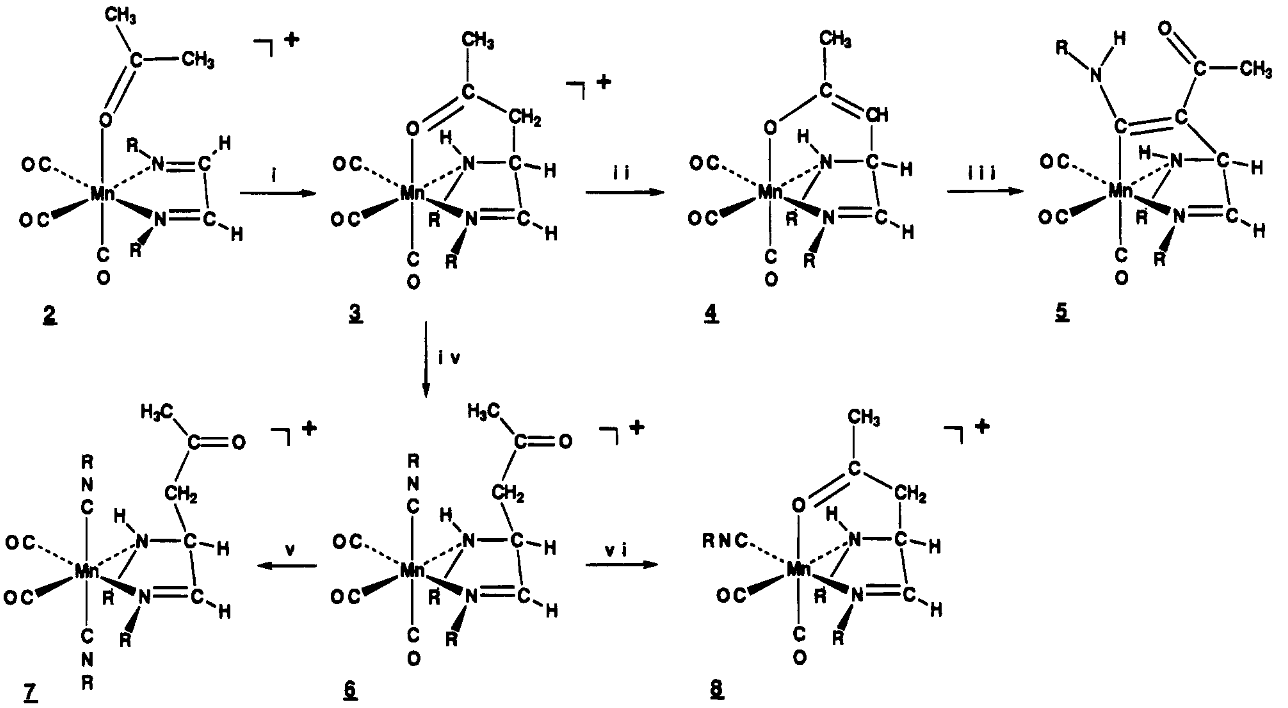
Scheme 1[a]



[a] Reagents and conditions: (i) stirring at room temperature, 3 days; (ii) KOH, room temperature, 15 min; (iii) CN^{t}Bu, room temperature, 30 h; (iv) CN^{t}Bu, room temperature 12 h; (v) CN^{t}Bu, refluxing acetone, 2.75 h; (vi) refluxing chloroform, 2 h.

Results and Discussion

In our work with manganese carbonyl complexes containing N,N-chelate ligands, we had observed that the reaction of *fac*-[Mn(CO)$_3$(^{t}BuN=CHCH=N^{t}Bu)(OClO$_3$)], **1**, with isocyanides, CNR, in acetone, gave the expected *fac*-[Mn(CO)$_3$(^{t}BuN=CHCH=N^{t}Bu)(CNR)]ClO$_4$,[6] but also small amounts of another product, which was not detected when the reaction was carried out in CH$_2$Cl$_2$. This prompted us to study the reaction of **1** with acetone.

As expected,[7] upon solution of *fac*-[Mn(CO)$_3$(^{t}BuN=CH-CH=N^{t}Bu)(OClO$_3$)], **1**, in acetone the perchlorate ligand is replaced by a solvent molecule to give *fac*-[Mn(CO)$_3$(^{t}BuN=CHCH=N^{t}Bu)(CH$_3$COCH$_3$)]ClO$_4$, **2**, as shown by conductivity measurements, $\Lambda_M = 130$ S cm^2 mol^{-1}. Stirring **2** for 3 days at room temperature leads to the formation of *fac*-[Mn(CO)$_3${^{t}BuN=CHCH(CH$_2$COCH$_3$)-N(H)^{t}Bu}]ClO$_4$, **3**, which can be isolated in good yield from the reaction mixture (i in Scheme 1).

The proposed structure for **3** is supported by spectroscopic data (see Table 1) and elemental analysis. Further support for the proposed structure arises from comparing these spectroscopic data with those of the related complex **8**, whose structure has been determined by X-ray diffraction studies, (see later). Thus, the ^{1}H NMR signal at 8.1 ppm and the ^{13}C NMR peak at 171.8 ppm are consistent with the presence of an imine group, HC=N. The IR ν_{CO} stretching band at 1666 cm^{-1}, as well as the sharp ^{13}C NMR resonance at 221.8 ppm are compatible with an oxygen-bonded acetone moiety. The IR band at 3218 cm^{-1} suggests the existence of a N—H bond. The ABX system at 3.2, 3.7, and 4.3 ppm in the ^{1}H NMR spectrum is concordant with the formation of a CH$_2$CH group. Finally, the three intense IR bands at 2045, 1956, and 1926 cm^{-1} indicate the presence of three carbonyl ligands in a *fac* disposition.

The acetone molecule which adds to the imine group in **2** to yield **3** should be the coordinated one rather than a solvent molecule (see Scheme 1), since *fac*-[Mn(CO)$_3$(^{t}BuN=CHCH=N^{t}Bu)Br][8] and *fac*-[Mn(CO)$_3$(CN^{t}Bu)(^{t}BuN=CHCH=N^{t}Bu)]ClO$_4$[6] remain unaltered after 10 days in acetone at room temperature.

The formation of **3** provides further support for some of the proposed mechanism for acetone intramolecular activation,[4] which suggests that this activation is the result of a cooperation between the metal center, to which the acetone is oxygen bonded, and a ligand 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 coordinated acetone by an imine nitrogen, but unlike in the above mechanisms, the transferred proton remains bonded to the nitrogen atom, the acetone remains O-bonded to the manganese, and the resulting acetone group CH$_3$COCH$_2$, does not attack the metal but the imine carbon atom.

Complex **3** possesses several acidic protons, but only one of the hydrogens in the methylene group of the ketone moiety is removed, when **3** is allowed to react with KOH in CH$_2$Cl$_2$ at room temperature, leading to the synthesis of the enolate derivative *fac*-[Mn(CO)$_3${^{t}BuN=CHCH(CH=C{O}CH$_3$)N(H)^{t}Bu}], **4**, in good yield (73%) (ii in Scheme 1). The product **4** was characterized spectroscopically (see Table 1) and by elemental analy-

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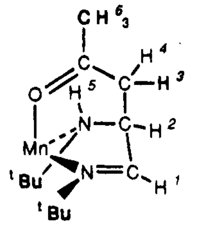
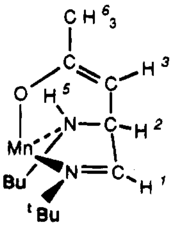
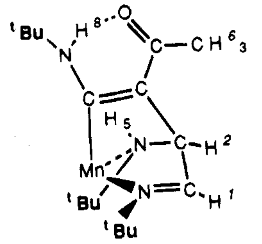
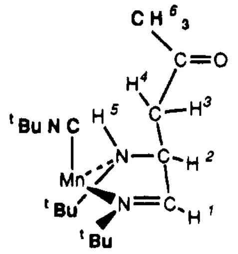
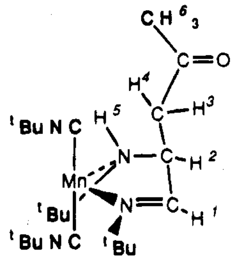
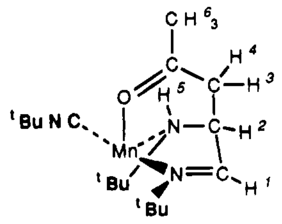
Table 1. Spectroscopic Data for the New Compounds

compound	infrared[a]	^{1}H NMR[b]	^{13}C{^{1}H} NMR[b]
 **3**	3218 w (ν_{NH}) 2046 s (ν_{CO}) 1958 s (ν_{CO}) 1929 s (ν_{CO}) 1666 m (ν_{CO})	8.1[c] (s, H^1) 4.7 (s, H^5) 3.2, 3.7, 4.3 {(H^3,H^4,H^2), ABX system, X = H^2 $\delta_A = 3.2$, $\delta_B = 3.7$, $\delta_X = 4.3$, $J_{AB} = 20$, $J_{BX} = 5$} 2.4 (s, H^6) 1.5 (s), 1.4 (s) {C(CH_3)$_3$}	221.8[c] (s,—C=O—Mn) 171.8 (s, CH^1) 65.4 (s), 59.3 (s) {C(CH$_3$)$_3$} 56.3 (s, CH^2) 41.6 (s, CH^3) 31.7 (s, CH^6_3) 30.7 (s), 27.8 (s) {(CH$_3$)$_3$}
 **4**	d 2021 s (ν_{CO}) 1919 s (ν_{CO}) 1896 s (ν_{CO}) 1640 m ($\nu_{C=C}$)	6.6[e] (d, H^1, $J_{H^2-H^1} = 2$) 3.7 (d, H^3, $J_{H^2-H^3} = 8$) 3.2 (s, H^5) 3.0 (dd, H^2, $J_{H^1-H^2} = 2$, $J_{H^3-H^2} = 8$) 2.0 (s, H^6) 1.2 (s), 0.8 (s) {(CH_3)$_3$}	167.9[f] {s, =C(—O)} 160.2 (s, CH^1) 75.3 (s, CH^3) 62.6 (s), 57.8 (s) {C(CH$_3$)$_3$} 59.1 (s, CH^2) 31.4 (s), 29.0 (s) {(CH$_3$)$_3$} 26.5 (s, CH^6_3)
 **5**	3197 w (ν_{NH}) 2005 s (ν_{CO}) 1913 s (ν_{CO}) 1890 s (ν_{CO})	13.6[c] (s, H^8) 7.9 (d, H^1, $J_{H^2-H^1} = 3$) 4.9 (d, H^2, $J_{H^1-H^2} = 3$) 2.7 (s, H^5) 2.0 (s, H^6) 1.5 (s), 1.4 (s), 1.2 (s) {(CH_3)$_3$}	238.5 (s, C=C—Mn) 181.9 (s, C=O) 166.3 (s, CH^1) 104.7 (s, C=C—Mn) 63.6 (s), 56.2 (s), 55.0 (s) {C(CH$_3$)$_3$} 62.9 (s, CH^2) 31.4 (s), 31.0 (s), 29.0 (s) {(CH$_3$)$_3$} 28.0 (s, CH^6_3)
 **6**	3229 w (ν_{NH}) 2177 m (ν_{CN}) 2044 s (ν_{CO}) 1977 s (ν_{CO}) 1944 s (ν_{CO}) 1720 m (ν_{CO})	7.9 (s, H^1) 4.8 (s, H^5) 4.5 (br, H^2) 3.5 (m, br, H^4) 3.2 (m, br, H^3) 2.3 (s, H^6) 1.6 (s), 1.5 (s), 1.3 (s) {(CH_3)$_3$}	206.8 (s, C=O) 173.2 (s, CH^1) 65.4 (s), 59.5 (s), 59.0 (s) {C(CH$_3$)$_3$} 60.1 (s, CH^2) 44.6 (s, CH^3) 30.6 (s, CH^6_3) 30.5 (s), 30.0 (s), 28.1 (s) {(CH$_3$)$_3$}
 **7**	3251 w (ν_{NH}) 2126 s (ν_{CN}) 1975 s (ν_{CO}) 1904 s (ν_{CO}) 1725 m (ν_{CO})	7.8 (s, H^1) 4.4 (br, H^2) 4.3 (s, H^5) 3.5 (dd, H^4, $J_{H^3-H^4} = 18$; $J_{H^2-H^4} = 2$) 3.2 (dd, H^3, $J_{H^4-H^3} = 18$; $J_{H^2-H^3} = 9$) 2.3 (s, H^6) 1.6 (s), 1.5 (s), 1.45 (s), 1.3 (s) {(CH_3)$_3$}	206.8 (s, C=O) 170.6 (s, CH^1) 64.8 (s), 58.8 (s), 58.5 (s), 58.0 (s) {C(CH$_3$)$_3$} 59.1 (s, CH^2) 45.9 (s, CH^3) 30.4 (s, CH^6_3) 30.6 (s), 30.3 (s), 30 (s), 28.2 (s) {(CH$_3$)$_3$}
 **8**	3245 w (ν_{NH}) 2151 m (ν_{CN}) 1955 s (ν_{CO}) 1878 s (ν_{CO}) 1677 m (ν_{CO})	8.0 (s, H^1) 4.4 (br), 4.4 (br) (H^2, H^5) 4.0 (d, H^4, $J_{H^3-H^4} = 22$) 3.0 (d, H^3, $J_{H^4-H^3} = 22$) 2.4 (s, H^6) 1.5 (s), 1.45 (s), 1.4 (s) {(CH_3)$_3$}	219.2 (s, C—O—Mn) 169.9 (s, CH^1) 64.4 (s), 58.4 (s), 58.2 (s) {C(CH$_3$)$_3$} 55.6 (s, CH^2) 41.5 (s, CH^3) 31.1 (s), 30.5 (s), 28 (s) {(CH$_3$)$_3$, CH^6_3}

[a] KBr dispersion for ν_{NH}, $\nu_{C=C}$, and ketone ν_{CO} absorptions. In CH_2Cl_2 for carbonyl ligand ν_{CO} bands. [b] In $CDCl_3$. For all NMR signals: δ in ppm, J in Hz. [c] CD_2Cl_2. [d] Several absorptions in the ν_{NH} range. [e] C_6D_6. [f] CH_2Cl_2/external D_2O.

sis. Thus, the ^{1}H NMR 3–5 ppm region contains only three signals, which correspond to the protons 2, 3, and 5 (see Table 1), instead of the four peaks observed for **3**. The ^{13}C NMR spectrum exhibits resonances at 167.9 and 75.3 ppm, which are assigned to the carbon atoms Mn—O—C=C and Mn—O—C=C, respectively, in the enolate moiety.[9] The three IR ν_{CO} bands of the carbonyl ligands appear at 2005, 1913, and 1890 cm^{-1}, at lower

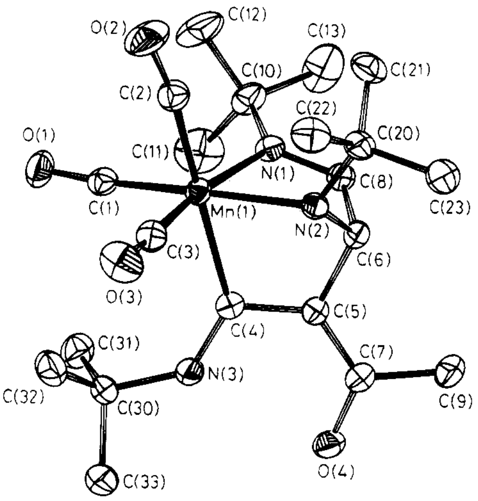


Figure 1. Diagram of the crystal structure of complex **5** as determined by single-crystal X-ray diffractometry. Protons are omitted for clarity.

wavenumbers than in **3** (2021, 1919, 1896 cm^{-1}), in accordance with the neutral nature of **4** and opposite to the cationic nature of **3**.

The tridentate ligand is further modified upon reaction of **4** with CN^{t}Bu in CH$_2$Cl$_2$, which leads to *fac*-[Mn(CO)$_3${^{t}BuN=CHCH(C{=CN(H)^{t}Bu}COCH$_3$)N(H)-^{t}Bu}], **5**, in good yield (76%) (iii in Scheme 1). The structure of **5** has been determined by X-ray difraction methods (see Figure 1). Its most prominent feature is certainly the resulting new tridentate ligand, and although two of the ligand arms are easily described as imine (C_6—C_8=N_1, in Figure 1) and amine (C_6—N_2, in Figure 1) moieties, the third fragment requires a more detailed description.

The atom arrangement in the third arm can be interpreted as the result of an isocyanide—enolate coupling, resulting in a C—C bond formation (C(5) – C(4), in Figure 1) and a hydrogen migration from the carbon atom of the former methyl group in the previously free acetone (C(5) in Figure 1) to the prior isocyanide nitrogen atom (N(3), in Figure 1). On the other hand, the atoms N(3), C(4), C(5), C(7), O(4), and H(3) in Figure 1, are roughly in the same plane, which can be explained by taking into account the existence of double bonds (C(4)=C(5) and C(7)=O(4)) and a hydrogen bond N(3)—H(3)—O(4). Actually, the double bonds should be delocalized to some extent along the C(4)—C(5)—C(7)—O(4) chain, since both the C(4)—C(5) and C(5)—C(7) distances, 1.423(3) and 1.415(3) Å, respectively, are long for a carbon—carbon double bond length, 1.34 Å, but short for sp^2 carbon—sp^2 carbon single bond, 1.48 Å,[10] and the C(7)—O(4) distance, 1.261(2) Å, is rather long for a carbon oxygen double bond, 1.20 Å.[10] The other interatomic distances fit well with single bond lengths, including the manganese vinyl carbon distance, Mn—C(4), 2.111(2) Å.[11]

The spectroscopic data for complex **5** are consistent with the solid state structure (see Table 1). Thus, the ^{13}C NMR resonance at 181.9 ppm, attributable to the carbonyl carbon of the former acetone, appears downfield of enolate carbon signal (167.9 ppm in complex **4**) but upfield of the uncoordinated ketone resonance (206.8 ppm in **6** and **7**, see later), which is in accordance with a C—O bond order between 1 and 2. On the other hand, the ^{13}C NMR peaks at 238.5 and 104.7 ppm, corresponding to the α and β vinyl carbons are in the low field extreme of the vinyl carbon resonances range.[12] The ^{1}H NMR low field resonance at 13.6 ppm as well as the IR ν_{NH} band at a rather low wavenumber, 3197 cm^{-1}, are in agreement with the presence of a N—H⋯O hydrogen bond.[13]

A possible mechanism for the formation of **5** is shown in Scheme 2. After the enolate moiety is replaced by the incoming isocyanide, the resulting intermediate **A** would tautomerize to **B**, where the carbanion would attack the isocyanide carbon, generating **C**, which would rearrange to yield **5**. The whole reaction could be interpreted as a typical double addition to an isonitrile carbon atom[14] followed by a hydrogen migration; that is, an electrophile (the manganese atom in **A**) and a

Table 2. Bond Lengths (Å) and Bond Angles (deg) with Esd's in Parentheses

Mn(1)—N(1)	2.102(2)	Mn(1)—N(2)	2.131(2)
Mn(1)—C(1)	1.780(2)	Mn(1)—C(2)	1.820(2)
Mn(1)—C(3)	1.790(2)	Mn(1)—C(4)	2.111(2)
O(1)—C(1)	1.160(3)	O(2)—C(2)	1.157(3)
O(3)—C(3)	1.152(3)	O(4)—C(7)	1.261(2)
N(1)—C(8)	1.279(3)	N(1)—C(10)	1.503(3)
N(2)—C(6)	1.494(3)	N(2)—C(20)	1.523(3)
N(3)—C(4)	1.340(3)	N(3)—C(30)	1.479(3)
C(4)—C(5)	1.423(3)	C(5)—C(6)	1.510(3)
C(5)—C(7)	1.415(3)	C(6)—C(8)	1.489(3)
C(7)—C(9)	1.511(3)	C(10)—C(11)	1.532(4)
C(10)—C(12)	1.513(4)	C(10)—C(13)	1.518(4)
C(20)—C(21)	1.519(3)	C(20)—C(22)	1.522(3)
C(20)—C(23)	1.537(3)	C(30)—C(31)	1.519(3)
C(30)—C(32)	1.527(3)	C(30)—C(33)	1.531(3)

N(2)—Mn(1)—N(1)	79.9(1)	C(1)—Mn(1)—N(1)	98.4(1)
C(1)—Mn(1)—N(2)	177.5(1)	C(2)—Mn(1)—N(1)	95.4(1)
C(2)—Mn(1)—N(2)	98.8(1)	C(2)—Mn(1)—C(1)	83.1(1)
C(3)—Mn(1)—N(1)	170.7(1)	C(3)—Mn(1)—N(2)	91.3(1)
C(3)—Mn(1)—C(1)	90.3(1)	C(3)—Mn(1)—C(2)	88.6(1)
C(4)—Mn(1)—N(1)	85.5(1)	C(4)—Mn(1)—N(2)	78.9(1)
C(4)—Mn(1)—C(1)	99.2(1)	C(4)—Mn(1)—C(2)	177.4(1)
C(4)—Mn(1)—C(3)	90.1(1)	C(8)—N(1)—Mn(1)	109.6(1)
C(10)—N(1)—Mn(1)	131.1(1)	C(10)—N(1)—C(8)	119.1(2)
C(6)—N(2)—Mn(1)	97.4(1)	C(20)—N(2)—Mn(1)	126.1(1)
C(20)—N(2)—C(6)	116.5(2)	C(30)—N(3)—C(4)	134.0(2)
O(1)—C(1)—Mn(1)	172.5(2)	O(2)—C(2)—Mn(1)	170.4(2)
O(3)—C(3)—Mn(1)	177.6(2)	N(3)—C(4)—Mn(1)	135.6(2)
C(5)—C(4)—Mn(1)	108.7(1)	C(5)—C(4)—N(3)	115.5(2)
C(6)—C(5)—C(4)	112.8(2)	C(7)—C(5)—C(4)	126.1(2)
C(7)—C(5)—C(6)	121.1(2)	C(5)—C(6)—N(2)	106.3(2)
C(8)—C(6)—N(2)	108.5(2)	C(8)—C(6)—C(5)	106.3(2)
C(5)—C(7)—O(4)	123.4(2)	C(9)—C(7)—O(4)	116.7(2)
C(9)—C(7)—C(5)	120.0(2)	C(6)—C(8)—N(1)	117.6(2)
C(11)—C(10)—N(1)	106.5(2)	C(12)—C(10)—N(1)	108.3(2)
C(12)—C(10)—C(11)	110.7(2)	C(13)—C(10)—N(1)	113.0(2)
C(13)—C(10)—C(11)	109.7(3)	C(13)—C(10)—C(12)	108.6(2)
C(21)—C(20)—N(2)	111.7(2)	C(22)—C(20)—N(2)	106.2(2)
C(22)—C(20)—C(21)	111.1(2)	C(23)—C(20)—N(2)	110.4(2)
C(23)—C(20)—C(21)	109.2(2)	C(23)—C(20)—C(22)	108.1(2)
C(31)—C(30)—N(3)	110.1(2)	C(32)—C(30)—N(3)	112.6(2)
C(32)—C(30)—C(31)	111.8(2)	C(33)—C(30)—N(3)	105.1(2)
C(33)—C(30)—C(31)	108.6(2)	C(33)—C(30)—C(32)	108.4(2)

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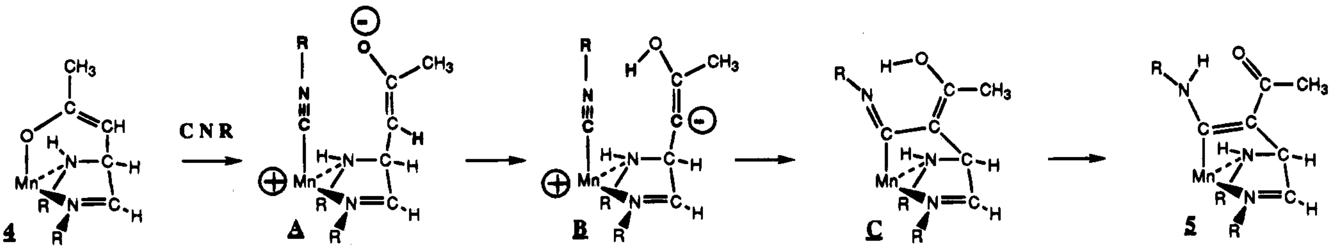
Scheme 2. Proposed Mechanism for the Formation of 5



nucleophile (the enolate carbanion in **B**) add to the isocyanide carbon atom, originating **C**, which then rearranges to give **5**. The conversion of **A** into **B** and that of **C** into **5** can be seen as en−ol tautomerizations, although in the last step the hydrogen atom migrates from the oxygen to a close nitrogen atom and not to the appropriate carbon atom.

It should be emphasized that the formation of complex **5** implies the total deprotonation of an acetone methyl group in three steps, corresponding to the synthesis of compounds **3**−**5**, respectively. This is even more remarkable because of the very mild conditions of the first and last steps.

Compound **3** shows another kind of reactivity. In fact, the ketone CO group in **3** is smoothly replaced by CN^tBu in acetone to afford *fac*-$[Mn(CO)_3(CN^tBu)\{^tBuN{=}CHCH(CH_2COCH_3)N(H)^tBu\}]ClO_4$, **6**, in 73% yield (iv in Scheme 1). Complex **6** has been characterized by IR and ^1H and ^{13}C NMR spectroscopies (see Table 1) and by elemental analysis. The proposed structure for **6** is also supported by comparison of its spectroscopic data with those of complex **7**, whose structure has been determined by single-crystal X-ray diffraction studies (see later). In particular, the IR ν_{CN} absorption at 2177 cm^{-1} and the three ν_{CO} bands at 2044, 1977, and 1944 cm^{-1} indicate that four of the six coordination positions are occupied by the isocyanide and three mutually cis carbonyl ligands, and therefore the ketone−amino−imino ligand should act in a bidentate fashion. This is supported by the IR ν_{CO} band at 1720 cm^{-1} and the ^{13}C NMR resonance at 206.8 ppm, which are consistent with a free, noncoordinated, ketone group.

Heating **6** in refluxing acetone in the presence of CN^tBu leads to the formation of *cis,trans*-$[Mn(CO)_2(CN^tBu)_2\{^tBuN{=}CHCH(CH_2COCH_3)N(H)^tBu\}]ClO_4$, **7**, in 76% yield (v in Scheme 1). The structure of **7** has been determined by X-ray crystallography.[5] The spectroscopic data (see Table 1) are in accordance with the solid state geometry. Thus, for example, the single IR ν_{CN} absorption at 2126 cm^{-1} is in agreement with a trans disposition of the two isocyanide ligands, while the two IR ν_{CO} bands at 1975 and 1904 cm^{-1} are consistent with the presence of two mutually cis carbonyl ligands; in a similar way, the IR ν_{CO} absorption at 1725 cm^{-1} and the ^{13}C NMR signal at 206.8 ppm are in accordance with a free ketone group.

Heating **6** in refluxing chloroform results in the formation of *cis*-$[Mn(CO)_2(CN^tBu)\{^tBuN{=}CHCH(CH_2COCH_3)N(H)^tBu\}]ClO_4$, **8**, in good yield (82%) (vi in Scheme 1). The structure of **8** has been obtained by single-crystal X-ray diffraction studies.[5] The spectroscopic data (see Table 1) are in agreement with the solid state structure. Thus, for instance, the IR ν_{CO} absorption at 1677 cm^{-1} and the ^{13}C NMR signal at 219.2 ppm are consistent with an oxygen coordinated ketone carbonyl group; the single IR ν_{CN} band at 2151 cm^{-1} and the two ν_{CO} IR bands at 1955 and 1878 cm^{-1} are compatible with the presence of an isocyanaide and two mutually cis carbonyl ligands.

A plausible mechanism for the formation of **8** could be envisioned in the following way: after the loss of one carbonyl CO ligand, the isocyanide moves to a position trans to the imine moiety, the ketone carbonyl group occupying the vacant position in the manganese coordination sphere, yielding **8**. The CO loss, a very common event upon heating carbonyl complexes, is probably the first step. Isocyanide migrations following decarbonylation are well documented in manganese carbonyl complexes containing N,N-chelate ligands;[6] in those cases the isocyanide and the chelate nitrogen atoms are proposed to be located in basal positions in the intermediate square pyramid.

The formation of **3** and **6**−**8** indicate the versatility of the ketone−amino−imino tridentate ligand, which is able to act in a bidentate (**6** and **7**) or tridentate fashion (**3** and **8**). The adaptability of the ligand certainly arises from the lability of the ketone group.[7]

Experimental Section

All reactions were carried out under a nitrogen atmosphere and in the absence of light. Solvents were dried and distilled under nitrogen. Petroleum ether was a fraction with bp 62−66 °C. Acetone, HPLC grade, was purchased from S.D.S. and used as received. Infrared spectra were recorded on a Perkin-Elmer 1720-X infrared spectrophotometer. Proton and carbon magnetic resonance spectra (NMR) were measured on a Bruker AC-300 instrument at 300.13 and 75.47 MHz, respectively. Chemical shifts are referred to internal TMS. ^{13}C NMR assignments are supported by DEPT experiments. Elemental analyses were obtained with a Perkin-Elmer 240-B microanalyzer.

Preparation of *fac*-$[Mn(CO)_3(^tBuN{=}CHCH{=}NH^tBu)(OClO_3)]$ (1). A mixture of *fac*-$[Mn(CO)_3(^tBuN{=}CHCH{=}N^tBu)Br]$ (0.30 g, 0.77 mmol), and $AgClO_4$ (0.177 g, 0.85 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 1 h. After filtration through Celite to eliminate the precipitated AgBr and the excess of silver perchlorate, the solvent was removed in vacuo and the residue was stirred with petroleum ether (30 mL) to give an orange solid (0.28 g, 90% yield). Anal. Calcd for $C_{13}H_{20}N_2O_7ClMn$ (**1**): C, 38.39; H, 4.96; N, 6.89. Found: C, 38.37; H, 5.09; N, 6.71. Infrared ν_{CO} bands (CH_2Cl_2, in cm^{-1}): 2045 (s), 1937 (s).

Preparation of *fac*-$[Mn(CO)_3\{^tBuN{=}CHCH(CH_2COCH_3)N(H)^tBu\}]ClO_4$, (3). A solution of *fac*-$[Mn(CO)_3(^tBuN{=}CHCH{=}N^tBu)(OClO_3)]$, **1** (0.30 g, 0.74 mmol), in acetone (30 mL) was stirred at room temperature for 3 days. After the solvent was evaporated, the residue was washed three times with petroleum ether (3 × 20 mL), giving a yellow solid (0.32 g, 93% yield). Crystallization from acetone/petroleum ether afforded yellow needles. Anal. Calcd for $C_{16}H_{26}N_2O_8ClMn$ (**3**): C, 41.35; H, 5.64; N, 6.03. Found: C, 41.23; H, 5.81; N, 6.06.

Note: Apparently, the acetone solvent should be HPLC quality; otherwise nonreproducible results can be obtained.

In the preliminary communication,[5] it was stated that the ^{13}C NMR of **3** in CD$_3$CN exhibits two close peaks for the ketone (at 223.6 and 223.6 ppm) and the imine (174.6 and 174.1 ppm) carbon atoms. However, only single peaks for these carbon atoms are observed in the ^{13}C NMR spectra of **3** in CD$_2$Cl$_2$ (see Table 1) and in CH$_3$CN/external D$_2$O (223.9 and 174.7 ppm); therefore it seems likely that those reported double peaks were rather artifacts.

Preparation of *fac*-[Mn(CO)$_3${^{t}BuN=CHCH(CH=C{O}-CH$_3$)N(H)^{t}Bu}]ClO$_4$ (4). A solution of *fac*-{Mn(CO)$_3${^{t}Bu-N=CHCH(CH$_2$COCH$_3$)N(H)^{t}Bu}]ClO$_4$, **3** (0.40 g, 0.86 mmol), in CH$_2$Cl$_2$ (50 mL) was stirred with KOH pellets (0.73 g, 13 mmol) for 15 min. After being transferred through a steel cannula, the solvent was evaporated to dryness and the residue dissolved in petroleum ether (40 mL). The resulting solution was then transferred again through a steel cannula, concentrated under reduced pressure, and stored in the refrigerator at −20 °C to give yellow crystals (0.23 g, 73% yield). Anal. Calcd for C$_{16}$H$_{25}$N$_2$O$_4$Mn (**4**): C, 52.75; H, 6.92; N, 7.69. Found: C, 52.45; H, 6.61; N, 7.46.

Preparation of *fac*-[Mn(CO$_3${^{t}BuN=CHCH(C{=CN-(H)^{t}Bu}COCH$_3$)N(H)^{t}Bu}] (5). CN^{t}Bu (0.10 mL, 0.88 mmol, d = 0.736 g/mL) was added to a solution of *fac*-[Mn(CO)$_3$-{^{t}BuN=CHCH(CH=C{O}CH$_3$)N(H)^{t}Bu}]ClO$_4$, **4** (0.15 g, 0.412 mmol), in CH$_2$Cl$_2$ (30 mL), and the resulting mixture was stirred for 30 h. After the solvent was removed, the residue was washed with petroleum ether (3 × 2 mL), affording a yellow solid (0.14 g, 76% yield). Crystals of **5**, suitable for X-ray diffraction studies, were obtained from CH$_2$Cl$_2$/diethyl ether at room temperature. Anal. Calcd for C$_{21}$H$_{34}$N$_3$O$_4$Mn (**5**): C, 56.37; H, 7.66; N, 9.39. Found: C, 56.29; H, 7.33; N, 9.33.

Preparation of *fac*-[Mn(CO)$_3$(CN^{t}Bu){^{t}BuN=CHCH-(CH$_2$COCH$_3$)N(H)^{t}Bu}]ClO$_4$ (6). A mixture of *fac*-[Mn(CO)$_3${^{t}-BuN=CHCH(CH$_2$COCH$_3$)N(H)^{t}Bu}]ClO$_4$, **3** (0.15 g, 0.32 mmol), and CN^{t}Bu (0.073 mL, 0.65 mmol, d = 0.736 g/mL) in acetone (20 mL) was stirred for 12 h. After evaporation of the solvent, the resulting oil was washed with petroleum ether (3 × 15 mL) to eliminate the excess of isocyanide. Recrystallization from CH$_2$Cl$_2$/diethyl ether at −20 °C afforded **6** as yellow crystals (0.13 g, 73% yield). Anal. Calcd for C$_{21}$H$_{35}$N$_3$O$_8$ClMn (**6**): C, 46.03; H, 6.44; N, 7.67. Found: C, 45.85; H, 6.67; N, 7.70.

Preparation of *cis,trans*-[Mn(CO)$_2$(CN^{t}Bu)$_2${^{t}BuN=CH-CH(CH$_2$COCH$_3$)N(H)^{t}Bu}]ClO$_4$ (7). CN^{t}Bu (0.16 mL, 1.42 mmol, d = 0.736 g/mL) was added to a solution of *fac*-[Mn-(CO)$_3$(CN^{t}Bu){^{t}BuN=CHCH(CH$_2$COCH$_3$)N(H)^{t}Bu}]ClO$_4$, **6** (0.2 g, 0.365 mmol), in acetone (30 mL), and the resulting mixture was heated under reflux for 2 h 45 min. After the solvent was removed, the residue was washed with petroleum ether (4 × 10 mL) to remove the excess of isocyanide. Recrystallization from CH$_2$Cl$_2$/diethyl ether at −20 °C gave yellow crystals of **7** (0.165 g, 76% yield). Anal. Calcd for C$_{25}$H$_{44}$N$_4$O$_7$ClMn (**7**): C, 49.79; H, 7.35; N, 9.29. Found: C, 50.01; H, 7.34; N, 9.33.

Preparation of *cis*-[Mn(CO)$_2$(CN^{t}Bu){^{t}BuN=CHCH-(CH$_2$COCH$_3$)N(H)^{t}Bu}]ClO$_4$ (8). A solution of *fac*-[Mn(CO)$_3$(CN^{t}Bu){^{t}BuN=CHCH(CH$_2$COCH$_3$)N(H)^{t}Bu}]ClO$_4$, **6** (0.15 g, 0.27 mmol), in chloroform (30 mL) was heated under reflux for 2 h. After filtration through Celite, petroleum ether (50 mL) was added and the resulting mixture was stored at −20 °C until orange crystals of **8** were obtained (0.1117 g, 82% yield). Anal. Calcd for C$_{20}$H$_{35}$N$_3$O$_7$ClMn (**8**): C, 46.21; H, 6.79; N, 8.08. Found: C, 46.39; H, 6.71; N, 7.99.

X-ray Data Collection, Structure Determination, and Refinement for Complex 5. A yellow crystal of dimensions 0.29 × 0.16 × 0.06 mm was mounted on a Enraf-nonius CAD-4 difractometer. Intensity data were collected using graphite-monochromated Mo Kα radiation. Unit cell dimensions were obtained using the setting angles of 25 reflections in the range 15° < θ < 20°. On the basis of systematic absences the space group was determined to be $P2_1/n$. A total of 4777 reflections were measured within the ***hkl*** range (0,0,−18) to (10,21,17) and 0° < θ < 25°. The $\omega-2\theta$ scan technique with a variable scan speed and a maximum scan time of 60 s/reflection was used. The intensity was checked by monitoring three standard reflections every 60 min. Final drift corrections were between 0.98 and 1.02. On all reflections profile analyses were performed.[15,16] Some double measured reflections were averaged, $R_{\mathrm{int}} = \Sigma(I - \langle I\rangle)/\Sigma I = 0.017$, resulting in 4148 unique reflections of which only 3155 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied, and data were reduced to $|F_o|$ values. The structure was solved by Patterson techniques using the program SHELXS86[17] and expanded by DIRDIF.[18] Isotropic least-squares refinement, using SHELX76[19] converged to R = 0.080. At this stage an empirical absorption correction was applied using DIFABS,[20] giving correction factors from 0.91 to 1.10, and as a result, a further decrease of R to 0.074 was observed. Anisotropic refinements followed by a difference Fourier synthesis allowed the location of some hydrogen atoms; the rest were geometrically placed, and all of them were refined riding on their parent atoms. All nonhydrogen atoms were anisotropically refined.

The final agreement factors were $R = 0.028$ and $wR = 0.030$ for the 3155 observed reflections and 365 parameters; this low ratio reflection/parameter led to rather high standard deviations in the structural calculations. The minimized function was $\Sigma w(F_o - F_c)^2$, with $w = 1/[\sigma^2(F_o) + 0.00025F_o^2]$, $\sigma(F_o)$ being derived from counting statistics. The maximum shift to esd ratio in the last full-matrix least-squares cycle was less than 0.005. The final difference Fourier map showed no peaks higher than 0.30 e Å^{-3} nor deeper than −0.35 e Å^{-3}. Atomic scattering factors were taken from ref 21. The plot was made with EUCLID.[22] Geometrical calculations were made with PARST.[23] All calculations were made on a MicroVax 3400 at the Scientific Computer Center of the University of Oviedo.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic temperature factors, torsion angles, and least-squares planes (13 pages). Ordering information is given on any current masthead page.

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