Reaction of CO and *tert*-Butyl Isocyanide with the Cluster [(C₅Me₅)₃Co₃(μ₂-H)₃(μ₃-H)];
Facile Hydrogen Transfer to Isocyanide forms [(C₅Me₅)₃Co₃(μ-H)(μ₃-η²-HC=NCMe₃)]

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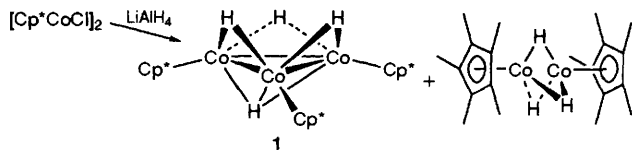
The reaction of [(C₅Me₅)₃Co₃(μ₂-H)₃(μ₃-H)] 1 with 2 equiv. of CO forms the biscarbonyl dihydride cluster [(C₅Me₅)₃Co₃(μ₃-CO)(μ₂-CO)(μ-H)₂] 2; *tert*-butyl isocyanide inserts into a Co–H bond of 1 to form the formimidoyl monohydride cluster [(C₅Me₅)₃Co₃(μ-H)(μ₃-η²-HC=NCMe₃)] 5, *via* the intermediate [(C₅Me₅)₃Co₃(μ₃-CNCMe₃)(μ₂-CNCMe₃)(μ-H)₂] 6.

In collaboration with Theopold and coworkers, we recently reported the synthesis of the unusual trinuclear tetrahydride cluster, [(C₅Me₅)₃Co₃(μ₂-H)₃(μ₃-H)] 1 and the dinuclear trihydride complex [(C₅Me₅)₂Co₂(μ-H)₃], from the reaction of [(C₅Me₅)CoCl]₂ with LiAlH₄ (Scheme 1).[1] Complex 1 is a reactive,[2] 46 electron cluster, which reacted rapidly with 1 atm CO at room temperature to fragment the cluster and produce mononuclear [(C₅Me₅)Co(CO)₂] 3 and H₂.[1] Here we report that 1 reacts with 2 equiv. of CO to form the 48 electron dicarbonyl dihydride cluster, [(C₅Me₅)₃Co₃(μ₃CO)(μ₂-CO)(μ-H)₂] 2. 1 also reacts with *tert*-butyl isocyanide at low temperature to form the analogous isocyanide cluster [(C₅Me₅)₃Co₃(μ₃-CNCMe₃)(μ₂-CNCMe₃)(μ-H)₂] 6, which was observed by low-temperature ¹H NMR spectroscopy. 6 rapidly inserts an isocyanide ligand into a cobalt–hydrogen bond of 6 to form the 48 electron formimidoyl cluster

[(C₅Me₅)₃Co₃(μ-H)(μ₃-η²-HC=NCMe₃)] 5, which was characterized by X-ray crystallography.

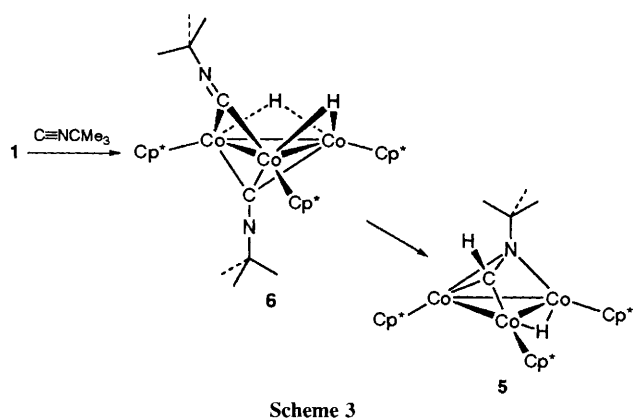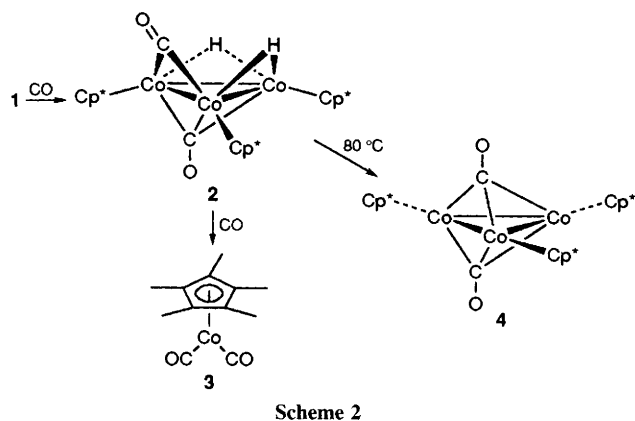Reaction of tetrahydride 1 with 2 equiv. of CO at room temperature led to the isolation of the 48 electron dicarbonyl dihydride cluster 2† in 60% yield (Scheme 2). In the IR spectrum of 2, intense absorbances at 1778 and 1652 cm⁻¹ indicated the presence of both a double bridged and triple bridged CO ligand. The ¹H NMR spectrum in C₆D₆ displayed a 2:1 ratio of C₅Me₅ peaks and a characteristic resonance for the μ-H ligands at δ −32.26. The ¹³C NMR spectrum displayed a single CO resonance at δ 270.9, indicating that the interconversion of the μ₂-CO and μ₃-CO ligands is rapid at room temperature. 2 is very similar to the clusters [(C₅Me₅)₃Rh₂M(μ₃-CO)(μ₂-CO)(μ-H)₂] (M = Co, Ir, Rh) reported by Stone *et al.*[3]

A C₆D₆ solution of 1 was monitored by ¹H NMR spectroscopy as small amounts (4 additions of < 1 equiv. CO) were progressively added. During the conversion of 1 to 2, only

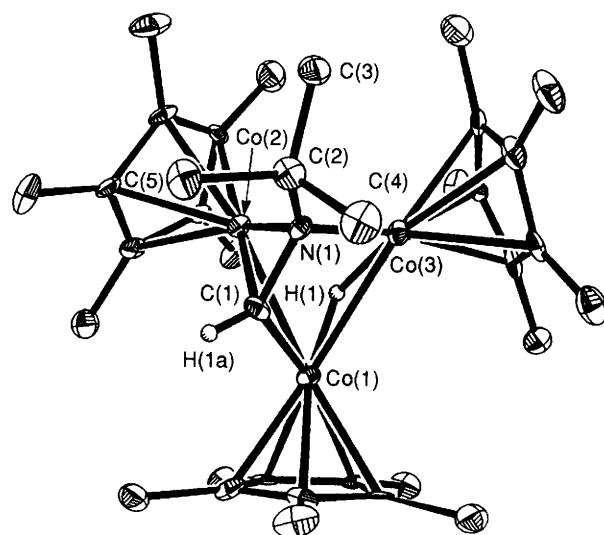[Cp*CoCl]₂ —LiAlH₄→

Scheme 1

Scheme 2

Scheme 3

Fig. 1 X-Ray crystal structure of **5**. Selected bond lengths (Å) and angles (°): Co(1)–Co(2) 2.557(1), Co(1)–Co(3) 2.621(1), Co(2)–Co(3) 2.525(1), Co(1)–C(1) 1.842(6), Co(2)–C(1) 1.968(5), Co(2)–N(1) 1.972(4), Co(3)–N(1) 1.912(4), C(1)–N(1) 1.346(7), Co(1)–C(1)–Co(2) 84.2(2), Co(2)–N(1)–Co(3) 81.1(2), C(1)–N(1)–C(2) 120.7(4), C(1)–Co(2)–N(1) 40.0(2), Co(1)–C(1)–N(1) 115.1(4), Co(3)–N(1)–C(1) 104.7(3), Co(2)–N(1)–C(2) 133.5(3) Co(3)–N(1)–C(2) 129.1(3).

C_5Me_5 signals for **1** (δ 62) and **2** (δ 1.56 and 1.63) were observed. The C_5Me_5 signal for $(C_5Me_5)Co(CO)_2$ (δ 1.59) was observed only after cluster **1** had been completely converted to **2**. Isolated **2** was quantitatively (96 ± 5% by ^1H NMR) converted to **3** upon exposure to 1 atm CO at room temperature for 1 h. These experiments demonstrate that CO reacts much faster with the 46 electron cluster **1** than with the 48 electron cluster **2** and that **2** is an intermediate in the formation of **3**.

When a C_6D_6 solution of **2** was heated at 80 °C in a sealed tube for 12 h, the known 46 electron dicarbonyl cluster, $[(C_5Me_5)_3Co_3(\mu_3\text{-}CO)_2]$ **4**[4] was formed nearly quantitatively [92 ± 5% by ^1H NMR; ^1H NMR (C_6D_6) δ 3.39; IR (hexane) 1681 cm^{-1}]. GC‡ of the gases over the solution showed the presence of H_2 and comparison with standard mixtures indicated a 3 : 1.5 ± 0.5 ratio of Co : H (75% yield of H_2 from **2**).

Because isocyanides are isoelectronic with CO, we expected the reaction of *tert*-butyl isocyanide with **1** to parallel the reaction of CO with **1**. In contrast, a surprisingly facile insertion of the isocyanide into a cobalt–hydrogen bond of **1** occurred. Reaction of **1** with 2.5 equiv. of *tert*-butyl isocyanide in benzene at room temperature for 12 h led to the isolation of the 48 electron formimidoyl cluster $[(C_5Me_5)_3Co_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HC=NCMe_3)]$ **5**§ in 52% yield (Scheme 3). X-Ray crystallo-

graphic analysis of **5** (Fig. 1) revealed a triangle of cobalt atoms capped on one face by an η^2-formimidoyl ligand bonded to all three cobalt atoms. The structure of the tricobalt core and bridging atoms of **5** is very similar to that of related clusters of Os,[5] Fe,[6] Re[7] and Ru.[8] The bridging hydride of **5** is intermediate between μ_2 and μ_3. While the projection of the hydride onto the tricobalt plane lies 0.19 Å within the tricobalt triangle, there are two short [1.41(5) and 1.65(5) Å] and one long [2.01(5) Å] Co–H distances.

Migratory insertion of CO into a M–H bond has been proposed as a key step in the catalytic hydrogenation of CO.[9] The direct insertion of isocyanide into a cobalt–hydrogen bond of **1** is therefore of interest as an analogue to cluster-catalysed CO reduction.[10] The insertion of isocyanide into a metal hydrogen bond of a trimetallic cluster has been previously observed for carbonyls of Fe,[11] Re,[7,12] Ru[13] and Os.[5] Owing to the importance of this facile insertion, we searched for intermediates in the reaction of **1** with *tert*-butyl isocyanide.

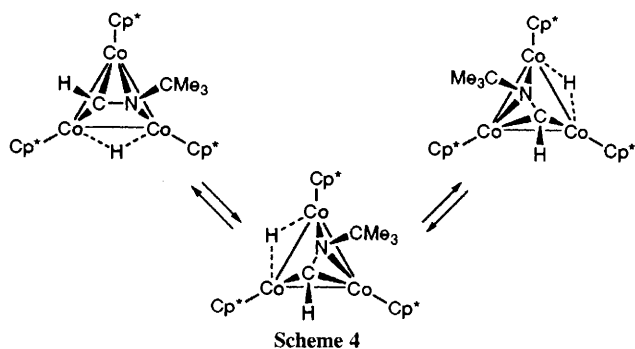When a [$^2H_8$]toluene solution of **1** and an excess of *tert*-butyl isocyanide was warmed from −80 to −35 °C and monitored by ^1H NMR spectroscopy, two new C_5Me_5 signals at δ 1.95 and 1.59 in a 2 : 1 ratio began to appear after 15 min, along with the C_5Me_5 signal for **5** (δ 1.86). The relative integration of the two signals reached a maximum of 35% after 2 h and then gradually decreased; the 2 : 1 ratio of the two signals remained constant throughout. The C_5Me_5 resonances at δ 1.95 (30 H) and 1.59 (15 H) and signals at 1.13 (18 H) and −20.05 (2 H) are assigned to the 48 electron bis(isocyanide) cluster **6**. The formation of **5** from **6** can be explained by insertion of one isocyanide into a cobalt–hydrogen bond to give the unobserved $[(C_5Me_5)_3Co_3(\mu\text{-}CNCMe_3)(\mu\text{-}H)(\mu_2\text{-}\eta^2\text{-}HC=NCMe_3)]$, followed by expulsion of isocyanide to generate **5**. Although the structure of **6** rests solely on spectroscopic data, the proposed structure is supported by the close analogy to the isoelectronic biscarbonyl cluster **2**.

Scheme 4

Although the solid-state structure of **5** clearly shows the presence of three nonequivalent C$_5$Me$_5$ ligands, the room temperature ^{1}H NMR spectrum of **5** in [^{2}H$_8$]-toluene displayed a single sharp resonance for the C$_5$Me$_5$ ligands at δ 1.88, and a single resonance for the *tert*-butyl group at δ 1.57. At −85 °C the C$_5$Me$_5$ ligands appeared as a 1 : 2 ratio of peaks at δ 1.94 and 1.81; this is consistent with a process in which a single terminus of the formimidoyl ligand oscillates between two cluster edges in concert with hydride migration between the same two edges (Scheme 4). However, we cannot distinguish which terminus of the formimidoyl ligand is fluctional. Similar 'windshield wiper' fluctuation has been observed in clusters possessing μ$_3$-η^2-formimidoyl,[7,11a,b] aminoacyl,[8,14] and alkynyl[15] ligands. Surprisingly, at −85 °C the *tert*-butyl resonance also appeared as a 2 : 1 ratio of peaks at δ 1.51 and 1.44, consistant with hindered rotation of the *tert*-butyl group.

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