

Oxygen initiated unprecedented condensation of propargylamine into the 1,3-di(propargylimino)propylateanion coordinated to cobalt(III)

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Condensation of coordinated propargylamine into the unprecedented 1,3-di(propargylimino)propylateanion, an analogue of the acetylacetonate anion, is initiated by dioxygen in the Co(II) polymeric trimethylacetate complex/ $\text{NH}_2\text{CH}_2\text{C}\equiv\text{CH}$ system; molecular structures of the intermediate complex, $\text{Co}(\text{O}_2\text{CCMe}_3)_2(\text{H}_2\text{NCH}_2\text{C}\equiv\text{CH})_4$ and final product $\text{Co}(\text{O}_2\text{CCMe}_3)_2(\text{NH}_2\text{CH}_2\text{C}\equiv\text{CH})_2[\text{N},\text{N}'\text{-(HC}\equiv\text{CCH}_2\text{NCHCHCHNCH}_2\text{C}\equiv\text{CH)}]$ were established by X-ray analysis.

The chemistry of transition metal complexes with propargylic amines is rather poorly studied. Here, we describe unexpected condensation of Co(II) coordinated propargylamine into the unprecedented 1,3-di(propargylimino)propylateanion bound to a Co(III) centre.

Upon reacting the cobalt(II) containing polymeric complex $[\text{Co}(\text{OH})_n(\text{O}_2\text{CCMe}_3)_{2-n}]_x$ or oligomeric complex $\text{Co}_6(\mu_3\text{-OH})_2(\text{O}_2\text{CCMe}_3)_{10}(\text{HO}_2\text{CCMe}_3)_4$ with propargylamine under an anaerobic atmosphere, the paramagnetic mononuclear complex $\text{Co}(\text{O}_2\text{CCMe}_3)_2(\text{H}_2\text{NCH}_2\text{C}\equiv\text{CH})_4$ **1** was obtained as the main product (95% yield)[†]. The four propargylamine molecules occupy the four positions in the equatorial plane [$\text{Co}-\text{N}$ 2.206(2)–2.214(2) Å] of the octahedral Co(II) atom according to X-ray diffraction data[‡] as shown in Fig. 1.

Complex **1** is fairly stable under Ar atmosphere in toluene solution containing an excess of propargylamine up to the solvent boiling point. However, complex **1** readily transforms in the diamagnetic cobalt(III) complex, $\text{Co}(\text{O}_2\text{CCMe}_3)_2(\text{NH}_2\text{CH}_2\text{C}\equiv\text{CH})_2[\text{N},\text{N}'\text{-(HC}\equiv\text{CCH}_2\text{NCHCHCHN-CH}_2\text{C}\equiv\text{CH)}]$ **2**, upon reaction with an excess of propargylamine (CH_2Cl_2 , 20 °C) in air; even traces of air initiate the reaction (Scheme 1).[§]

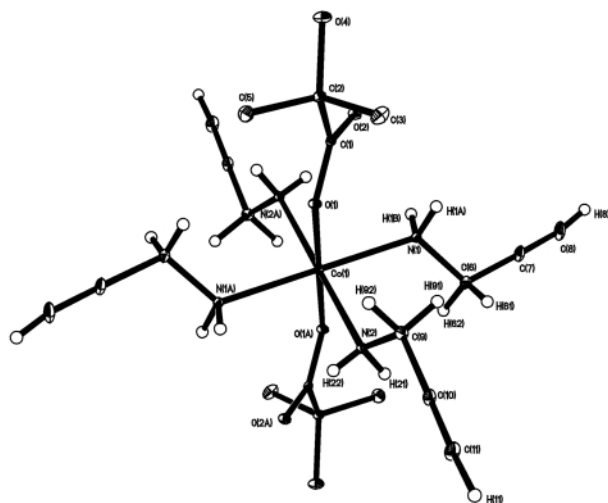
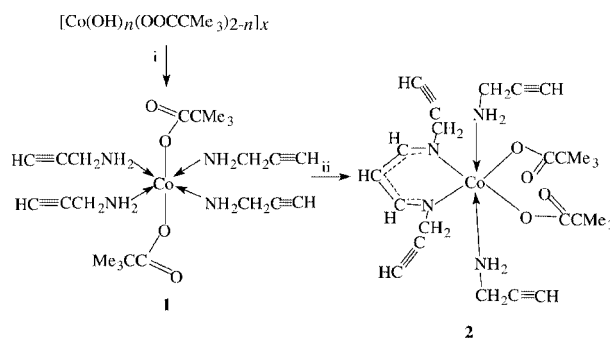


Fig. 1 Molecular structure of $\text{Co}(\text{O}_2\text{CCMe}_3)_2(\text{H}_2\text{NCH}_2\text{C}\equiv\text{CH})_4$ **1**; Co–O 2.064(1), C–N 1.452(3)–1.453(3), C≡C 1.158(4)–1.162(4) Å.



Scheme 1 Interconversions of cobalt(II/III) complexes. Reagents and conditions: i, 4 equiv. propargylamine, CH_2Cl_2 , Ar atmosphere; ii, 1–2 equiv. propargylamine, CH_2Cl_2 or toluene, in air.

According to an X-ray diffraction study[‡] the Co(III) atom has an octahedral environment with two propargylamine ligands occupying apical positions [$\text{Co}-\text{N}$ 1.974(2) Å] and three anionic ligands [two O_2CCMe_3 groups ($\text{Co}-\text{O}$ 1.976(2) Å) and one N,N' -coordinated RNCHCHCHNR ($\text{R} = \text{propargyl}$) fragment ($\text{Co}-\text{N}$ 1.936(2) Å)] in the equatorial plane of the complex coordination sphere as shown in Fig. 2. The metal atom and the planar $\text{C}-\text{N}=\text{CHCHCH}=\text{N}-\text{C}$ fragment lie in the same plane

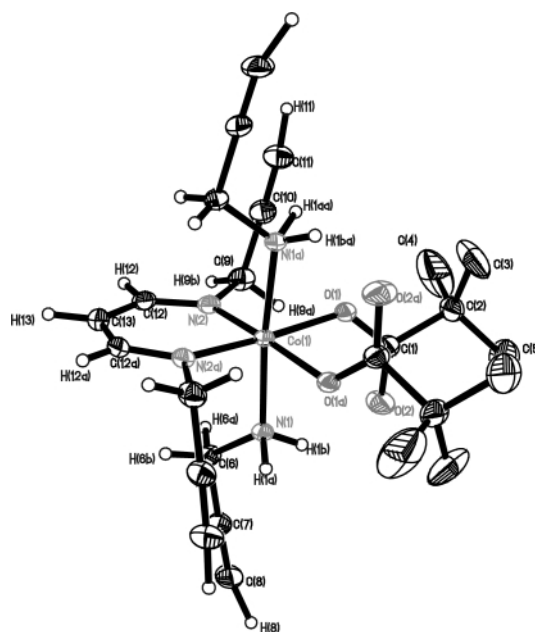


Fig. 2 Molecular structure of $\text{Co}(\text{O}_2\text{CCMe}_3)_2(\text{NH}_2\text{CH}_2\text{C}\equiv\text{CH})_2[\text{N},\text{N}'\text{-(HC}\equiv\text{CCH}_2\text{NCHCHCHNCH}_2\text{C}\equiv\text{CH)}]$ **2**; C=C 1.167(5) Å in the propargylamine ligands and 1.172(6) Å in the 1,3-di(propargylimino)propylateanion.

forming an aromatic system with shortened C=N bonds [1.303(4) Å] lying in the same plane of the H atoms [C–C–H 118.4(9)°] and equivalent C(H)–C(H) bonds [1.375(4) Å]. This geometry is very similar to that observed in six-membered metal–acetylacetonate rings.^{2,3}

Complex **2** could be also prepared *via* direct reaction between a cobalt trimethylacetate polymer and propargylamine (reagent ratio Co: L = 1: 5–6) in air in toluene solution at 20 °C.

The reaction of an oligomeric nonanuclear nickel(II) complex and an excess of propargylamine gives rise to the complex Ni(O₂CCMe₃)₂L₄ **3**.⁴ Geometric parameters of complex **3** are very similar to those of complex **1**. Unlike cobalt complex **1**, the nickel compound **3** is stable in air and does not react with propargylamine present in excess even at elevated temperature in solution. This fact suggests that the redox properties of the metal centre and its capability to be involved in one-electron transfer reactions are of importance for the observed amine condensation to form complex **2**. A study addressed toward mechanistic aspects of the reaction is in progress.

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Notes and references

† Propargylamine (11.58 mmol, 0.638 g) was added gradually to an CH₂Cl₂ solution (40 ml) of Co₆(μ₃-OH)₂(O₂CCMe₃)₁₀(HO₂CCMe₃)₄ (0.322 mmol, 0.583 g) or 0.5 g of the polymeric complex [Co(OH)_n(O₂CCMe₃)_{2–n}]_x (ratio propargylamine:Co = 4:1) under Ar atmosphere and the solution was stirred at 20 °C. Then the solvent was evaporated *in vacuo* to 10 ml and cooled to –5 °C. Pale-pink crystals of complex **1** which formed were separated and dried *in vacuo* (yield 95%). Single crystals suitable for X-ray investigation were prepared by slow cooling of the hot concentrated solution of **1** in CH₂Cl₂. [Co(O₂CCMe₃)₂(H₂NCH₂C≡CH)₄] **1**. Anal. Calc for C₂₂H₃₈CoN₄O₄: C, 54.89; H, 7.90; N, 11.64. Found: C, 55.1; H, 8.0; N, 11.7%. IR, (KBr pellet), ν/cm⁻¹: 3450m, 3352m, 3308s, 3234m, 2963s,

2944s, 2870m, 1672s, 1579vs, 1481vs, 1419vs, 1363s, 1221s, 1098m, 1011s, 980w, 894m, 795w, 645m, 635s, 610s, 570m. μ_{eff} = 4.96 μ_B (293 K).

‡ *Crystal data*: for **1**: C₂₂H₃₈CoN₄O₄, *M* = 481.49, triclinic, space group *P*1̄, μ(Mo-Kα) = 6.63 cm⁻¹, *R*₁ = 0.0463, *wR*₂ = 0.1310; *a* = 6.528(3), *b* = 10.634(4), *c* = 11.041(4) Å, α = 66.36(2), β = 79.60(2), γ = 75.89(2)°; *V* = 678.0(5) Å³; *T* = 20 °C; *Z* = 1, collected/independent reflections 3675/3388 (*R*_{int} = 0.0265). For **2**: C₂₅H₃₇CoN₄O₄·0.5C₆H₆, *M* = 555.58; monoclinic space group, *C*2/*c*, μ(Mo-Kα) = 6.63 cm⁻¹; *R*₁ = 0.0483, *wR*₂ = 0.1214; *a* = 14.830(3), *b* = 15.354(3), *c* = 15.282(3) Å, β = 94.83(3)°, *V* = 3467.4(12) Å³; *T* = 20 °C; *Z* = 4, collected/independent reflections: 3101/3101.

§ Propargylamine (19.91 mmol, 1.095 g) was added gradually to an toluene solution (40 ml) of Co₆(μ₃-OH)₂(O₂CCMe₃)₁₀(HO₂CCMe₃)₄ (0.553 mmol, 1 g) or 0.9 g of polymeric complex [Co(OH)_n(O₂CCMe₃)_{2–n}]_x (ratio propargylamine:Co = 5–6:1) and the pink suspension of complex **1** was stirred in air at 100 °C for 1–2 h. until formation of a red–brown solution. This solution was kept at 20 °C for 7–9 days after which brown prisms of Co(O₂CCMe₃)₂(NH₂CH₂C≡CH)₂[*N,N*-(HC≡CCH₂NCHCHCHNCH₂-C≡CH)] **2** were formed. Crystals of complex **2** were separated and dried *in vacuo* (yield 18%). Anal. Calc for C₂₅H₃₇CoN₄O₄: C, 58.14; H, 7.17; N, 10.85. Found: C, 57.8; H, 7.4; N, 10.5%. IR, (KBr pellet), ν/cm⁻¹: 3296m, 3222m, 3024m, 2963m, 2938m, 2887m, 1771w, 1740w, 1672w, 1610s, 1592s, 1573s, 1511vs, 1462w, 1407s, 1376s, 1345s, 1221s, 1036s, 894w, 746m, 63 vs, 542m. Single crystals suitable for X-ray investigation were prepared by slow cooling of a hot concentrated solution of **2** in benzene.

CCDC 182/1652. See <http://www.rsc.org/suppdata/cc/b0/b000004n/> for crystallographic files in .cif format.

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