# Unusual condensation of propargylamine. Generation of the 1,3-di(propargylimino)propane anion coordinated to the cobalt(III) atom

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The reaction of propargylamine with the hexanuclear complex $Co^{II}_6(\mu_3\text{-}OH)_2(OOCCMe_3)_{10}(HOOCCMe_3)_4$ or the polymer $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ under an argon atmosphere afforded the unstable paramagnetic tetramine complex $Co^{II}(OOCCMe_3)_2(H_2NCH_2C{\equiv}CH)_4$ (**1**). In air, if an excess of propargylamine is present, the latter complex is transformed into the complex $Co^{III}(OOCCMe_3)_2(NH_2CH_2C{\equiv}CH)_2[\eta^2\text{-}N,N'\text{-}(HC{\equiv}CCH_2N{=}CHCH{=}N{-}CH_2C{\equiv}CH)]$ (**2**) containing a new ligand, *viz.*, the 1,3-di(propargylimino)propane anion, which is a formal analog of the acetylacetonate anion. In contrast to propargylamine, 1,3-diaminopropane reacted with the $Co^{II}$ trimethylacetate clusters in air to produce the cationic complex $[Co^{III}\{1,3\text{-}(NH_2)_2(CH_2)_3\}_2(OOCCMe_3)_2]^+OOCCMe_3^-$ (**3**) without entering into condensation reactions. The structures of the resulting complexes were determined by X-ray diffraction analysis.

**Key words:** propargylamine, 1,3-di(propargylimino)propane monoanion, 1,3-diaminopropane, cobalt complexes, oxidation, X-ray diffraction analysis.

Aromatic monoamines are readily oxidized in the presence of iron(III) salts or manganese dioxide to form azo compounds.[1,2] Oxidation of aniline under the action of $Os^{IV}$ or $Ru^{III}$ compounds gave rise to monomeric complexes in which the oxidation product of the amine, *viz.*, *N*-phenyl-*o*-quinonediimine, is bound to the metal atoms.[3,4] The authors of the cited studies assumed that these reactions proceeded through intermediate formation of coordinated nitrenes. Unlike aromatic amines, alkyl derivatives do not enter into analogous reactions. There are only a few examples of chemical or electrochemical oxidative dehydrogenation of alkylamines coordinated to metal atoms. Generally, these transformations are accompanied by an increase in the C—N bond order of the starting amine $R{-}CH_2{-}NH_2$ giving rise to the aldimine $-CH{=}NH$ or nitrile $-C{\equiv}N$ groups.[5] In this case, propargylamine $R{-}CH_2{-}NH_2$ ($R = -C{\equiv}CH$), which potentially bears two functional groups of different nature, *viz.*, $NH_2$ and $C{\equiv}CH$, would be expected to be more active under the action of an oxidizer due to coordination to the metal center. In the present study, we examined the reactions of $Co^{II}$ trimethylacetate complexes with propargylamine and 1,3-diaminopropane.

## Results and Discussion

The reactions of propargylamine with cobalt(II) trimethylacetate complexes, the $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ polymer, or the hexanuclear $Co_6(\mu_3\text{-}OH)_2(OOCCMe_3)_{10}(HOOCCMe_3)_4$ complex[6] under anaerobic conditions afforded the paramagnetic monomer $Co(OOCCMe_3)_2(H_2NCH_2C{\equiv}CH)_4$ (**1**, $\mu_{eff}$ = 4.96 μB at 293 K) in high yield (95%) (Scheme 1). Complex **1** whose structure was determined by X-ray diffraction analysis (Fig. 1, Table 1) is similar to the analogous nickel(II) complex $Ni(OOCCMe_3)_2(H_2NCH_2C{\equiv}CH)_4$ prepared previously.[7] In molecule **1**, the $Co^{II}$ atom is bound to four propargylamine ligands through the amino groups, which are located in the equatorial plane (Co—N 2.206(2)—2.214(2) Å), and two monodentate-coordinated trimethylacetate ligands (Co—O 2.064(1) Å). The geometric characteristics of the acetylene fragments of the peripheral propargylamine ligands are virtually identical to the corresponding values known for such groups (C≡C 1.158(4)—1.162(4) Å).[8] However, it should be noted that the Co—N bond lengths are substantially

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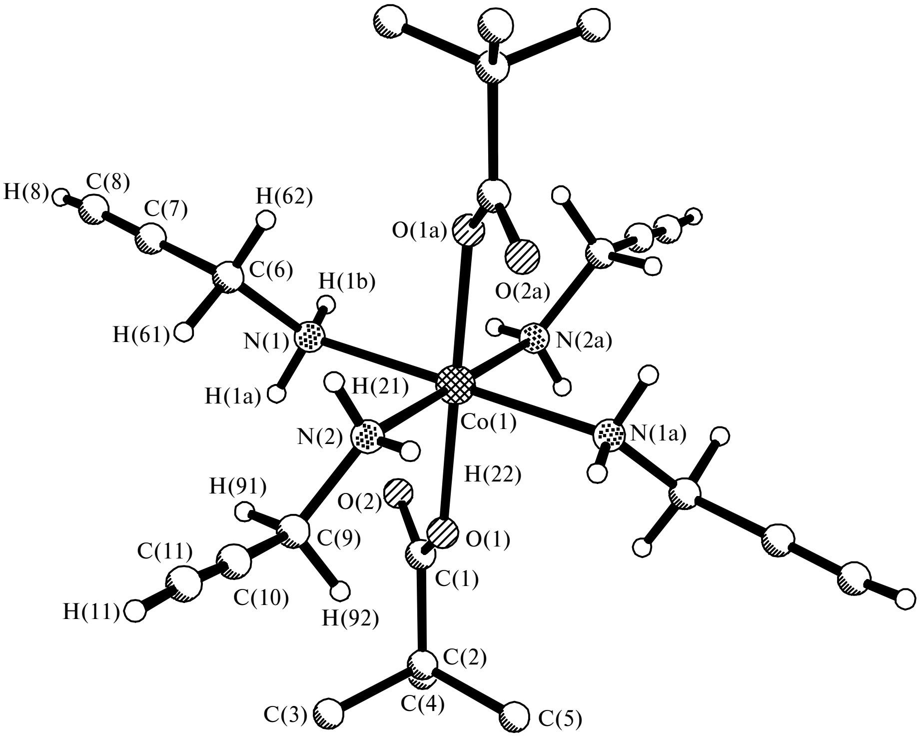


**Fig. 1.** Structure of the complex $Co(OOCCMe_3)_2(H_2NCH_2C{\equiv}CH)_4$ (**1**).

larger than the corresponding values in the binuclear complex $Py_2Co_2(\mu\text{-}OOCCMe_3)_4$ with the "China-latter" structure[9] due apparently to the electron-excessive character of the cobalt(II) atom (19 electrons) in complex **1**.

In the crystal, there are in addition rather short intermolecular nonbonded contacts between the H atoms of the amino groups and the O atoms of the carboxylate fragments, which are not coordinated to the metal atom; N—H...O are in the range of 2.15(2)—2.22(2) Å (Fig. 2).

These intermolecular hydrogen bonds can also be responsible for weakening of the Co—N bonds.

However, neither analogous intermolecular hydrogen bonds nor a high excess of electrons (the 20-electron configuration) in the isostructural nickel(II) complex $Ni(OOCCMe_3)_2(H_2NCH_2C{\equiv}CH)_4$[7] cause elongation of the metal—nitrogen bonds. The N—M distances in the $Ni^{II}$ complex are somewhat shorter (2.146(2)—2.160(2) Å) than those in complex **1**, whereas the O—M bond lengths in both compounds are virtually identical.[6,7] Unlike the nickel derivative, cobalt complex **1** is unstable in solutions and is oxidized in air even at 20 °C (Scheme 1) to form new complex **2** (Fig. 3). The latter compound contains the 1,3-di(propargylimino)propane monoanion (**A**) as one of the ligands. This ligand can be formally considered as a product of condensation of three propargylamine molecules. In the course of the reaction, the Co atom was oxidized, and the resulting complex $Co(OOCCMe_3)_2(NH_2CH_2C{\equiv}CH)_2[\eta^2\text{-}N,N'\text{-}(HC{\equiv}CCH_2N{=}CHCHCH{=}N{-}CH_2C{\equiv}CH)]$ (**2**) was diamagnetic.

**Table 1.** Selected geometric characteristics of complex **1**

| Bond | $d$/Å | Angle | ω/deg |
|---|---|---|---|
| Co(1)—O(1) | 2.064(1) | O(1)—Co(1)—N(1) | 92.89(6) |
| Co(1)—N(1) | 2.214(2) | O(1)—Co(1)—N(2) | 89.22(6) |
| Co(1)—N(2) | 2.206(2) | O(1′)—Co(1)—N(1) | 87.11(6) |
| O(1)—C(1) | 1.265(2) | O(1′)—Co(1)—N(2) | 90.78(6) |
| O(2)—C(1) | 1.241(2) | N(2)—Co(1)—N(1) | 90.96(7) |
| N(1)—C(6) | 1.453(3) | N(2′)—Co(1)—N(1) | 89.04(7) |
| N(2)—C(9) | 1.452(3) | C(1)—O(1)—Co(1) | 127.37(11) |
| C(6)—C(7) | 1.467(4) | C(6)—N(1)—Co(1) | 121.89(14) |
| C(7)—C(8) | 1.158(4) | C(9)—N(2)—Co(1) | 121.42(14) |
| C(9)—C(10) | 1.471(4) | O(2)—C(1)—O(1) | 124.4(2) |
| C(10)—C(11) | 1.162(4) | N(1)—C(6)—C(7) | 114.5(2) |
| | | N(2)—C(9)—C(10) | 113.9(2) |
| | | C(8)—C(7)—C(6) | 178.6(4) |
| | | C(11)—C(10)—C(9) | 177.9(4) |

According to the data of X-ray diffraction analysis, the coordination environment around the $Co^{III}$ atom in molecule **2** is a distorted octahedron formed by the monodentate-coordinated pivalate anions, the chelating ligand **A**, and two propargylamine molecules (Co—N 1.974(2) Å) located in the apical positions. The equatorial plane in this complex contains two O atoms of the carboxylate groups (Co—O 1.976(2) Å) and two N atoms of the anion **A** (Co—N 1.936(2) Å). The six-membered metallocycle formed by the anion **A** and the Co atom is planar (see Fig. 3). As a result, the metal atom in complex **2** formally has the favorable 18-electron configuration, which is reflected in the strength of the Co—N and Co—O bonds (Table 2).

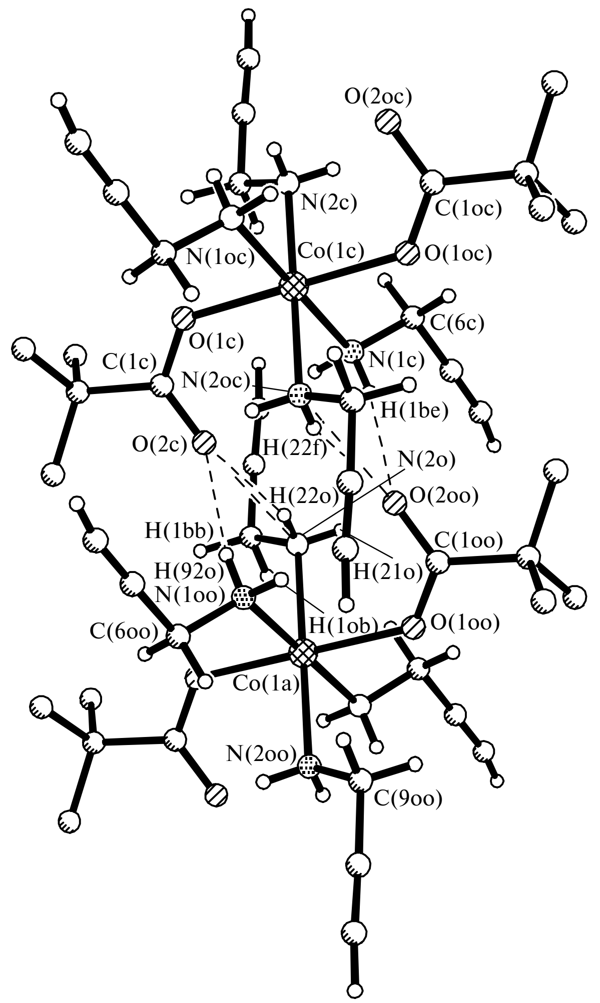
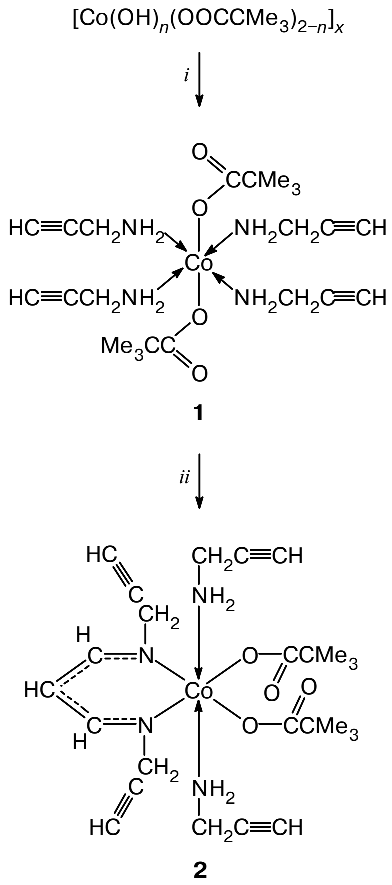


**Fig. 2.** Fragment of the molecular packing of complex **1**.

The fact that the reaction of the Co$^{II}$ complex with propargylamine afforded the planar six-membered metallocycle involving the previously unknown chelating ligand **A**, which is a formal analog of the acetylacetonate anion, gave impetus to the study of the reactions of cobalt(II) trimethylacetates with 1,3-diaminopropane. It appeared that the reaction of diaminopropane with polymeric cobalt carboxylate $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ in acetonitrile at 20 °C in air gave rise to the mononuclear diamagnetic ionic cobalt (III) complex, $[Co\{1,3\text{-}(NH_2)_2(CH_2)_3\}_2(OOCCMe_3)_2]^+(OOCCMe_3)^-$ (**3**). The amino groups of diaminopropane were not oxidized even upon prolonged refluxing of complex **3** in acetonitrile. Like compound **1**, cation **3** has a typical structure of a complex with four amine ligands (Fig. 4, Table 3). In the cation of complex **3**, the Co$^{III}$ atom is coordinated by four N atoms of the amino groups of two diaminopropane ligands, which are located in the equatorial plane (Co—N 1.968(2)—1.978(2) Å; two independent molecules per asymmetric unit), and two O atoms of the carboxylate fragments occupying the axial positions (Co—O 1.923(1)—1.934(1) Å). The Co$^{III}$ atoms have the

**Scheme 1**



**Reagents and conditions:** *i.* 4 equiv. of $NH_2CH_2C≡CH$, $CH_2Cl_2$, under an argon atmosphere; *ii.* 1—2 equiv. of $NH_2CH_2C≡CH$, toluene, in air.

**Table 2.** Selected geometric characteristics of complex **2**

| Bond | *d*/Å | Angle | ω/deg |
|---|---|---|---|
| Co(1)—O(1) | 1.935(2) | O(1)—Co(1)—N(1) | 95.39(9) |
| Co(1)—N(1) | 1.976(2) | O(1)—Co(1)—N(2) | 91.19(10) |
| Co(1)—N(2) | 1.936(2) | O(1′)—Co(1)—O(1) | 85.23(12) |
| O(1)—C(1) | 1.274(3) | O(1′)—Co(1)—N(1) | 80.71(9) |
| O(2)—C(1) | 1.215(4) | O(1)—Co(1)—N(2′) | 172.51(8) |
| N(1)—C(6) | 1.461(4) | N(2)—Co(1)—N(1) | 93.11(10) |
| N(2)—C(9) | 1.473(4) | N(1)—Co(1)—N(1′) | 174.74(14) |
| N(2)—C(12) | 1.303(4) | N(2′)—Co(1)—N(1) | 90.51(10) |
| C(6)—C(7) | 1.471(4) | C(1)—O(1)—Co(1) | 132.1(2) |
| C(7)—C(8) | 1.167(5) | C(6)—N(1)—Co(1) | 122.8(2) |
| C(9)—C(10) | 1.461(5) | C(9)—N(2)—Co(1) | 119.5(2) |
| C(10)—C(11) | 1.172(6) | C(12)—N(2)—Co(1) | 124.7(2) |
| C(12)—C(13) | 1.375(5) | C(12)—N(2)—C(9) | 115.7(3) |
| C(13)—C(12′) | 1.375(4) | O(2)—C(1)—O(1) | 125.2(3) |
| | | N(1)—C(6)—C(7) | 111.9(3) |
| | | C(8)—C(7)—C(6) | 178.7(4) |
| | | C(10)—C(9)—N(2) | 112.1(3) |
| | | C(11)—C(10)—C(9) | 178.3(5) |
| | | N(2)—C(12)—C(13) | 127.3(3) |
| | | C(12′)—C(13)—C(12) | 122.9(4) |

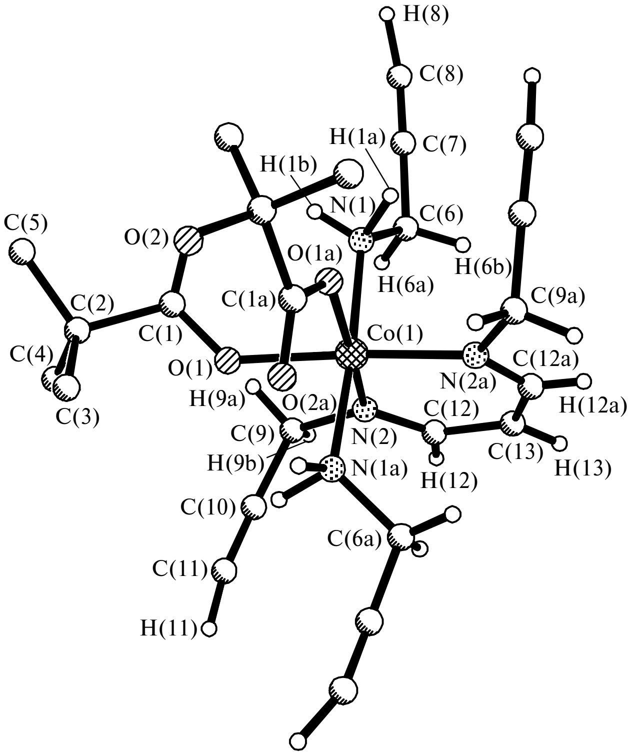


**Fig. 3.** Structure of complex **2**.

favorable saturated 18-electron configuration resulting in substantial strengthening of the metal—ligand bonds compared to the corresponding bonds involving the Co$^{II}$ atom

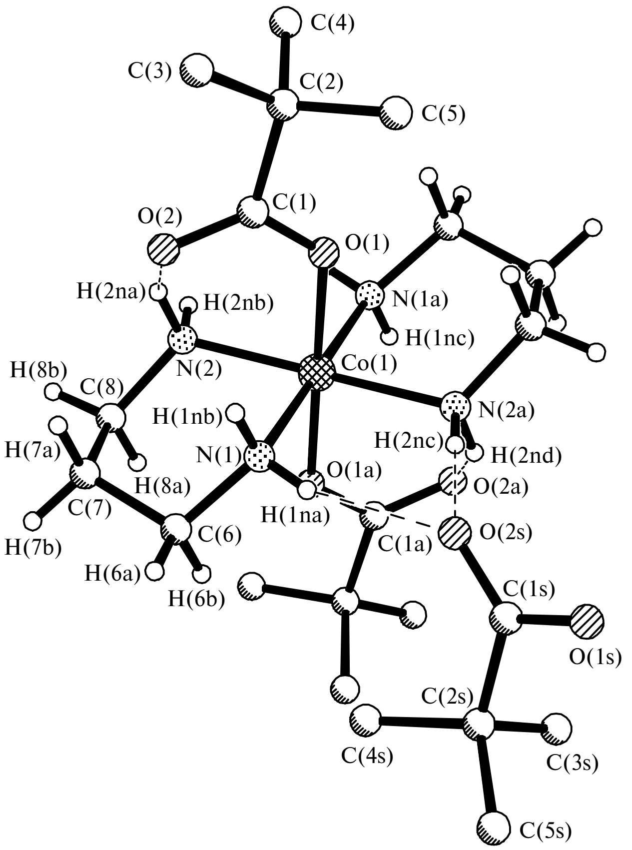


**Fig. 4.** Molecular structure of complex **3** (one of two independent molecules is shown).

**Table 3.** Selected geometric characteristics of the Co[1,3-(NH$_2$)$_2$(CH$_2$)$_3$]$_2$(OOCCMe$_3$)$_2^+$ cation in complex **3**

| Molecule A | | Molecule B | |
|---|---|---|---|
| Bond | *d*/Å | Bond | *d*/Å |
| Co(1)—O(1) | 1.934(1) | Co(2)—O(3) | 1.923(1) |
| Co(1)—N(1) | 1.978(2) | Co(2)—N(3) | 1.970(2) |
| Co(1)—N(2) | 1.971(2) | Co(2)—N(4) | 1.968(2) |
| O(1)—C(1) | 1.292(2) | O(3)—C(9) | 1.289(2) |
| O(2)—C(1) | 1.240(3) | O(4)—C(9) | 1.237(3) |
| N(1)—C(6) | 1.483(3) | N(3)—C(14) | 1.492(3) |
| N(2)—C(8) | 1.473(3) | N(4)—C(16) | 1.483(3) |
| C(6)—C(7) | 1.521(3) | C(14)—C(15) | 1.522(3) |
| C(7)—C(8) | 1.518(3) | C(15)—C(16) | 1.522(3) |
| Angle | ω/deg | Angle | ω/deg |
| O(1)—Co(1)—N(1) | 91.01(6) | O(3)—Co(2)—N(3) | 87.69(7) |
| O(1)—Co(1)—N(2) | 91.26(6) | O(3)—Co(2)—N(4) | 89.13(6) |
| O(1)—Co(1)—N(1′) | 88.99(6) | O(3′)—Co(2)—N(3) | 92.31(7) |
| O(1′)—Co(1)—N(2) | 88.74(6) | O(3′)—Co(2)—N(4) | 90.87(6) |
| N(2)—Co(1)—N(1) | 89.03(7) | N(4)—Co(2)—N(3) | 88.40(7) |
| N(2)—Co(1)—N(1′) | 90.97(7) | N(4′)—Co(2)—N(3) | 91.60(7) |
| C(1)—O(1)—Co(1) | 128.91(13) | C(9)—O(3)—Co(2) | 128.80(13) |
| C(6)—N(1)—Co(1) | 118.95(12) | C(14)—N(3)—Co(2) | 118.82(14) |
| C(8)—N(2)—Co(1) | 119.01(12) | C(16)—N(4)—Co(2) | 119.25(13) |
| O(2)—C(1)—O(1) | 124.7(2) | O(4)—C(9)—O(3) | 125.0(2) |
| N(1)—C(6)—C(7) | 111.7(2) | N(3)—C(14)—C(15) | 111.5(2) |
| C(8)—C(7)—C(6) | 113.3(2) | C(16)—C(15)—C(14) | 114.2(2) |
| N(2)—C(8)—C(7) | 112.2(2) | N(4)—C(16)—C(15) | 111.2(2) |

in complex **1** in spite of noticeable intramolecular hydrogen bonding between the protons of the amino groups and the free oxygen atoms of the terminal trimethylacetate ligands (N—H...O(OCO) 2.10(3)—2.14(4) Å) and the carboxylate anion (1.87(3) Å) (see Fig. 4). High stability of the coordinated diaminopropane molecules to oxidation indicates that hydrogen bonds are of secondary importance in transformations of coordinated amines.

The mechanism of formation of complex **2** containing this unusual ligand is poorly understood and remains to be explored. In our opinion, noteworthy are the following possible key reactions whose analogs have been described in the literature.[10]

1. Dismutation of propargylamine yielding dipropargylamine (apparently, catalyzed by cobalt complexes):

$$2\,\text{PrgNH}_2 \longrightarrow (\text{Prg})_2\text{NH} + \text{NH}_3,$$

where Prg = $-\text{CH}_2-\text{C}{\equiv}\text{CH}$.

2. One-electron oxidation of propargylamine giving rise to the N-centered radical:

$$\text{PrgNH}_2 + \text{Ox} \longrightarrow \text{PrgNH}^{\bullet} + \text{Red},$$

where Ox = $\text{Co}^{\text{II}}/\text{O}_2$, $\text{Co}^{\text{III}}$, *etc.*

3. The addition of $\text{PrgNH}^{\bullet}$ at the triple bond of dipropargylamine or at the double bond of isomeric allenylpropargylamine against the Markovnikoff rule:

$$\text{PrgNH}^{\bullet} + \text{CH}_2{=}\text{C}{=}\text{CHNHPrg} \longrightarrow$$
$$\longrightarrow \underset{\textbf{4}}{\text{PrgNH}-\text{CH}_2-\text{C}^{\bullet}{=}\text{CHNHPrg}}.$$

4. Isomerization of vinylic radical **4** producing energetically more favorable allylic radical **5** in which the free valence is stabilized through the interaction with the lone electron pairs of the nitrogen atoms:

$$\text{PrgNH}-\text{CH}_2-\text{C}^{\bullet}{=}\text{CHNHPrg} \longrightarrow$$
$$\longrightarrow \underset{\textbf{5a}}{\text{PrgNH}-\text{CH}^{\bullet}-\text{CH}{=}\text{CHNHPrg}} \longleftrightarrow$$
$$\longleftrightarrow \underset{\textbf{5b}}{\text{PrgNH}-\text{CH}{=}\text{CH}-\text{CH}^{\bullet}\text{NHPrg}}.$$

5. Oxidative dehydrogenation of radical **5** to form the anionic ligand **A**:

$$\text{PrgNH}\overset{\cdots}{-}\text{CH}\overset{\cdots}{-}\text{CH}\overset{\cdots}{-}\text{CH}\overset{\cdots}{-}\text{NHPrg} \xrightarrow[-2\,\text{H}^+,\ -\text{e}]{}$$
$$\longrightarrow \text{PrgN}\overset{\cdots}{-}\text{CH}\overset{\cdots}{-}\text{CH}\overset{\cdots}{-}\text{CH}\overset{\cdots}{-}\text{NPrg}\,\rceil^{-}.$$

All the above-mentioned reactions serve only as models of more complex processes proceeding, apparently, in the inner coordination sphere of the cobalt atoms.

The ligand **A** is a derivative of malonaldehyde, which does not exist in the free state. The presence of such a ligand in complex **2** exemplifies the possibilities in the organic synthesis provided by the coordination chemistry.

Apparently, the ability of the cobalt atom to readily enter into one-electron redox transformations plays a key role in the reaction under consideration. Thus the reactions of propargylamine with nickel(II) trimethylacetate clusters in the presence of atmospheric oxygen afforded a mononuclear complex, which is a structural analog of **1**, stable to oxidation.[7] This inertness is apparently arises from rather high resistance of the nickel atom in the octahedral ligand environment (the 20-electron configuration) to the electron transfer.

## Experimental

Operations associated with the synthesis of the complexes were carried out under an inert atmosphere or in air using anhydrous solvents. The starting $\text{Co}^{\text{II}}$ trimethylacetate complexes were synthesized according to known procedures.[11] Propargylamine and 1,3-diaminopropane were purchased from Fluka. The IR spectra of the complexes were recorded on a Specord M-80 instrument in KBr pellets. The static magnetic susceptibilities $\chi'_\text{m}$ were measured using the Faraday method in the temperature range of 77—300 K on an instrument at the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences.[12] The effective magnetic moments were calculated according to the following formula:

$$\mu_\text{eff} = (8\chi'_\text{M}T)^{1/2}.$$

**Syntheses of the complexes. Tetrakis-propargylamino-dipivalatocobalt(II), $\mathbf{Co(OOCCMe_3)_2(H_2NCH_2C{\equiv}CH)_4}$ (1).** Propargylamine (0.64 g, 11.6 mmol) was added to a solution of the complex $\text{Co}_6(\mu_3\text{-OH})_2(\text{OOCCMe}_3)_{10}(\text{HOOCCMe}_3)_4$ (0.58 g, 0.32 mmol) or $[\text{Co(OH)}_n(\text{OOCCMe}_3)_{2-n}]_x$ (0.5 g) in $\text{CH}_2\text{Cl}_2$ (40 mL) and the reaction mixture was stirred under an atmosphere of argon at 20 °C for 1 h. The solution was concentrated *in vacuo* to 10 mL and the residue was cooled to −5 °C. The dark-pink crystals that precipitated were separated by decantation and dried *in vacuo*. Complex **1** was obtained in a yield of 0.88 g (95% with respect to the initial amount of cobalt). Found (%): C, 55.1; H, 8.0; N, 11.7. $\text{C}_{22}\text{H}_{38}\text{CoN}_4\text{O}_4$. Calculated (%): C, 54.89; H, 7.90; N, 11.64. IR, $\nu/\text{cm}^{-1}$: 3450 m, 3352 m, 3308 s, 3234 m, 2963 s, 2944 s, 2870 m, 1672 s, 1579 v.s, 1481 v.s, 1419 v.s, 1363 s, 1221 s, 1098 m, 1011 s, 980 w, 894 m, 795 w, 645 m, 635 s, 610 s, 570 m.

Crystals suitable for X-ray diffraction study were obtained by slow cooling of a hot concentrated solution of **1** in $\text{CH}_2\text{Cl}_2$ to 20 °C.

**Bis-propargylamino-1,3-di(propargylimino)propanatodipivalatocobalt(III), $\mathbf{Co(OOCCMe_3)_2(NH_2CH_2C{\equiv}CH)_2[\eta^2\text{-}\mathit{N,N'}\text{-}(HC{\equiv}CCH_2N{=}CHCHCH{=}N{-}CH_2C{\equiv}CH)]}$ (2).** A solution of $\text{Co}_6(\mu_3\text{-OH})_2(\text{OOCCMe}_3)_{10}(\text{HOOCCMe}_3)_4$ (1 g, 0.55 mmol) or $[\text{Co(OH)}_n(\text{OOCCMe}_3)_{2-n}]_x$ (0.9 g) in toluene (40 mL) and propargylamine (1.09 g, 19.91 mmol) were stirred under an atmosphere of argon until a pink suspension of complex **1** formed. Then benzene (10 mL) was added to the suspension and the mixture was heated in air to 100 °C for 2 h. The resulting brown-red solution was kept in air at ~20 °C for 7 days. The crystals that formed were separated by decantation, washed with cold ether, and dried under a stream of argon. The yield of $\mathbf{2}\cdot0.5\text{C}_6\text{H}_6$ was 0.31 g (18%). Found (%): C, 60.8; H, 7.4; N, 10.3. $\text{C}_{28}\text{H}_{40}\text{CoN}_4\text{O}_4$. Calculated (%): C, 60.52; H, 7.26; N, 10.08. IR, $\nu/\text{cm}^{-1}$: 3296 m, 3222 m, 3024 m, 2963 m, 2938 m, 2887 m, 1771 w, 1740 w, 1672 w, 1610 s, 1592 s, 1573 s, 1511 v.s, 1462 w, 1407 s, 1376 s, 1345 s, 1221 s, 1036 s, 894 w, 746 m, 635 v.s, 542 m.

The crystals obtained in the synthesis were suitable for X-ray diffraction analysis.

**Bis-1,3-diaminopropanopivalatocobalt(III) pivalate, $\mathbf{Co[1,3\text{-}(NH_2)_2(CH_2)_3]_2(OOCCMe_3)_2{}^+OOCCMe_3{}^-}$ (3).** A solution of 1,3-diaminopropane (0.28 g, 3.8 mmol) in benzene (10 mL) was added to a suspension of the polymer $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ (0.5 g, 1.9 mmol) in acetonitrile (50 mL). The pink suspension that formed was refluxed in air for 20 min until the precipitate was completely dissolved. The resulting brown-red solution was concentrated to 15 mL and kept at ~20 °C for one day. The green crystals that formed were separated by decantation, washed with cold ether, and dried under a stream of argon. The yield of $\mathbf{4} \cdot 0.5C_6H_6$ was 0.34 g (32%). Found (%): N, 5.3; C, 52.5; H, 9.4. $CoC_{24}H_{50}O_6N_2$. Calculated (%): N, 5.10; C, 52.46; H, 9.11. IR (KBr), $\nu/cm^{-1}$: 3288 m, 3248 s, 3112 m, 2960 s, 2895 s, 2872 m, 1696 w, 1616 s, 1591 s, 1560 v.s, 1480 s, 1456 m, 1392 s, 1344 v.s, 1216 v.s, 1128 w, 1056 s, 920 m, 896 m, 784 m, 688 w, 632 m, 568 w, 528 m, 472 w.

The crystals obtained in the synthesis were suitable for X-ray diffraction analysis.

**X-ray diffraction study.** The X-ray intensity data sets for complexes **1** and **2** were collected on an automated four-circle Siemens P3/PC diffractometer (graphite monochromator, $T$ = 22 °C, $\theta$-$2\theta$ scanning technique). The unit-cell parameters were determined and refined based on 24 equivalent reflections with $2\theta < 24$—28°. In both cases, three strong standard reflections with $0 < \chi < 65°$ were monitored after each 100 reflections. The intensities of the standard reflections showed no decrease in the course of data collection, and therefore, the corresponding corrections were ignored. The experimental data for complex **3** was collected on an automated Bruker AXS SMART diffractometer equipped with a CCD detector (graphite monochromator, $T$ = 110 °C, $\omega$ scanning technique, scan step was 0.3°, frames were exposed for 30 s) using a standard procedure.[13] The semiempirical absorption correction was applied.[14] The crystallographic parameters and details of the refinement of all structures are given in Table 4.

**Table 4.** Crystallographic parameters of complexes **1**, **2**, and **3**

| Parameter | **1** | **2** | **3** |
|---|---|---|---|
| Molecular formula | $C_{22}H_{38}CoN_4O_4$ | $C_{25}H_{37}CoN_4O_4 \cdot 0.5C_6H_6$ | $C_{21}H_{47}CoN_4O_6 \cdot 0.5C_6H_6$ |
| Space group | $P\bar{1}$ | $C2/c$ | $P\bar{1}$ |
| $a$/Å | 6.528(3) | 14.830(3) | 10.6992(8) |
| $b$/Å | 10.634(4) | 15.354(3) | 11.9759(9) |
| $c$/Å | 11.041(4) | 15.282(3) | 12.7886(9) |
| $\alpha$/deg | 66.36(2) | 90 | 73.8870(10) |
| $\beta$/deg | 79.60(2) | 94.83(3) | 65.3220(10) |
| $\gamma$/deg | 75.89(2) | 90 | 88.324(2) |
| $V$/Å$^3$ | 678.0(5) | 3467.4(12) | 1423.4(2) |
| $Z$ | $1^a$ | $4^b$ | $2^c$ |
| $\rho_{calc}$/g cm$^{-3}$ | 1.179 | 1.064 | 1.282 |
| $\mu$/cm$^{-1}$ | 6.63 | 5.27 | 6.45 |
| Radiation | Mo-K$\alpha$ ($\lambda$ = 0.71073 Å) | | |
| Number of measured reflections | 3675 | 3101 | 12413 |
| Number of reflections with $I > 4\sigma$ | 3388 | 3101 | 7924 |
| $R_1$ | 0.0463 | 0.0483 | 0.0468 |
| $wR_2$ | 0.1310 | 0.1214 | 0.1190 |

[a] The molecule occupies the crystallographic inversion center.
[b] The molecule is located on a twofold axis.
[c] Two independent molecules occupy crystallographic inversion centers.

The structures of complexes **1**, **2**, and **3** were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The positions of the hydrogen atoms of the propargyl ligands and of the amino groups of 1,3-diaminopropane were located from difference Fourier syntheses and refined isotropically. The positions of the remaining H atoms were calculated geometrically and refined using the riding model. All calculations were carried out with the use of the SHELX97 program package.[15] The principal geometric parameters of complexes **1**, **2**, and **3** are given in Tables 1—3, respectively.

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