

Sr₃[Co(CN)₃] and Ba₃[Co(CN)₃]: Highly Reduced Cobaltates

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Nitridometalates and carbometalates of the transition metals *M* have been extensively investigated with respect to their structural chemistry and their peculiar chemical bonding features [1–5]. Our recent research on the reactions of electropositive alkaline-earth or rare-earth metals with transition metals and nitrogen as well as carbon accentuated the ambivalent role played by carbon which is able to react both as electron donor as well as electron acceptor. Reactions under oxidizing conditions (excess N₂) led to nitridometalate-carbodiimides (e. g. Sr₆[Co¹⁺N₂]₂[CN₂] [6], (Sr₆N)[Co¹⁺N₂]₂[CN₂]₂ [7]), whereas reactions under inert conditions and in absence of N resulted in carbometalates (e. g. La_{3.67}[Fe¹⁺(C₂)₃] [8]). Preliminary investigations on similar quaternary systems under reducing conditions (without excess N₂) led to low-valency cyano-nitridometalates such as Sr₂[NNi⁰(CN)] [9] with the lowest oxidation state of nickel in nitrido-compounds observed so far. Shifting our focus towards compounds containing CN groups appeared to be promising in this respect.

Preparation

Single-phase powders of the highly air and moisture-sensitive phases, Sr₃[Co(CN)₃] and Ba₃[Co(CN)₃], are obtained by treatment of pressed pellets of AE₂N (AE = Sr, Ba) with Co, graphite, and NaCN in the molar ratio AE:Co:C:N = 3:1:3:2.5 under Ar at temperatures of about 1200 K. Single crystals of the Ba phase were obtained at 1023 K whereas single crystals of Sr₃[Co(CN)₃] could not successfully be grown up to now. Great care was taken to keep the nitrogen content at a suitable (low) level. Higher nitrogen contents inevitably led to the formation of (AE₆N)[CoN₂]₂[CN₂]₂ [7] or other carbodiimides.

Crystal Structure

As shown in Figure 1, the crystal structures of Ba₃[Co(CN)₃] (*P*6₃/*m*, No. 176, *a* = 905.26(11) pm, *c* = 577.35(9) pm, *V* = 409.75(10) 10⁶ pm³) and Sr₃[Co(CN)₃] (*P*6₃/*m*, No. 176, *a* = 869.26(1) pm, *c* = 540.65(1) pm) are closely related to the nitridometalates AE₃[MN₃] (AE = Sr, Ba; *M* = Cr,

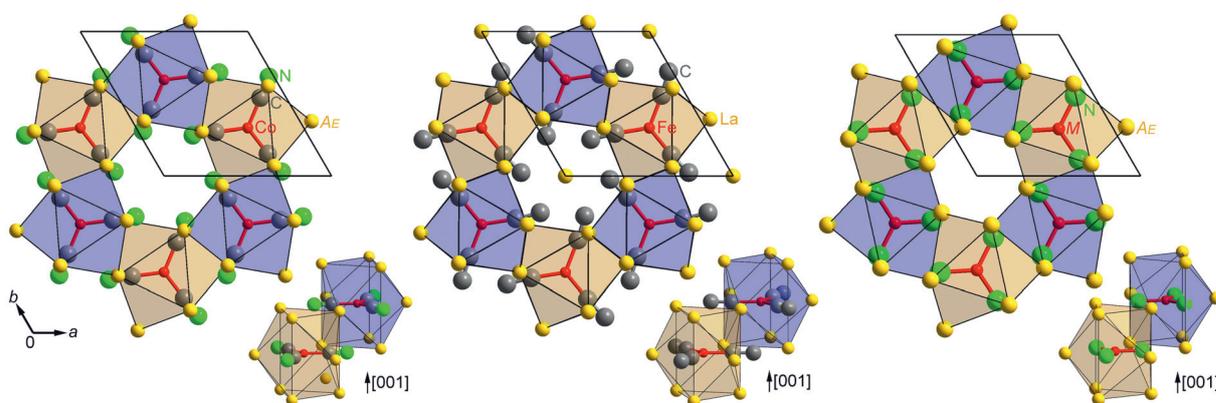


Fig. 1: Comparison of the closely related crystal structures of AE₃[Co(CN)₃] (left), La_{3.67}[Fe(C₂)₃] [8] (center), and AE₃[FeN₃] [10] (right). The channels running along [001] are filled in the case of La_{3.67}[Fe(C₂)₃] [8] only.



Fig. 2: The complex anion $[\text{Co}(\text{CN})_3]^{6-}$ (left) together with trigonal planar complexes in a cyanocuprate [18] and a carbonylcobaltate [15]. Values for distances in $[\text{Co}(\text{CO})_3]^{3-}$ are based on theoretical calculations [15].

Mn, Fe) [10] and the carbometalate $\text{La}_{3,67}[\text{Fe}(\text{C}_2)_3]$ [8]. If the (CN) ligands are considered as formally mono-atomic species, the compounds $A\text{E}_3[\text{Co}(\text{CN})_3]$ and $A\text{E}_3[\text{MN}_3]$ are strictly isotypic. The same structural motif is also present in $\text{La}_{3,67}[\text{Fe}(\text{C}_2)_3]$, although in this latter compound, the channels along [001] are occupied by chains of additional La atoms resulting in a threefold superstructure along *c*. Predominant structural features of $A\text{E}_3[\text{Co}(\text{CN})_3]$ are isolated trigonal-planar complex anions $[\text{Co}(\text{CN})_3]^{6-}$ (Fig. 2) arranged to form layers with a stacking sequence $\cdots\text{ABAB}\cdots$ along [001]. Large voids are present above and below the $[\text{Co}(\text{CN})_3]^{6-}$ complexes (Fig. 1). The CN species are octahedrally coordinated by one Co and five AE; the coordination polyhedron around AE is best described as a highly distorted trigonal bipyramid $\text{AE}(\text{CN})_5$.

Crystal Chemistry

At first glance, the isotypic compounds under consideration could be regarded as cyanocobaltates(3-) with the ionic formula $A\text{E}^{2+}_3[\text{Co}^{3-}(\text{CN})_3]$, although such uncommonly electron-rich and highly reduced cyanometalates are not known up to date. The interatomic distances $\text{AE}-\text{C}/\text{N}$ ($d(\text{Ba}-\text{N})$: 274.2(3) pm – 334.7(3) pm, $d_{\text{ave}} = 302.4$ pm; $d(\text{Sr}-\text{N})$: 252(3) pm – 331(1) pm, $d_{\text{ave}} = 288$ pm) correspond well with data from related compounds containing complex anions [11]. However, the C–N distances ($\text{Sr}_3[\text{Co}(\text{CN})_3]$: 125(1) pm and $\text{Ba}_3[\text{Co}(\text{CN})_3]$: 123.5(5) pm) are remarkably long compared to cyanometalates, which in general form a rather homogeneous group with short distances $d(\text{C}\equiv\text{N}) = 113$ pm – 116 pm [12].

From a structural point of view, a trigonal-planar coordination of Co is quite rare: besides $[\text{Co}^{2+}\text{O}_3]^{4-}$ in $A_4[\text{CoO}_3]$ [13] and $[\text{Co}^{2+,3+}\text{S}_3]$ in $A_9\text{Co}_2\text{S}_7$ [14], only the carbonyl complexes

$A_3[\text{Co}(\text{CO})_3]$ [15] and the nitrosyl complex $(\text{Co}(\text{NO})_3)$ [16] are known. The variety of tricyanometalate complexes is also small [12] ($[\text{Cu}(\text{CN})_3]^{2-}$, $[\text{Ag}(\text{CN})_3]^{2-}$, $[\text{Zn}(\text{CN})_3]^-$, $[\text{Cd}(\text{CN})_3]^-$, and $[\text{Hg}(\text{CN})_3]$). The bond lengths $d(\text{Co}-\text{C})$ in $\text{Sr}_3[\text{Co}(\text{CN})_3]$ (174(1) pm) and $\text{Ba}_3[\text{Co}(\text{CN})_3]$ (176.9(3) pm) are comparable to $\text{Na}_3[\text{Co}(\text{CO})_3]$ (177 pm, based on theoretical calculations) [15] and $\text{Na}[\text{Co}(\text{CO})_4]$ (176.2 pm) [17], whereas in the hexacyanocobaltates(III) $[\text{Co}(\text{CN})_6]^{3-}$ typical distances of 188 pm – 190 pm are observed [12].

Spectroscopic Characterisation

Whereas the high negative oxidation state of cobalt in the alkaline-earth cyanocobaltates is very unusual with respect to the large family of cyanometalates of transition elements, this situation reminds of carbonylmetalates (e.g. $\text{Na}_3[\text{Co}(\text{CO})_3]$ [15]) and trinitrosylcobalt $\text{Co}(\text{NO})_3$ [16]. Since there are no structural data available for $[\text{Co}(\text{CO})_3]^{3-}$ and $\text{Co}(\text{NO})_3$, vibration spectroscopy (Tab. 1) provides good insight into the chemical bondings involved. Typical CN valence vibrations in cyano complexes are observed in a rather small range between 2000 cm^{-1} and 2200 cm^{-1} depending on ionicity, electronegativity, oxidation state, and other factors. In organic compounds frequencies of 1700 cm^{-1} – 1600 cm^{-1} for double bonds (C=N), and about 1000 cm^{-1} for single bonds (C–N) are reported.

The symmetry of the complex anion $[\text{Co}(\text{CN})_3]^{6-}$ is C_{3h} with only small deviation from D_{3h} ($\angle\text{Co}-\text{C}-\text{N} = 179.3(2)^\circ$). The factor group analysis results in 10 fundamentals for both symmetries:

$$\Gamma_{\text{vib}}(C_{3h}) = 3 A'(\text{RE}) + 2 A''(\text{IR}) + 4 E'(\text{IR}, \text{RE}) + 1 E''(\text{RE})$$

Out of these, only the CN stretching modes (A' : $\nu_s = 1671$ cm^{-1} / 1700 cm^{-1} , E' : $\nu_{\text{as}} = 1682$ cm^{-1} / 1696 cm^{-1}) are relevant for this work. All other modes are found in the region below 600 cm^{-1} (CoC_3 stretching (A' : ν_s , E' : ν_{as}) $\text{Co}-\text{C}-\text{N}$ bending (A' : δ , E' : δ), CoC_3 bending (A'' : γ , E' : δ), $\text{Co}-\text{C}-\text{N}$ torsion (A'' : γ , E'' : τ)). However, it is important to note, that the CoC_3 stretching modes are observed in the region of ≈ 600 cm^{-1} , whereas the corresponding values in other cyanometalates are ≈ 400 cm^{-1} , indicating a much stronger Co–C interaction in $A\text{E}_3[\text{Co}(\text{CN})_3]$.

Tab. 1: C–N and C–O distances [pm] together with CN and CO stretching frequencies [cm^{-1}] in IR and Raman spectra of $A\text{E}_3[\text{Co}(\text{CN})_3]$ in comparison with related cyano- and carbonylmetalates.

	IR	Raman	$d(\text{C-N})/$ $d(\text{C-O})$	[Ref.]
$\text{Sr}_3[\text{Co}(\text{CN})_3]$	1671	1682– 1725	125(1)	this work
$\text{Ba}_3[\text{Co}(\text{CN})_3]$	1700	1696	123.5(5)	this work
$\text{Na}_2[\text{Cu}(\text{CN})_3] \cdot 3\text{H}_2\text{O}$	2090– 2111	2090– 2122	113–116	[18]
$\text{Cs}[\text{Hg}(\text{CN})_3]$	2156– 2162	2157– 2164	109–119	[19]
$\text{K}_3[\text{Co}(\text{CN})_6]$	2128– 2131	2135– 2153	116(2)	[20]
$\text{Na}[\text{Co}(\text{CO})_4]$	1886	1918	115(1)	[17]
$\text{Na}_3[\text{Co}(\text{CO})_3]$	1614		126*	[15]

*from theoretical calculations

The low values for the CN stretching modes ($1671 \text{ cm}^{-1} - 1725 \text{ cm}^{-1}$) in $\text{Sr}_3[\text{Co}(\text{CN})_3]$ and $\text{Ba}_3[\text{Co}(\text{CN})_3]$ along with the elongated C–N distances (125 pm/123.5 pm) are unprecedented in cyanometalate chemistry. In carbonyl metalates, due to the strong metal–CO π -backbonding the high negative charges of the metal are distributed via the π^* -CO orbitals. In result the ligand is effectively reduced as shown for $\text{Na}[\text{Co}(\text{CO})_4]$ [17] and $\text{Na}_3[\text{Co}(\text{CO})_3]$ [15]. A similar behavior was not observed for any cyanometalates up to now. In $A\text{E}_3[\text{Co}(\text{CN})_3]$, however, a partial reduction of the ligands and simultaneous strengthening of the Co–C bond appears to significantly affect the bond lengths and the vibration frequencies.

The compounds $A\text{E}_3[\text{Co}(\text{CN})_3]$ are diamagnetic and insulating. X-ray absorption spectra (XAS) at the Sr–K edge of $\text{Sr}_3[\text{Co}(\text{CN})_3]$ [21] are consistent with a Sr^{2+} charge for the strontium sites. Electron spin resonance (ESR) data unambiguously support the exclusive presence of paired electrons and rule out the existence of any type of radicals in $A\text{E}_3[\text{Co}(\text{CN})_3]$.

The local electronic configuration of Co in $\text{Sr}_3[\text{Co}(\text{CN})_3]$ was investigated by means of X-ray photoelectron spectroscopy (XPS) and XAS. The XAS measurements were performed at the Dragon

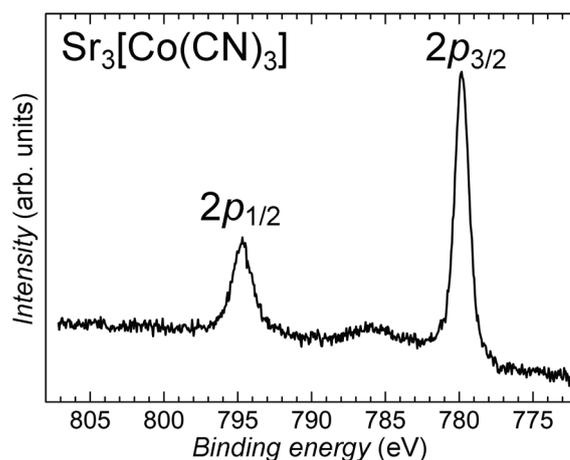


Fig. 3: Co $2p_{3/2}$ and $2p_{1/2}$ core level X-ray photoelectron spectrum of $\text{Sr}_3[\text{Co}(\text{CN})_3]$.

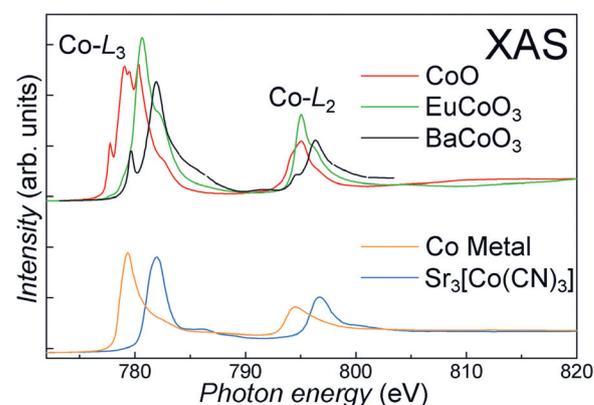


Fig. 4: Co- $L_{2,3}$ XAS spectra of $\text{Sr}_3[\text{Co}(\text{CN})_3]$, CoO, BaCO_3 , EuCoO_3 , and Co metal.

beamline of the synchrotron NSRRC in Taiwan. The XPS spectrum shown in Figure 3 consists of two narrow lines representing the spin-orbit split Co $2p_{3/2}$ and $2p_{1/2}$ states of Co. The simplicity of the spectral line shape is remarkable. The absence of any significant satellite peak, the featureless shape of the line, and the extremely narrow line-width (1.1 eV) provide evidence for a closed shell configuration of Co $3d$ [22, 23]. In addition, the symmetric shape of the peaks without the high-energy tail – typically found for metallic systems – also indicates that $\text{Sr}_3[\text{Co}(\text{CN})_3]$ has a considerable band gap [22, 23].

Further support for the above results can be inferred from the XAS measurements. Figure 4 displays the isotropic Co- $L_{2,3}$ ($2p \rightarrow 3d$) XAS measured on $\text{Sr}_3[\text{Co}(\text{CN})_3]$ at 300 K (blue curve). The Co $2p$ core-hole spin-orbit coupling roughly splits the spectrum into two parts, namely the L_3 and L_2 white line regions. Figure 4 also includes the Co-

$L_{2,3}$ spectra of CoO (red), EuCoO₃ (green), and BaCoO₃ (black) which are characterized by well-defined Co valence states, 2+, 3+ and 4+, respectively. Figure 4 also includes the spectrum of elemental Co metal (orange) for comparison.

It is well-known that XAS spectra are highly sensitive to the valence state [24]. For transition metal ions with an open 3*d*-shell, an increase in the valence state of the metal ion by one causes a shift of the Co- $L_{2,3}$ white lines by one or more eV towards higher energies as illustrated by the CoO, EuCoO₃, and BaCoO₃ spectra. Yet, the high energy of the white lines of Sr₃[Co(CN)₃] should not be interpreted in terms of a Co valence of 4+ or more. On the contrary, the lack of sharp multiplet features is fully consistent with the closed 3*d*¹⁰ shell assignment from XPS. The absorption features are then given by the rather broad structures of the conduction band. Furthermore, the observation of the white lines of Sr₃[Co(CN)₃] at energies higher than those of elemental Co metal indicates that the material is an insulator with an appreciable band gap, probably of order of 2 eV.

Quantum Chemical Calculations

The calculated density of states (DOS) [25] for Ba₃[Co(CN)₃] (Fig. 5) shows six groups of peaks denoted A0, A1, A2, B, C, D within the energy range between -20 eV and the Fermi level (set to 0 eV). A calculated band gap of about 0.7 eV indicates semiconducting behaviour which is consistent with the experimental data. Due to the purely technical character of the atomic sphere regions and the associated atomic sphere projected DOS, a more founded site projection has been additionally calculated, namely the QTAIM atomic site projection [26,27] for regions A – D (Tab. 2). Obviously, for regions A – C the dominating QTAIM atoms correspond to the ones dominating the atomic sphere projected local DOS. Regions A – C are identified as the expected ones for a metalate with the transition metal in *d*¹⁰ configuration, namely the nominal Ba-5*p* (A0, 18 e⁻/ f.u.), the CN-*ss*σ (A1, 6 e⁻/ f.u.), the CN-*ss*σ* (A2, 6 e⁻/ f.u.), CN-*pp*σ/π (B, 18 e⁻/ f.u.), and the Co-3*d* (C, 10 e⁻/ f.u.) orbitals. The most interesting and novel part corresponds to DOS region D, where it is to be noted that 77% of the electrons are not contained inside any atomic sphere.

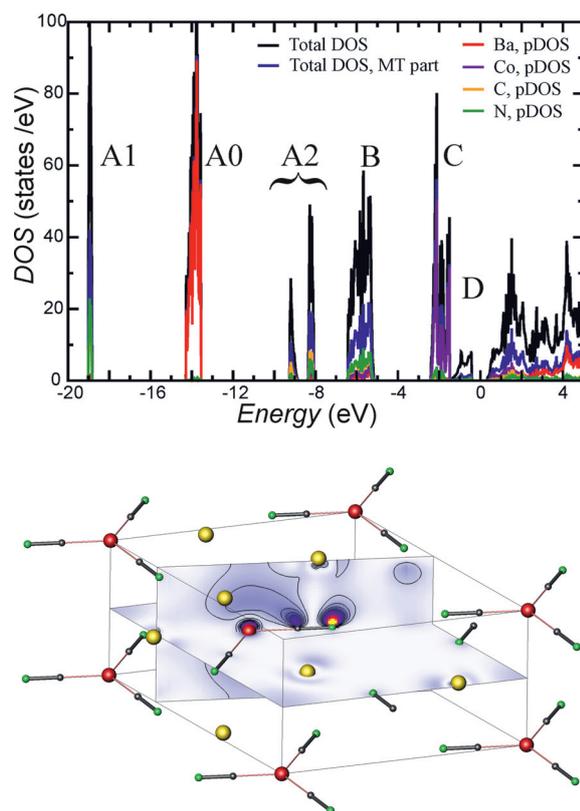


Fig. 5 top: DOS for Ba₃[Co(CN)₃]; bottom: electron density for DOS D; spheres denote atoms (Co: red, C: black, N: green, Ba: yellow).

Tab. 2: QTAIM atomic site projection of DOS regions A0 – D. The portion of electrons of each unit per f.u. is given in %. QTAIM effective charges Q^{eff} from the total electron density are given. They are identical to the ones obtained in sum from DOS A0 – D.

	e ⁻ / f.u.	3 Ba	1 Co	3 CN
DOS A0	18	93%	0.4%	6%
DOS A1	6	3%	0.2%	97%
DOS A2	6	6%	12%	83%
DOS B	18	7%	8%	85%
DOS C	10	7%	65%	29%
DOS D	2	27%	21%	53%
Q^{eff}		Ba ^{1.4+}	Co ^{0.0}	(CN) ^{1.4-}

The corresponding electron density plot (Fig. 5) reveals an interaction between a CN- $pp\pi^*$ and a diffuse Co state with a node within the molecular plane. From the electronic occupation ($2 e^-$ f.u.), region D can be identified to belong to the A'' representation of the site symmetry group C_{3h} of the cobalt atom, for which only the p_z orbital contribution is strictly allowed at the Γ point of the Brillouin zone (BZ). At other points of the BZ other states could, in principle, mix, but this does not significantly happen as is proven by the shape of the partial electron density around Co. The QTAIM atomic site projection of DOS region D (Tab. 2) reveals a portion of 53% of the electrons belonging to the CN groups, 21% belonging to the Co atoms, and 27% to the Ba atoms. Thus, the highest occupied band (HOCO) with its 2 electrons is to be attributed mainly to the three CN groups, leaving Co with oxidation state 1^- and each CN ligand being significantly reduced with a formal charge according to $CN^{1.67^-}$. These results, obtained by a formal procedure, are consistent with the QTAIM effective charges $Co^{0.0}$ and $CN^{1.4^-}$ (Tab. 2). The latter are expected to lie always somewhat closer in value to ± 0 than the formal ones [28].

The occupation for the CN- $pp\pi^*$ antibonding orbital is compatible with the experimentally observed long distance C–N (123.5(5) pm) and the comparably low C–N stretching frequency (1680 cm^{-1}). The short distance Co–C (176.9(3) pm) could be explained by the partial Co–C $pp\pi$ bond established in the HOCO by stabilizing delocalization of the CN π^* orbital towards the transition metal.

Future Perspectives

In conclusion, the air and moisture-sensitive isotypic phases $A E_3[Co(CN)_3]$ are the first examples of highly reduced cyanometalates, containing the complex anion $[Co(CN)_3]^{6-}$ with a closed-shell configuration of Co and significantly reduced CN ligands. The results of the investigations of the physical properties and of the quantum chemical calculations form a consistent picture of these unusual highly reduced compounds. The resulting oxidation state 1^- for Co and the five remaining negative charges belonging to the three CN ligands are unprecedented in inorganic chemistry.

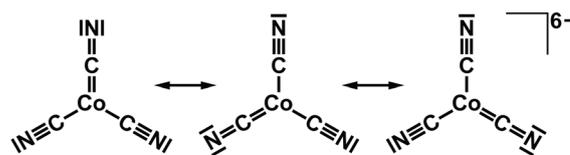


Fig. 6: Mesomeric forms of $[Co(CN)_3]^{6-}$

By taking into account the occupation of CN- $pp\pi^*$ antibonding orbitals, the long C–N distance and the low C–N stretching frequency, as well as the short Co–C distance it is conceivable that the three CN groups of the complex anion are further reduced and symmetry related equivalent to $([Co^{1-}(CN)^{1.67^-}]_3)^{6-}$. However, for ease of understanding, an approximate basic description implies stabilization by mesomeric forms $[Co^{1-}(CN)^3-(CN)^{-2}]^{6-}$ (Fig. 6) including the $(CN)^{3-}$ ligand which corresponds to a $12 e^-$ system, isoelectronic with the O_2 molecule, and called a percyano-group. Consequently, the complex anion can be described as a *monopercyano-dicyano-cobaltate (1-)*. Formally, $[Co(CN)_3]^{6-}$ as well as $[Co(CO)_3]^{3-}$ and $[Co(NO)_3]$, represent exceptionally rare examples of 3-coordinate, 18-electron systems which are isoelectronic to Krypton.

Future research will be focused on related electron-rich systems of the neighboring elements Fe and Mn as well as on corresponding carbonyl compounds.

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