Homoleptic Isocyanide Metalates

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Isocyanides are derived from CO by replacing the oxygen atom with the isoelectronic—but less electronegative—NR unit. Therefore it is not surprising that isocyanides also form stable metal complexes that are similar to metal carbonyls in terms of composition and structure. Remarkably, however, up to the middle of this century a large number of neutral and anionic metal carbonyl complexes was without exception opposed only by homoleptic isocyanide complex cations.[1–5] These compounds were either obtained by the exhaustive alkylation of cyanometalates or by treatment of metal salts with the free ligand.[1]

The first homoleptic metal carbonyl, $[NiCO_4]$, was already described in 1890,[6] whereas information about the first analogous isocyanide systems, $[Ni(CNPh)_4]$ and $[Ni(CNC_6H_4OEt)_4]$, only dates back to the 1950s.[7, 8] Even to date the number of neutral homoleptic metal carbonyls known clearly exceeds that of the corresponding isocyanide complexes (Table 1).[3] On the other hand homoleptic carbonyl metal cations have—compared to the numerous stable isocyanide complexes of metals in positive oxidation states—been one of the missing links in the field of carbonyl chemistry for nearly a hundred years. Recent research, however, has provided us with the missing information about isolable and thermally surprisingly stable salts with cations such as $[Au(CO)_2]^+$, $[Hg(CO)_2]^{2+}$, $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os), and $[Ir(CO)_6]^{3+}$, if one does not take into consideration complexes such as $[M(CO)_6]^+$ (M = Mn, Tc, Re) that have been known for a longer time.[9] There are also blank areas in the field of isocyanide complex chemistry, which have remained for more than a century: homoleptic isocyanide metalates $[M_n(CNR)_m]^{x-}$, to which a large number of—partly highly reduced—carbonyl analogues $[M_n(CO)_m]^{x-}$ correspond.[10, 11]

It was deduced from preparative results, IR data, electrochemical studies, and theoretical calculations that CO—as a weak σ-donor, but excellent π-acceptor ligand—is ideally suited to stabilize metal complexes in oxidation states ≤0. In contrast, alkyl and aryl isocyanides proved to be much stronger σ-donor, but poorer π-acceptor ligands than CO. It has, however, to be emphasized that the acceptor capability of CNR can be tuned within certain limits by the nature of R. [5]

Not unexpectedly, these bonding concepts did not encourage efforts to prepare homoleptic carbonyl metal cations or isocyanide metalate anions. Therefore it is not all that surprising that the above-mentioned carbonyl metal cations were discovered by researchers working on fluorine chemistry and not those working on organometallic chemistry.[9]

Essentially at the same time as these studies, Cooper et al. reported on the synthesis, structure, and reactivity of $K[Co(CNXyl)_4]$ (Xyl = 2,6-$Me_2C_6H_3$), the first isocyanide

Table 1. Fully characterized cationic and neutral homoleptic metal–isocyanide complexes.[3]

Group 5	6	7	8	9	10	11
$[V(CNR)_6]^+$	$[Cr(CNR)_6]$ $[Cr(CNR)_6]^+$ $[Cr(CNR)_6]^{2+}$ $[Cr(CNR)_6]^{3+}$ $[Cr(CNR)_7]^{2+}$	$[Mn(CNR)_6]^+$	$[Fe(CNR)_5]$ $[Fe_2(CNR)_9]$	$[Co_2(CNR)_8]$ $[Co(CNR)_5]^+$ $[Co(CNR)_5]^{2+}$ $[Co_2(CNR)_{10}]^{2+}$	$[Ni(CNR)_4]$ $[Ni_4(CNR)_7]$ $[Ni(CNR)_4]^{2+}$	$[Cu(CNR)_4]^+$
	$[Mo(CNR)_6]$ $[Mo(CNR)_7]^{2+}$		$[Ru(CNR)_5]$ $[Ru_2(CNR)_9]$ $[Ru_2(CNR)_{10}]^{2+}$	$[Rh(CNR)_4]^+$ $[Rh_2(CNR)_8]^{2+}$ $[Rh_2(CNRNC)_4]^{2+}$[a]	$[Pd_3(CNR)_6]$ $[Pd_2(CNR)_6]^{2+}$ $[Pd_3(CNR)_8]^{2+}$ $[Pd(CNR)_4]^{2+}$	$[Ag(CNR)_2]^+$
	$[W(CNR)_6]$ $[W(CNR)_7]^{2+}$	$[Re(CNR)_6]^+$	$[Os(CNR)_5]$ $[Os_2(CNR)_{10}]^{2+}$	$[Ir(CNR)_4]^+$	$[Pt_3(CNR)_6]$ $[Pt_7(CNR)_{12}]$ $[Pt(CNR)_4]^{2+}$ $[PdPt(CNR)_6]^{2+}$ $[Pt_2(CNR)_6]^{2+}$	$[Au(CNR)_2]^+$

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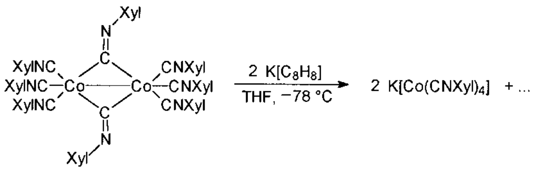
metalate.[12] Such exotic complexes are now well on the way to becoming familiar reagents in the synthetic arsenal of preparative chemists.

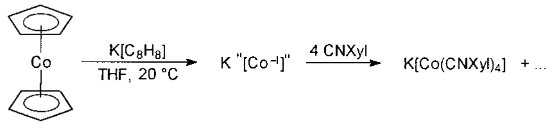
Preparation

The synthesis of the orange-yellow complex K[Co(CNXyl)$_4$] was initially achieved by substituting all ethene ligands in K[Co(C$_2$H$_4$)$_4$] with xylyl isocyanide [Eq. (a)].[12] Subsequently, this compound was prepared analogously to carbonyl metalates by reducing octakis(isocyanide)dicobalt [Eq. (b)] or cobaltocene with potassium naphthalenide [Eq. (c)].[13] The potassium napthalenide reduction of [Co(CNR)$_5$)BF$_4$] as well as [Co(CNR)$_4$I$_2$] also afforded the desired compound in similar good yields (70–80%). Burgundy-red solutions in THF of the thermally unstable and not isolable salts K$_2$[Ru(CNR)$_4$] (R = Xyl, *t*Bu) were obtained analogously at −78 °C [Eq. (d)].[14] The existence of isocyanide ruthenates was supported by derivatization with Ph$_3$SnCl and other trapping reagents (see below). The same strategy was successfully applied for the synthesis of the manganate ion [Mn(CNXyl)$_5$]$^-$. Black-red crystals of the compound [K([18]crown-6)][Mn(CNXyl)$_5$] were isolated in 53% yield from the blood-red THF solution, which was generated by the reduction of [Mn(CNXyl)$_5$Cl] and subsequent addition of [18]crown-6 [Eq. (e)].[15]

$$\mathrm{K[Co(C_2H_4)_4]} + 4\ \mathrm{XylNC} \xrightarrow[-78\,^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{K[Co(CNXyl)_4]} + 4\ \mathrm{C_2H_4} \tag{a}$$



(b)



(c)

$$\mathrm{[Ru(CNR)_4Cl_2]} \xrightarrow[\mathrm{THF},\ -78\,^\circ\mathrm{C}]{4\ \mathrm{K[C_8H_8]}} \mathrm{K_2[Ru(CNR)_4]} + 2\,\mathrm{KCl} + \dots \tag{d}$$

R = Xyl, *t*Bu

$$\mathrm{[Mn(CNXyl)_5Cl]} \xrightarrow[-78\,^\circ\mathrm{C}\ \ \mathrm{THF}]{2\,\mathrm{K[C_8H_8]}} \mathrm{K[Mn(CNXyl)_5]} \xrightarrow{[18]\mathrm{crown\text{-}6}} \mathrm{[K([18]crown\text{-}6)][Mn(CNXyl)_5]} \tag{e}$$

Chemical Properties

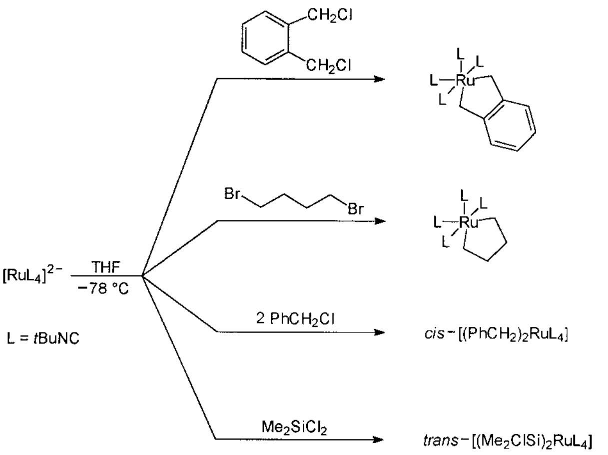
In analogy to carbonyl metalates,[11] the presented extremely reactive anions are transformed into stable neutral complexes by reaction with equivalent amounts of Ph$_3$SnCl [Eqs. (f)–(h)]. The compound K$_2$[Ru(CN*t*Bu)$_4$] also oxidatively adds electrophiles with Si and C as central atoms [Eqs. (i)–(l)]. In contrast, the alkylation of pentakis(isocyanide)manganate with methyl iodide or ethyl iodide[16] took a different course and can be compared to the methylation of [Fe(CN*t*Bu)$_5$].[17] In both cases the alkylation at the metal center was followed by the insertion of two isocyanide ligands under the formation of 1,4-diazabutadien-2-yl-complexes [Eq. (m)]. If *t*BuNC was added before the methylation, the mixed complex [Mn(XylNC)$_3$(*t*BuNC){XylN=C–C(Me)=NXyl}] was formed.[16]

$$\mathrm{[Co(CNXyl)_4]^-} + \mathrm{Ph_3SnCl} \longrightarrow \mathrm{[Ph_3SnCo(CNXyl)_4]} + \mathrm{Cl^-} \tag{f}$$

$$\mathrm{[Ru(CNR)_4]^{2-}} + 2\,\mathrm{Ph_3SnCl} \longrightarrow trans\text{-}\mathrm{[Ru(CNR)_4(SnPh_3)_2]} + 2\,\mathrm{Cl^-} \tag{g}$$

R = Xyl, *t*Bu

$$\mathrm{[Mn(CNXyl)_5]^-} + \mathrm{Ph_3SnCl} \longrightarrow \mathrm{[Mn(CNXyl)_5(SnPh_3)]} + \mathrm{Cl^-} \tag{h}$$

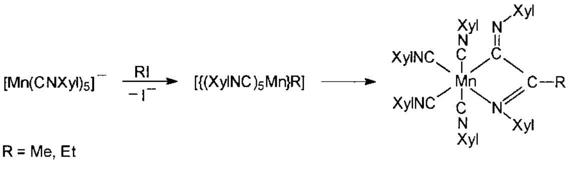


(i)

(j)

(k)

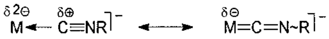
(l)

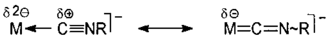


(m)

Bonding and Structures

The negative charge results in strong metal-CN-π-back donation by which the antibonding π*-CN-orbitals are filled (Scheme 1). Thus, the wavenumbers of the $\tilde{\nu}$ (CN) stretching





Scheme 1. The strong metal-CN-π-back donation in homoleptic isocyanide metalates under participation of antibonding π*-CN-orbitals.

vibrations of the terminal xylyl isocyanide ligands were shifted from $\tilde{\nu} = 2150, 2115\ \text{cm}^{-1}$ in the cation $[Co(CNXyl)_5]^+$ to $\tilde{\nu} = 2010\ \text{cm}^{-1}$ in neutral $[Co_2(CNXyl)_8]$ to $\tilde{\nu} = 1815\ \text{cm}^{-1}$ in the anion $[Co(CNXyl)_4]^-$. In the free ligand $\tilde{\nu}$(CN) was determined at $2116\ \text{cm}^{-1}$ (Table 2).

Table 2. CN vibrational stretching frequencies $\tilde{\nu}$(CN) $[\text{cm}^{-1}]$ of homoleptic isocyanide complexes.

Isocyanide complex	$\tilde{\nu}$(CN) $[\text{cm}^{-1}]$	Solvent	Ref.
$[Co(CNXyl)_4]^-$[a]	1890 sh, 1815 br.	THF	[12, 13]
$[Co_2(CNXyl)_8]$	2010, 1680	THF	[13]
$[Co(CNXyl)_5]^+$	2150, 2115	THF	[13]
$[Ru(CNXyl)_4]^{2-}$	1670 vs	THF	[14]
$[Ru(CN\textit{t}Bu)_5]$[b]	2059 sh, 2032 s, 1832 s br.	n-C_6H_{14}	[18]
$[Fe(CN\textit{t}Bu)_5]$	2110 sh, 2005 s, 1830 s	n-C_6H_{14}	[18]
$[Fe(CNXyl)_5]$	2036 sh, 1978 vs, 1870 sh	n-C_6H_{14}	[18]
$[Mn(CNXyl)_5]^-$	1920 s, 1710 m	THF	[15]

[a] $\tilde{\nu}$(CNXyl) (in THF) = $2116\ \text{cm}^{-1}$. [b] $\tilde{\nu}$(CN*t*Bu) (in CCl_4) = 2145 s, 2115 w, 2079 w.

The X-ray structure analyses of $[K(dme)][Co(CNXyl)_4]$ and $[K([18]crown\text{-}6)dme](Mn(CNXyl)_5)]$ (dme = 1,2-dimethoxyethane) feature besides discrete cations discrete distorted tetrahedral $[Co(CNXyl)_4]^-$ and trigonal-bipyramidal $[Mn(CNXyl)_5]^-$ ions, respectively. The isocyanide ligands of the cobaltate ion are nonlinear, their C-N-C angles range between 147.7(9) and 165.2(14)°. In contrast, the structure of the manganate ion resembles that of the homoleptic neutral complex $[Fe(CN\textit{t}Bu)_5]$.[17, 18] The valence angles at the axial isocyanide ligands are markedly more obtuse (163°) than those at the equatorial isocyanide ligands (143–149°). This can be explained with a more effective π-back-bonding from the negatively charged metal center to the equatorial isocyanide ligands. Accordingly, we find nearly linear C-N-C units in cationic isocyanide complexes, in which π-back-bonding is of only marginal importance.[4, 19–23]

Outlook

With the first results on the synthesis, structure, and reactivity of the homoleptic isocyanide metalates $[Co(CNXyl)_4]^-$, $[Ru(CNR)_4]^{2-}$ (R = Xyl, *t*Bu), and $[Mn(CNXyl)_5]^-$ the door to the chemistry of this class of compounds has been opened significantly. It has been impressively demonstrated that the capability of isocyanides to stabilize metals in negative oxidation states has probably been underestimated. In view of the versatile chemistry of carbonyl metalates one eagerly awaits the further development of isocyanide metalate chemistry.

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