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Reaction of cyanamide and their derivatives with $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$

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Dedicated to Prof. Dr. Dr. h.c. mult. Wolfgang A. Herrmann.

Abstract

The reaction of cyanamide and its derivatives with the $(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF)$ and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2(THF)$ complexes affords the cyanamide substituted complexes of types $(\eta^5\text{-}C_5H_5)Mn(CO)_2(NCN(R')(R''))$ (**2a**–**d**) and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2(NCN(R')(R''))$ (**3a**–**e**). All complexes were characterized by spectroscopy (^1H, ^{13}C NMR, IR), elemental and mass spectroscopy analysis. Complex **2b** $(\eta^5\text{-}C_5H_5)Mn(CO)_2(NCN(CH_3)_2)$ was additionally examined by single crystal X-ray structure determination.

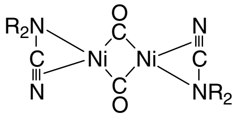
Keywords: Carbonyl complex; Cyanamide; Cyclopentadienyl; Half sandwich complex; Manganese

1. Introduction

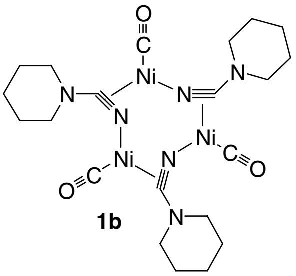
Cyanamides are amino-functionalized nitriles of biological and synthetic interest which display high reactivity. Despite the well developed coordination chemistry of organonitrils [1] and biological and synthetic interest of cyanamide ($NCNH_2$) and $NCNC(NH_2)_2$ [2], there have been few reports on the reactivity of cyanamide ligands, and the activation of cyanamide by transition metals remains to be explored further.

The main reaction for this ligand class is polymerization, which is known now for a long time. Oligomerization and cocyclotrimerization of acetylene leads to dicyandiamide [3] and pyridine derivatives [4]. The reaction for the dicyandiamide is catalyzed by various bases [5], where the latter one is catalyzed by cobalt carbonyl or half-sandwich complexes of cobalt [6]. The formation of cyanamidium salts (highly substituted ureas, isoureas and guanidines) is catalyzed by Lewis acids ($SbCl_5$, $FeCl_3$) [7]. Despite the breadth of these reactions little is known about the fundamental organometallic chemistry of cyanamide complexes.

The first reports of cyanamide complexes were published in 1962 by Bock et al. [8]. In a reaction of dialkylcyanamide with an excess of $Ni(CO)_4$, they obtained an orange air sensitive complex and postulated the dimeric complex **1a** [9].



1a



1b

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Spectroscopic data later confirmed this proposed structure, and were consistent with a coordination of the cyanamide ligand by the free electron pair of the amine nitrogen and the π-electrons of the CN-triple bond [10]. A bridging cyanamide complex coordination was also observed for $Mo_2(OCH_2C(CH_3)_3)_6(\mu\text{-}NCNMe_2)$ by Chisholm et al. in 1983 [11]. In 1966 Kogmann and Mattes published a solid state structure of the piperidine μ-cyanamide nickel complex **1b**; in contrast to **1a** a trimeric structure was obtained [12], with a triangulo Ni_3-core, terminally bonded carbonyl ligands and bridging cyanamide ligands. Each cyanamide bridges two nickel atoms, forming a N-σ-bond to one nickel atom and a C≡N-π-bond to the other nickel atom.

The adducts of cyanamide and dimethylcyanamide at bis(cyclopentadienyl)tetracarbonyldimolybdenum published by Chisholm and Cotton some years later were structurally equivalent to the coordination behavior of the trimeric form **1b** [13].

Cyanamide chromium and molybdenum carbonyl complexes of the general formula $L_nM(CO)_{6-n}$ were prepared by Bock and Tom Dieck [14]. In these complexes, the cyanamide ligand is coordinated "end on" acting as a σ-donor ligand with weak π-acceptor ability and no bridging coordinations are observed (Scheme 1). Complexes of this type have been structurally characterized first by Fischer in 1978 [15].

These ambidentate ligands also participate in a variety of organometallic reactions. Published reports on reactivity include the metal-centered cleavage of cyanamide [16], hydrogenation of NCN systems [17], dehydrogenation reaction by electron rich Mo(0) and W(0) complexes [18], deprotonation or deamination of cyanoguanidine to give $NCNC(NH)NH_2^-$ or $NCNCN^-$ derivatives [19], or the formation of cyanamide complexes of, e.g., $NCNR_2$ (R = Me, Et) with Pt(II) [20] and Fe(II) [21] precursors.

Cyanamide half-sandwich complexes were not known at the beginning of our work [22]. Thus we have focused on a family of manganese Cp-complexes [$(\eta^5\text{-}C_5H_5)Mn(CO)_3$ (**2**) and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$ (**3**)] to investigate the reactivity of $NCNH_2$ and its derivatives with these complexes. In the following discussion, we present the synthesis and a structure of cyanamide manganese Cp-complexes, which help to further understand the organometallic chemistry of these intriguing complexes.

$$n(R_2N\text{-}CN) + M(CO)_6 \xrightarrow[-\ n(CO)]{} (R_2NCN)_nM(CO)_{6-n}$$

M = Cr, Mo
n = 1,2,3

Scheme 1. Preparation of cyanamide substituted chromium and molybdenum carbonyl complexes.

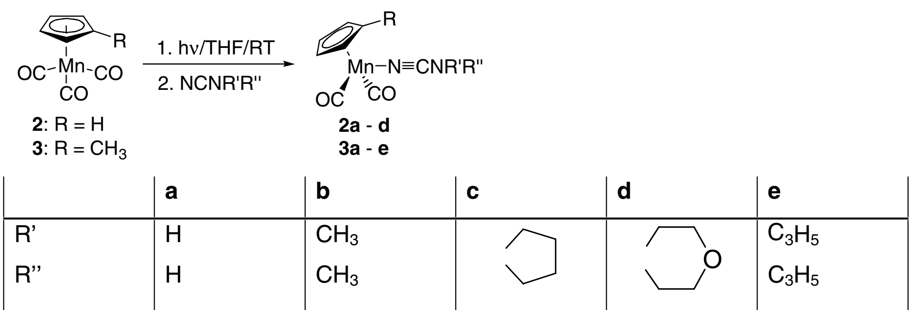
2. Results and discussion

The reaction of the solvent substituted complexes of the half-sandwich precursor complexes $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ (**2**) and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$ (**3**) with cyanamide and its derivatives at room temperature resulted in moderate yields of the desired complexes **2a**–**d** and **3a**–**e**, respectively (Scheme 2). These complexes display a structural motif similar to that of the isocyanide complex $Cp(CO)_2$-$MnCNC(Cr(CO)_5)NCCl_2$, which was first reported by Beck and Fehlhammer [23]. Complexes **2a**–**d** and **3a**–**e** appear to be relatively stable toward the atmosphere in the solid state, but are highly air sensitive and decompose within minutes in solution in the presence of oxygen. The stability of these complexes is increased by alkyl substitution at the Cp-ring (**3**) and at the cyanamide fragment (**b**–**d**).

Strong ν(N≡C) bands in the range of 2304–2252 cm^{-1} were observed in the IR-spectra of complexes **2a**–**d** and **3a**–**e**. Upon coordination to metals, the free ligands (**a**–**e**) shift to shorter wavelengths for the ν(N≡C) band by 30–50 cm^{-1} (Table 1). The observed ν(N≡C) stretching frequencies are comparable to those reported for the related complexes [15,18,20,21,32]. Further evidence of these coordination modes is provided in the solid state X-ray structure of **2b** shown in Fig. 1. Crystal data and

Table 1
CN-valence vibration (cm^{-1}) of complexes **2a**–**d** and **3a**–**e** in THF compared to the corresponding free ligand

	2	3	Free ligand
a	2304	2304	2248
b	2259	2258	2216
c	2255	2254	2209
d	2257	2255	2216
e		2252	2213



Scheme 2. Preparation of complexes **2a**–**d** and **3a**–**e**.