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Preliminary communication

ORGANOMETALLIC ANIONS CONTAINING ISONITRILE LIGANDS

II*. THE SYNTHESIS AND REACTION CHEMISTRY OF CYCLOPENTADIENYLMOLYBDENUM DICARBONYLMETHYLISONITRILE ANION

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Summary

The anion, $(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3^-$, has been prepared and spectroscopically investigated. The results show that the isonitrile ligand readily and extensively engages in metal to ligand π-backbonding. This anion undergoes chemical reaction via halide displacements producing a variety of neutral complexes containing isonitrile ligands. In reactions with $CH_2(Cl)CN$, $(CH_3)_3GeBr$, $(CH_3)_3SnCl$, and $(C_6H_5)_3PbI$ in THF at —78°, the compounds $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)R$ ($R = CH_2CN$, $Ge(CH_3)_3$, $Sn(CH_3)_3$, and $Pb(C_6H_5)_3$) have been prepared. These results demonstrate the synthetic value of the new reagent.

Recent studies have shown isonitrile molecules to be unusually versatile ligands [2]. This undoubtedly arises from their ability to bond through both σ-donation and π-backbonding.

In an effort to further investigate the importance of the π-backbonding component we have initiated a study of organometallic anions which contain isonitrile ligands, in hopes of (1) obtaining some evidence as to the extent in which isonitrile ligands might engage in π-backbonding, and (2) generating suitable intermediates which might be valuable for further use in syntheses of isonitrile complexes. We report here the results of our studies of the anion $(\eta^5\text{-}C_5H_5)Mo(CO)_2CHCN_3^-$ (I). Reduction of the complex $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)Cl$ with Na(Hg) in tetrahydrofuran at room temperature gives, upon filtration, a light yellow solution containing the anion I. This is supported by the PMR spectrum taken in tetrahydrofuran-d_8 which shows resonances at τ 5.05(5) (C_5H_5) and 7.10(3) ($N—CH_3$) ppm. The infrared spectrum (in THF) shows absorptions at 1710, 1765, and 1875 cm^{-1}. The two lower energy absorptions may be assigned

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[*] For part I see ref. 1.

TABLE 1

MELTING POINTS, IR AND NMR DATA OF THE COMPOUNDS PREPARED

Compound	M.p. (°C)	Infrared (cm^{-1}) [a]	PMR (τ, ppm)
$(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3CH_2CN$	78-80	2205 w, 2163 m, 1080 w 1970 s, 1913 m, 1908 s	4.70(C_5H_5); 4.87(C_5H_5); 6.40 (CH_3) 6.43(CH_3); 8.77(CH_2); 8.85(CH_2) [b]
$(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3Ge(CH_3)_3$	137.5-139.5	2142 m, 1960 m, 1937 m 1890 m, 1878 s	4.96(C_5H_5); 5.02(C_5H_5); 6.61(N—CH_3); 6.56(N—CH_3); 9.48(Ge—CH_3); 9.54(Ge—CH_3) [b]
$(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3Sn(CH_3)_3$	112-113.5	2139 m, 2110 (sh), 1947 m 1927 m, 1883 m, 1871 s	5.01(C_5H_5); 5.07(C_5H_5); 6.53(N—CH_3); 6.62 (N—CH_3); 9.68(Sn—CH_3); 9.73(Sn—CH_3) [b] $J(^{117,119}Sn–H) \cong 45$ Hz
$(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3Pb(C_6H_5)_3$	152.5-154.4 (dec.)	2125 m, 1969 s, 1945 (sh) 1899 s, 1890 (sh)	2.60(C_6H_5). 4.60(C_5H_5). 4.83(C_5H_5) 6.27(CH_3). 6.95(CH_3) [c]

[a] In C_6H_{12}. [b] In $CDCl_3$. [c] In acetone-d_6.

to the CO stretches, and their low frequencies attest to the anionic character of the complex. The absorption at 1875 cm^{-1} must be assigned to the CN stretching vibration, as there are no other absorptions observed in the multiple bond stretching region. The low frequency[*] of this absorption also supports the anionic character of the complex, but more importantly indicates that the ligand is now extensively engaged in π-backbonding.

In addition, the anion has proven to be a very effective intermediate for use in the synthesis of a variety of isonitrile complexes. In reactions with the compounds CH_2ClCN, $(CH_3)_3GeBr$, $(CH_3)_3SnCl$, and $(C_6H_5)_3PbI$ in tetrahydrofuran at −78°, the compounds $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CHCN_3)R$ ($R = CH_2CN$, $Ge(CH_3)_3$, $Sn(CH_3)_3$, and $Pb(C_6H_5)_3$) have been prepared[**]. Pertinent spectral and physical properties are listed in Table 1. As indicated by the infrared spectra, all compounds apparently exist as a mixture of *cis* and *trans* isomers [3].

Addition of deoxygenated acetic acid to solutions of the anion, followed by solvent evaporation and hexane extraction, yields yellow-brown crystals on cooling to −78°. These can be dried at low temperature, but melt when warmed to room temperature. The PMR spectrum of this oil in benzene shows resonances at τ 5.15(5) (C_5H_5); 7.83(3) (CH_3); and 15.05(1) (H). The high field resonance is indicative of the Mo—H bond [4]. The infrared spectrum shows absorptions at 2136 (CN), 1963 (CO), and 1900 (CO) cm^{-1}, and strongly indicates formulation of the compound as $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)H$. The hydride is thermally unstable and undergoes complete decomposition in a few hours at room temperature to give mainly $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$ [5] and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$, in approximately a 3/1 ratio. We have not been able to identify the expected decomposition product, $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)]_2$. It may be that this dimer is comparatively unstable and decomposes to the more stable unsubstituted and monosubstituted dinuclear species.

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[*] This reduction in frequency is nearly 300 cm^{-1} from that in the free ligand which occurs at 2160 cm^{-1}.

[**] Satisfactory elemental analyses have been obtained for these compounds.