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Preliminary communication

ORGANOMETALLIC ANIONS CONTAINING ISONITRILE LIGANDS

I. THE SYNTHESIS OF CYCLOPENTADIENYLIRONCARBONYL METHYLISONITRILE HYDRIDE AND ITS REACTIONS WITH GROUP IVB ALKYL HALIDES

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Summary

Reduction of the dimer, $[(\eta^5\text{-}C_5H_5)Fe(CO)CNCH_3]_2$, with sodium amalgam in tetrahydrofuran leads to the formation of the hydride, $(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_3)H$. It engages in a base-catalyzed reaction with Group IVB halides to form compounds of the type $(\eta^5\text{-}C_5H_5)FeCO(CNCH_3)R$, ($R = CH_2CN$, $Ge(CH_3)_2Cl, Sn(CH_3)_3$) and also $Hg[Fe(\eta^5\text{-}C_5H_5)(CO)(CNCH_3)]_2$. It is proposed that the hydride reacts via the anion, $(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_3)^-$, which is formed by base-induced deprotonation.

To date, there have been very few reports on the syntheses of organometallic anions containing isonitrile ligands [1]. Thus, in an effort to produce and study the physical and reaction chemistry of such species, we have carried out the reduction of the dimer [2], $[(\eta^5\text{-}C_5H_5)_5Fe(CO)(CNCH_3)]_2$ (I) with sodium amalgam in tetrahydrofuran at −15°. During the reduction a green intermediate solution is formed which is slowly converted* to an orange-brown solution. Carefully prepared samples of this latter solution show only two infrared absorptions in the CO and CN stretching region. These are at 2140 and 1935 cm^{-1}, and are characteristic of terminally coordinated carbonyl and isonitrile ligands. Chromatographic analysis ($Al_2O_3/6\%H_2O$) of the reduction solutions leads to the isolation of a thermally and oxidatively unstable yellow compound. Its infrared spectrum in tetrahydrofuran is identical to that observed in the reduction solution, indicating that it is by far the major component. Its

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*The latter transformation takes approximately 15 minutes at −15°, and only a matter of seconds when warmed to room temperature. In reductions carried out at room temperature the green intermediate is not observed.

PMR spectrum in C_6H_6 shows resonances at τ 5.58(5), 7.83(3) and 22.15(1). The very high field resonance of intensity 1 strongly indicates that the compound may be formulated as the hydride, $(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_3)H$ (II). In behavior similar to $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ [3], it readily decomposes to the dimer $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_3)]_2$.

Freshly prepared reduced solutions of the hydride are very useful for the synthesis of new organometallic complexes containing isonitrile ligands. Thus, reaction with the halides RCl (R = CH_2CN, $(CH_3)_2GeCl$ and $(CH_3)_3Sn$) in THF at −78° has led to the synthesis of the corresponding complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_3)R$. In a similar reaction, the compound $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_3)]_2Hg$ has also been prepared from HgI_2*. Pertinent spectral and physical properties are listed in Table 1. As expected, compounds III and IV show the presence of diastereotopic methylene protons and methyl groups as a result of the asymmetric coordination environment around the iron atom. The presence of more than one carbonyl absorption suggests the occurrence of different rotameric configurations. These may be formed by partial internal rotations around the Fe—C and Fe—Ge bonds [4]. Attempts to prepare compounds possessing iron—silicon bonds have so far been fruitless. The reason for this is not entirely clear, but similar observations have been made previously [5]. Recently, it has been speculated that iron—silicon bonds may even be weaker than iron—carbon bonds in systems of this type [6]. This could account for a relative instability.

TABLE 1

SPECTRAL AND PHYSICAL PROPERTIES OF THE COMPOUNDS III-VI

Compound	M.p. (°C)	Color	Infrared[a, b] (cm^{-1})	PMR (τ)[c]
$(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_3)(CH_2CN)$ (III)	<25	Orange	2200 m 2156 s(br) 1970 s(sh), 1960 s	5.80(5)[d] C_5H_5 7.67(3) $N{-}CH_3$ $\left.\begin{array}{l}9.02(1)\\9.08(1)\end{array}\right\}CH_2$
$(\eta^5\text{-}C_5H_5)FeCO(CNCH_3)Ge(CH_3)_2Cl$ (IV)	57-60	Yellow	2145 m(br) 1966 m, 1954 s	5.73(5) C_5H_5 7.75(3) $N{-}CH_3$ $\left.\begin{array}{l}8.90(3)\\8.92(3)\end{array}\right\}GeCH_3$
$(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_3)Sn(CH_3)_3$ (V)	33.5-34.5	Yellow	2108 m 1936 s	9.52(9)[e] $Sn(CH_3)_3$ 5.80(5) C_5H_5 7.77(3) $N{-}CH_3$
$[(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_3)]_2Hg$ (VI)	130-131	Orange	2090 m(vbr) 1971 w 1915 s(br)	5.67(5) C_5H_5 7.67(3) $N{-}CH_3$

[a] C≡O and C≡N stretching region. [b] C_6H_{12} solvent. [c] C_6H_6 solvent. [d] Relative intensity. [e] $J(^{117,119}Sn) \cong 42$ Hz.

Evidence for the mechanistic course of the reaction between the hydride and these halides was obtained from the following experiment. When filtered over a sintered glass frit, freshly prepared solutions of the hydride were highly

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*Satisfactory elemental analysis have been obtained for these new compounds.

active* toward reaction with chloracetonitrile, but when filtered over a short column of $Al_2O_3/6\%H_2O$, the hydride became completely unreactive. It could, however, be reactivated by addition of a tetrahydrofuran solution of potassium isobutoxide, and good yields of the product III were again obtained. The base activation strongly suggests that the active species is probably the anion, $(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_3)^-$, formed by deprotonation of the hydride. The observation that solutions of the hydride plus isobutoxide show only the absorptions due to the hydride indicates that the equilibrium 1 lies very largely

$$(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_3)(H) \rightleftharpoons (\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_3)^- + H^+ \qquad (1)$$

on the side of the associated species even in very basic solvents. Similar equilibria have been observed for other systems [7].

We do not yet know the identity of the species which activates the freshly prepared solutions of the hydride, but tetrahydrofuran is the most likely source of the proton originally used in its formation and a basic species which may be present could be an enolate anion formed by the decomposition of deprotonated tetrahydrofuran [8]. Further studies are in progress.

While the organometallic anion in this work is of limited existence, it is synthetically very effective. We believe that a general category of organometallic anions containing isonitrile ligands may be prepared and serve as the basis for the synthesis of a vast number of neutral complexes in which isonitrile ligands have been incorporated into the coordination sphere of metal atoms.

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*Yields of 70% or greater are common.