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Preliminary communication

THREE COMPOUNDS FROM THE REACTION BETWEEN DICARBONYL(METHYLCYCLOPENTADIENYL)(TETRAHYDROFURAN)-MANGANESE AND 4-CYANOPYRIDINE

RENATE GROSS and WOLFGANG KAIM
Institut für Anorganische Chemie der Universität, Niederurseler Hang,
D-6000 Frankfurt am Main 50 (F.R.G.)

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Summary

The isolation and characterization of two mononuclear complexes and one binuclear compound from the reaction between dicarbonyl(methylcyclopentadienyl)(tetrahydrofuran)manganese and 4-cyanopyridine are reported. The competition between the pyridine and nitrile nitrogen centers for coordination with the (η^5-$C_5H_4CH_3$)$Mn(CO)_2$ fragment results in the formation of two mononuclear complexes, of which the N^1-coordinated isomer is more stable.

Although recent studies of dicarbonyl(cyclopentadienyl)manganese (I) complexes with N-heterocyclic ligands have involved alkyl, aryl, pyridyl, alkoxy, nitro, acyl, and halogen substituted pyridines [1—3], no such complexes have previously been reported with the ambident cyanopyridine ligands. This gap is the more conspicuous because there is a standard route [1—4] for synthesis of such species (cf. eq. 1) and cyanopyridines have long been employed as ligands [5,6], especially with other d^6 metal fragments such as $[Ru(NH_3)_5]^{2+}$ [6,7] and $M(CO)_5$ (M = Cr, Mo, W) [8—11]. While with pentammineruthenium(II) mono- [6] and bi-nuclear [7] species were readily obtained, the pentacarbonylmetal fragments were reported to give only mononuclear complexes with coordination invariably occurring at the pyridine nitrogen [8-11].

In continuation of our efforts to synthesize elusive [3] $CpMn(CO)_2$ complexes [12], we report here the successful synthesis, separation, and spectroscopic characterization of mono- and bi-nuclear dicarbonyl(methylcyclopentadienyl)manganese complexes with 4-cyanopyridine.

The title compounds were prepared from 4-cyanopyridine and the photo-

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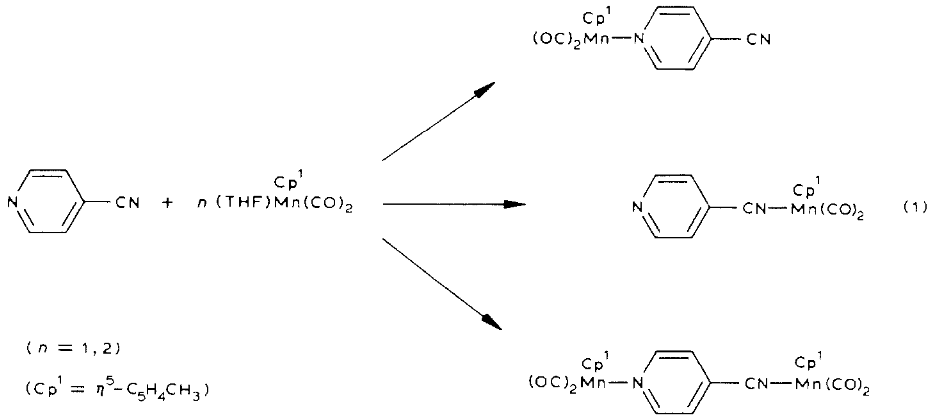
generated [1,4] solvent complex $MnCp^1(CO)_2(THF)$ in tetrahydrofuran (eq. 1). Although both 1/1 and 1/2 ratios of the reactants yielded predominantly the desired complexes, there were always significant amounts of the other compounds present, and low-temperature (—20° C) column chromatography proved to be necessary to separate three species, one bi- and two mono-nuclear complexes.



The complexes were eluted with increasingly polar solvents in the order (4-cyanopyridino-*N*^{1})dicarbonyl(methylcyclopentadienyl)manganese, (4-cyanopyridino-*CN*^{4})dicarbonyl(methylcyclopentadienyl)manganese, and (μ-4-cyanopyridino-*N*^{1},*CN*^{4})tetracarbonylbis(methylcyclopentadienyl)dimanganese. The compounds were characterized by analytical and spectroscopic techniques (cf. Table 1). The nitrile-coordinated mononuclear complex proved to be the most labile, undergoing conversion rapidly to the other isomer and the binuclear species at room temperature.

The fact that both mononuclear and the binuclear species are formed in reaction 1 demonstrates nicely that the $MnCp^1(CO)_2$ fragment readily coor-

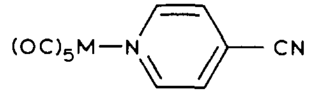
TABLE 1

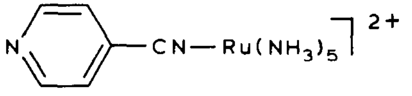
NITRILE AND CARBONYL INFRARED STRETCHING FREQUENCIES ν (cm^{-1}) FOR *CN*- AND *N*-COORDINATED COMPLEXES OF $MnCp^1(CO)_2$ FRAGMENTS IN THF SOLUTION ($Cp^1 = \eta^5$-$C_5H_4CH_3$) cp: 4-cyanopyridine; tn: terephthalonitrile (1,4-dicyanobenzene)

Complex	ν(CN)	ν(CO)[a]			
		A_1		B_1	
		b	c	b	c
(tn)$MnCp^1(CO)_2$	2205(m)[d]	1940	—	1880	—
(cp-*CN*^{4})$MnCp^1(CO)_2$	2215(m)	1942	—	1883	—
(cp-*N*^{1},*CN*^{4})$[MnCp^1(CO)_2]_2$	2200(m)	1946	1928	1885	1860
(cp-*N*^{1})$MnCp^1(CO)_2$	2238(w)[e]	—	1928	—	1861
(pyrazine)$MnCp^1(CO)_2$ [f]	—	—	1930	—	1865
(pyrazine)$[MnCp^1(CO)_2]_2$ [f]	—	—	1928	—	1855

[a] All bands very strong. [b] Bands of nitrile-coordinated metal fragments. [c] Bands of $MnCp^1(CO)_2$ fragments coordinated to heterocyclic nitrogen. [d] Only one CN stretching frequency observed, cf. refs. 4, 13.
[e] ν(CO) 2243 cm^{-1} for the free cp ligand, ref. 6. [f] Ref. 12.

dinates to both sites of the unsymmetrically bridging ligand 4-cyanopyridine. This behaviour contrasts with that of pentacarbonylmetal fragments of Group 6*d* which only yield mononuclear pyridine-coordinated complexes [8—11]. The low-spin d^6 metal fragment $[Ru(NH_3)_5]^{2+}$, on the other hand, yields mono- and bi-nuclear complexes not only of 4-cyanopyridine but also of 1,4-dicyanobenzene (terephthalonitrile) [7] ; Clarke and Ford reported the formation of the nitrile-coordinated mononuclear (4-cyanopyridine)pentammineruthenium(II) complex (eq. 2) in a kinetically-controlled reaction [6].





(2)

(M = Cr,Mo,W)

In the case of the organometallic manganese fragments, the infrared spectroscopic results (Table 1) clearly indicate that two different mononuclear complexes are formed, and that in the more stable compound the organometallic Mn^I fragment prefers the more basic [6] heterocyclic nitrogen center for coordination. In the complex eluted first by column chromatography, the CN stretching band is almost unchanged in frequency and (low) intensity by coordination of one manganese fragment, whereas with the second mononuclear species and the binuclear complex (which must have a $MnCp^1(CO)_2$ fragment coordinated to the cyano group) there is a distinct decrease in frequency and an increase of intensity in the ν(CN) band, both effects resulting from coordination of a back-bonding metal fragment to a nitrile group [4,6,13].

Both CO stretching frequencies show a clear dependence on whether the coordination of $MnCp^1(CO)_2$ has occurred at the heterocyclic nitrogen ($\nu(CO) \simeq 1930$ and $1860\ cm^{-1}$, cf. pyridine [1] and pyrazine complexes [12]) or at the cyano group ($\nu(CO) \simeq 1945$ and $1880\ cm^{-1}$ [4]). Thus, it appears that in the reaction with 4-cyanopyridine the mobile [12] dicarbonyl(methylcyclopentadienyl)manganese fragment has some thermodynamic preference for coordination at the more basic heterocyclic nitrogen center, but, it is also capable of binding to the nitrile group.

More detailed studies of the electronic structures of these complexes are in progress, the system presented here constitutes a remarkable case of coordinative ambivalence, and extension of this work will focus on other factors which determine the coordination preference of dicarbonyl(cyclopentadienyl)manganese fragments for either the nitrile or the pyridine nitrogen site in cyanopyridines.

Experimental

All procedures were carried out under dry argon with rigorously dried solvents under subdued light.

In a typical experiment intended to give predominantly mononuclear complexes, 3.3 g (15 mmol) of $MnCp^1(CO)_3$ were photolyzed at —40°C in 250 ml THF to yield the solvent complex $MnCp^1(CO)_2$)THF). This solution was then allowed to react with 1.56 g (15 mmol) of 4-cyanopyridine in a Schlenk tube for 24 h at room temperature. After removal of the solvent the residue was chromatographed on a Florisil column at −20° C. Pure hexane first eluted unchanged MnCp^1(CO)$_3$, hexane/toluene yielded a purple-red zone of the pyridine-coordinated mononuclear complex, and toluene/ether gave the light-brown fraction of the nitrile-coordinated mononuclear species. Finally, pure THF eluted some of the purple binuclear complex; the yield of the latter was improved by starting with a 1/2 ratio of ligand and manganese compound. The complexes were crystallized from THF/hexane at −30° C, yields of purified compounds ranging from 10—20%.

(4-Cyanopyridino-N^1*)dicarbonyl(methylcyclopentadienyl)manganese(I).* ^{1}H NMR (300 MHz; C_6D_6): δ 1.13 (s, 3H), 3.86 (s, 2H), 3.98 (s, 2H), 5.66 (d, 2H), 8.10 (d, 2H), $^3J_{2,3}$ 6 Hz. UV/VIS (THF): ν 20 100 cm^{-1}. Found: C, 57.05; H, 3.88; N, 9.42; Mn, 18.75. $C_{14}H_{11}MnN_2O_2$ calcd.: C, 57.16; H, 3.77; N, 9.52; Mn, 18.67%.

(4-Cyanopyridino-CN^4*)dicarbonyl(methylcyclopentadienyl)manganese(I).* ^{1}H NMR (300 MHz; C_6D_6): δ 1.55 (s, 3H), 4.03 (s, 2H), 4.23 (s, 2H), 6.01 (d, 2H), 8.08 (d, 2H), $^3J_{2,3}$ 6 Hz. UV/VIS (THF): ν 22 500 cm^{-1}.

(μ-4-Cyanopyridino-N^1*,CN*^{4}*)tetracarbonylbis(methylcyclopentadienyl)-dimanganese(I).* ^{1}H NMR (300 MHz; C_6D_6): δ 1.16 (s, 3H), 1.54 (s, 3H), (s, 2H), 4.02 (s, 4H), 4.23 (s, 2H), 5.32 (d, 2H), 8.07 (d, 2H), $^3J_{2,3}$ 6.4 Hz. UV/VIS (THF): ν 18 400 cm^{-1}. Found: C, 54.41; H, 3.87; N, 5.76; Mn, 22.85. $C_{22}H_{18}Mn_2N_2O_4$ calcd.: C, 54.56; H, 3.75; N, 5.78; Mn, 22.69%.

Dicarbonyl(methylcyclopentadienyl)terephthalonitrile)manganese(I) was prepared as previously described [4].

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