Journal of Organometallic Chemistry, 71 (1974) 91—96
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CYANIDE AND ISOCYANIDE METAL COMPLEXES

V*. POLYCYANO CYCLOPENTADIENYL-MOLYBDENUM AND -MANGANESE COMPOUNDS

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(Received October 15th, 1973)

Summary

Cyanide replaces first the halide and then the carbonyl groups in cyclopentadienyldicarbonyltriodomolybdenum(IV) to give $C_5H_4RMo(CO)_2(CN)_3$ and $K_2[C_5H_4RMo(CN)_5]$ (R = H or Me).

Photolysis of methylcyclopentadienyltricarbonylmanganese with cyanide gives crude $K_3[C_5H_4MeMn(CN)_3]$, recognised by alkylation to $K_2[C_5H_4MeMn(CN)_2CNEt]$ and $K[C_5H_4MeMn(CNEt)_2CN]$, in addition to $K[C_5H_4MeMn(CO)_2CN]$. The latter has been protonated and alkylated to $C_5H_4MeMn(CO)_2CNR$ (R = H viz. Me) and regenerated from these products with KCN.

Introduction

In Part II [2] we suggested that molybdenum(IV) complexes such as the dicarbonyl trihalides $C_5H_5Mo(CO)_2X_3$ should be good precursors of polycyano derivatives in view of the known preference for high oxidation states for such compounds. We have confirmed this and here describe the results of our experiments together with evidence for the existence of the manganese(I) compound $[C_5H_4MeMn(CN)_3]^{3-}$.

Results and discussion

The readily available [3, 4] triodomolybdenum compound $C_5H_5Mo(CO)_2I_3$, as well as its ring-methyl derivative $(C_5H_4Me)Mo(CO)_2I_3$, reacted with potassium cyanide in alcoholic solution in two distinct stages. Following reaction at room temperature, the solutions contained the tricyanodicarbonyl

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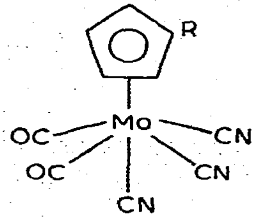
* For Part IV, see ref. 1.

TABLE 1

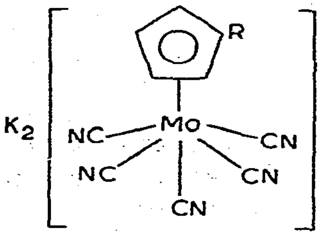
SPECTRAL DATA FOR THE MOLYBDENUM COMPOUNDS

Compound		Infrared maxima (cm^{-1}) (Nujol mulls)		^{1}H NMR signals[a] (τ ppm)	
		ν(CO)	ν(CN)	C_5H_4R	CH_3
$C_5H_5Mo(CO)_2I_3$		2068, 2027		3.5	
$C_5H_5Mo(CO)_2(CN)_3$	(I: R = H)	2135, 2020	2215, 2183, 2175(sh)	3.8	
$C_5H_4MeMo(CO)_2(CN)_3$	(I: R = Me)	2120, 2000	2220, 2185, 2170(sh)	4.0	7.7
$K_2[C_5H_5Mo(CN)_5]$	(II: R = H)		2180, 2109, 2095	4.8*	
$K_2[C_5H_4MeMo(CN)_5]$	(II: R = Me)		2170, 2100, 2080	4.9*	7.9*
$[C_5H_4MeMo(CO)_3]_2$		1970, 1935, 1925		4.6	7.75

[a] NMR spectra in $CDCl_3$ except where asterisked, when they were measured in D_2O.



(I)



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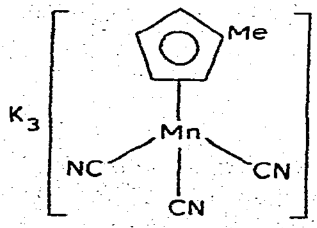

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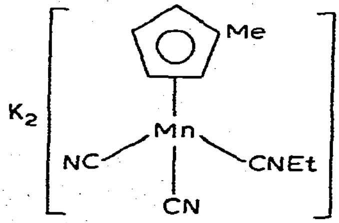
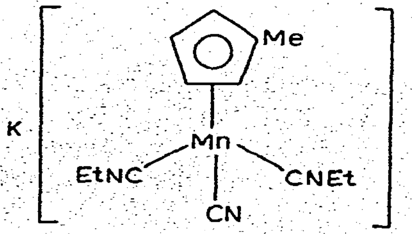


(IV)



(V)

complexes (I: R = H or Me) whereas reaction in refluxing methanol gave the pentacyano derivatives (II). The initial displacement of iodide rather than carbonyl contrasts with the behaviour [2] of the cobalt(III) analogue, $C_5H_5Co(CO)I_2$ and with the reported [3] reaction (eqn. 1) of the corresponding bromo complex with pyridine.

$$C_5H_5Mo(CO)_2Br_3 + 2\,C_5H_5N \rightarrow C_5H_5Mo(NC_5H_5)_2Br_3 + 2\,CO \qquad (1)$$

The sensitivity of all the new cyanides towards air and moisture discouraged further chemical study, but satisfactory analytical data were obtained for three of the compounds [the methyl-substituted pentacyanide (II: R = Me) was not isolated pure] and their spectra (see Table 1) support the structural assignments. Table 1 includes as comparison spectral data of cyclopentadienyl molybdenum(I) carbonyl and molybdenum(IV) carbonyl halide derivatives. Perhaps the most striking features in these spectra are the very high carbonyl stretching frequencies and correspondingly low field cyclopentadienyl ^1H NMR signals of the carbonyl cyanides as expected for the high oxidation state of the metal.

Although irradiation of cyclopentadienyltricarbonylmanganese with potassium cyanide had only been reported [5] to yield a monocyano complex, $[C_5H_5Mn(CO)_2CN]^-$, further study of this system was prompted by the possibility that polycyano species might be accessible if the corresponding hydrogen isocyanide complex, $C_5H_5Mn(CO)_2(CNH)$, obtained by protonation [5] suffers preferential displacement of CO (before CNH) by cyanide.

Because of the greater availability of the methyl-substituted precursor, $C_5H_4MeMn(CO)_3$, we converted this by the known routes [5] to the corresponding intermediates, the potassium salt, $K[C_5H_4MeMn(CO)_2CN]$, and the "free acid", $C_5H_4MeMn(CO)_2CNH$, which were fully characterised. Reaction of the latter with potassium cyanide merely regenerated the former, but whereas this could be attributed to simple deprotonation, the exactly analogous behaviour of the methyl isocyanide complex, $C_5H_4MeMn(CO)_2CNMe$, shows that preferential replacement of the isocyanide before carbonyl must occur according to eqn. 2.

$$C_5H_4MeMn(CO)_2CNR + KCN \rightarrow K[C_5H_4MeMn(CO)_2CN] + CNR \qquad (2)$$

(R = H or Me)

The methyl isocyanide complex used for this reaction, was readily formed by alkylation of the potassium salt with methyl iodide, following established precedents [2, 6, 7].

However, as reported for the lower homologue [5], during the formation of the salt $K[C_5H_4MeMn(CO)_2CN]$ by irradiation of the corresponding tricarbonyl with potassium cyanide, a small amount of yellow solid precipitated. Infrared examination indicated the absence of carbonyl groups and led us to repeat this reaction with excess of cyanide. The precipitate thus obtained in markedly increased yield had infrared maxima, including $\nu(CN)$ 2124, 2115 cm^{-1}, consistent with its formulation as the tricyano complex (III), but could not be purified. Its suspension in methanol was therefore heated with a suspension of triethyloxonium tetrafluoroborate and the soluble product so obtained

TABLE 2

SPECTRAL DATA FOR THE MANGANESE COMPOUNDS

Compound	Ref.	Infrared maxima [a] (cm^{-1})			^1H NMR signals (τ ppm) [b]		
		ν(CO)	ν(CN)	ν(CNR)	C_5H_4R	C—CH_3	CNR
$Na[C_5H_5Mn(CO)_2CN]$	5	1905, 1829*	2058*		5.68 [c]		
$K[C_5H_4MeMn(CO)_2CN]$		1915, 1820	2055		5.57	8.1	
$C_5H_5Mn(CO)_2CNH$	5	1919, 1859*		2016*	5.83 [d]		5.8(br) [d]
$C_5H_4MeMn(CO)_2CNH$		1920, 1860		2010			
$C_5H_5Mn(CO)_2CNC_6H_{11}$	8,9,11	1949, 1896 [e]		2120			
$C_5H_4MeMn(CO)_2CNMe$		1945, 1896		2180	5.6	8.1	6.2
$K_3[C_5H_4MeMn(CN)_3]$ [f] (III)			2127, 2115				
$K_2[C_5H_4MeMn(CN)_2$-$CNEt]$ (IV)			2085, 2070	2140	5.6 [g]	8.25 [g]	6.5(q), 8.7(t) [g]
$K[C_5H_4MeMn(CNEt)_2$-$CN]$ (V)			2050	2150, 2120	5.5 [g]	8.2 [g]	6.4(q), 8.6(t) [g]

[a] IR spectra as Nujol mulls except where asterisked when they were measured on KBr discs. [b] Integrals showed the expected signal ratios in all cases; peaks are singlets unless otherwise indicated. Spectra in $CDCl_3$ except where indicated otherwise. [c] In $(CD_3)_2CO$. [d] In C_6D_6. [e] 1957, 1905 in cyclohexane solution [11]. [f] Too insoluble for NMR study. [g] In D_2O.

was separated chromatographically giving two new salts. Analysis and spectroscopic examination left no doubt that these must be formulated as the mono- and di-alkylated compounds (IV) and (V) and hence proves that the precursor is indeed the tricyanomanganese(I) complex (III). The relevant spectral data are in Table 2 together with those of the other new manganese complexes and, for comparison literature data for ring-unsubstituted analogues where available. The incompleteness of the alkylation (contrast refs. 2 and 6) may be due to the heterogeneity of the reaction mixture.

Experimental

For general directions see Part III [6].

Methylcyclopentadienyl)dicarbonyltriiodomolybdenum(IV)

Following the method for the unsubstituted compound [3], a benzene solution of iodine (0.76 g, 3 mmol) was added dropwise to a stirred solution of bis[(methylcyclopentadienyl)tricarbonylmolybdenum] [10] (0.52 g, 2 mmol) in benzene (100 ml). After stirring for 1 h the mixture was kept in the dark at room temperature for 24 h. The black crystalline precipitate was collected, washed with benzene and n-pentane and dried in vacuo. The triiodo compound so obtained (0.61 g, 50%) may be further purified by chromatography using anhydrous ethanol as eluant; it has m.p. 47°. (Found: C, 15.4; H, 0.8; I, 62.6. $C_8H_7I_3MoO_2$ calcd.: C, 15.7; H, 1.1; I, 62.3%.)

Cyclopentadienyldicarbonyltricyanomolybdenum(IV), (I: R = H)

Potassium cyanide (0.18 g, 2.8 mmol) in absolute ethanol (≈ 400 ml) was added with stirring to cyclopentadienyldicarbonyltriiodomolybdenum(IV) [3] (0.61 g, 1 mmol) in ethanol (50 ml). After stirring at room temperature overnight the solution was filtered, evaporated to dryness under reduced pressure, and the residue crystallised from chloroform. The tricyano compound (I:

R = H) (0.214 g, 42%) was obtained as brown crystals, m.p. 105° (dec.), giving yellow solutions in polar organic solvents. (Found: C, 41.0; H, 1.9; N, 14.5. $C_{10}H_5MoN_3O_2$ calcd.: C, 40.7; H, 1.6; N, 14.2%.)

(Methylcyclopentadienyl)dicarbonyltricyanomolybdenum(IV), (I: R = Me)

This compound (0.12 g, 38%) was obtained similarly from the above methyl-substituted triiodo compound (0.63 g, 1 mmol) as brown crystals, m.p. 95° (dec.). (Found: C, 42.9; H, 2.6; N, 13.9. $C_{11}H_7MoN_3O_2$ calcd.: C, 43.2; H, 2.3; N, 13.7%.)

Dipotassium cyclopentadienylpentacyanomolybdate(IV), (II: R = H)

Potassium cyanide (0.36 g, 5.6 mmol) in methanol (400 ml) was added to cyclopentadienyldicarbonyltriiodomolybdenum(IV) [3] (0.61 g, 1 mmol) and the mixture was refluxed overnight. The product was filtered off, washed with carbon tetrachloride and extracted with water. The aqueous solution was evaporated to dryness under reduced pressure to give the brown air-sensitive dipotassium salt (II: R = H) (0.13 g, 33%), m.p. 225° (dec.). (Found: C, 32.8; H, 1.4; N, 19.3. $C_{10}H_5K_2MoN_5$ calcd.: C, 32.5; H, 1.4; N, 19.0%.)

II (R = Me) was formed similarly, but was not isolated in a pure state.

Potassium (methylcyclopentadienyl)dicarbonylcyanomanganate(I), K[MeC$_5$H$_4$-Mn(CO)$_2$CN]

Following the method for the cyclopentadienyl analogue [5] a mixture of (methylcyclopentadienyl)tricarbonylmanganese (I) (2.2 g, 10 mmol) and potassium cyanide (0.65 g, 10 mmol) in methanol (500 ml) was irradiated overnight, the yellow precipitate then filtered off and the filtrate evaporated to dryness under reduced pressure. The residue was chromatographed using methanol as eluant to give the monocyano compound (1.3 g, 50%) as a yellow solid, m.p. 117° (dec.), soluble in water and in organic solvents. (Found: C, 42.5; H, 3.0; N, 5.2. $C_9H_7KMnNO_2$ calcd.: C, 42.35; H, 2.75; N, 5.5%.)

(Methylcyclopentadienyl)(hydrogen isocyanide)dicarbonylmanganese(I)

The preceding potassium salt (0.51 g, 2 mmol) was dissolved in water (40 ml) and stirred with phosphoric acid (20 ml, 2*N*) for 15 min. The product was extracted with ether (3 × 20 ml), the extract dried ($MgSO_4$) and evaporated under reduced pressure, leaving yellow crystals (0.2 g, 46%), m.p. 67° (dec.). A sample was further purified for analysis by sublimation at 20 mmHg. (Found: C, 50.1; H, 3.9; N, 6.2. $C_9H_8MnNO_2$ calcd.: C, 49.8; H, 3.7; N, 6.45%.) Photolysis of this compound with an equivalent quantity of potassium cyanide in methanol solution (18 h) regenerates the cyano complex, K[MeC$_5$H$_4$Mn(CO)$_2$CN] (65%).

(Methylcyclopentadienyl)(methyl isocyanide)dicarbonylmanganese(I)

Potassium (methylcyclopentadienyl)dicarbonylcyanomanganate(I) (0.51 g, 2 mmol) and methyl iodide (5 ml, 80 mmol) were refluxed overnight in acetonitrile (100 ml). The solution was filtered, evaporated under reduced pressure and the residue dissolved in dichloromethane. Addition of light petroleum to the filtered dichloromethane solution precipitated the product (0.31 g, 67%) as an air-sensitive orange solid, m.p. 57° (dec.). (Found: C, 52.1; H, 4.5; N, 5.9. $C_{10}H_{10}MnNO_2$ calcd.: C, 52.0; H, 4.4; N, 6.1%.) Photolysis of this compound with an equivalent quantity of potassium cyanide in methanol solution (18 h) regenerates the cyano complex, $K[MeC_5H_4Mn(CO)_2CN]$ (72%).

Tripotassium (methylcyclopentadienyl)tricyanomanganate(I), (III)

The yellow precipitate noted in the formation of potassium (methylcyclopentadienyl)dicarbonylcyanomanganate(I) increased significantly at the expense of the latter, when a large excess (1.95 g, 30 mmol) of potassium cyanide was employed in the photolysis. It is extremely air-sensitive, turning brown on exposure. Its structure as salt (III) follows from its infrared spectrum, which in addition to the bands listed (Table 2) included bands attributable to the methylcyclopentadienyl group, but no carbonyl bands, and from the following ethylation.

Ethylation of the tripotassium salt, (III)

Triethyloxonium tetrafluoroborate (4.2 g, 22 mmol) was added to a suspension of the tricyanide (III) (0.66 g, 2 mmol) in methanol (50 ml) and the mixture refluxed overnight, then filtered and the filtrate evaporated under reduced pressure. The residue was redissolved in methanol and chromatographed to give two orange bands. After elution and rechromatography, the first band yielded the dialkylated product (V) (0.15 g, 25%) as a yellow solid, m.p. 110° (dec.). (Found: C, 50.75; H, 5.7; N, 13.5. $C_{13}H_{17}KMnN_3$ calcd.: C, 50.5; H, 5.5; N, 13.6%.) The second band similarly yielded the salt (IV) (51 mg, 8%) as an orange solid, m.p. 96°. (Found: C, 41.6; H, 3.6; N, 12.9. $C_{11}H_{12}K_2MnN_3$ calcd.: C, 41.4; H, 3.8; N, 13.2%.)

The same products were obtained in better overall yields [62 mg, 20% of (V) and 32 mg, 10% of (IV)] in a single process from (methylcyclopentadienyl)-tricarbonylmanganese(I) (0.3 g, 1 mmol) when irradiation with potassium cyanide (0.26 g, 4 mmol) in methanol (500 ml) was carried out in the presence of triethyloxonium tetrafluoroborate (1.90 g, 10 mmol), thus obviating the isolation of the air-sensitive intermediate (III).

Acknowledgements

The authors thank Dr. P. Bladon and his staff for spectra, Mr. F.R. Daubney and his staff for analyses and the University of Strathclyde for a Studentship (to JAD).

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