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METAL COMPLEXES OF HETEROCYCLES III*. ACETYLPYRROLYL AND INDOLYL COMPLEXES

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In part I[2] we described π-pyrrolyl complexes of the types $(CO)_3MnC_4H_4N$ and $C_5H_5FeC_4H_4N$ in which the pyrrole nucleus was either unsubstituted or bore one or more methyl substituents. Extension to functionally substituted and polycyclic pyrroles has proved more difficult and it is shown in the preceding paper[1] that N-metal complexes become more stable in these cases. We have however succeeded in characterising both iron and manganese complexes bearing acetyl substituents on the pyrrole ring and π-complexes of manganese from 2-methylindole and from tetrahydrocarbazole. These complexes are obtained from the potassium salt of the heterocycle by the method employed previously[2]. In contrast to the alkylindoles, indolylpotassium reacted in more complex fashion with pentacarbonyl bromomanganese to give a product $C_9H_8Mn(CO)_3$ which is receiving further study.

The proton magnetic resonance spectra of the new acetylpyrrolyl complexes are tabulated below together with those of the alkyl-substituted compounds described previously[2]. The different substitution patterns of these complexes allow clearcut identification of all the observed peaks. The frequencies of the ring protons α to the nitrogen atom which occur at $\tau = 3.4$–3.9 in the free pyrroles are shifted upfield by *ca.* 0.5 τ (to $\tau = 3.9$–4.3) in the manganese and by *ca.* 1 (to $\tau = 4.7$–4.9) in the iron complexes. Those of the β-protons suffer a similar, but even greater, displacement from $\tau = 3.7$–4.4 in the parent pyrrole to $\tau = 4.6$–5.1 in the manganese and $\tau = 5.5$–5.8 in the iron complexes.

EXPERIMENTAL

All reactions were conducted under a nitrogen atmosphere.

Tricarbonyl-π-(3-acetyl-2-methylpyrrolyl)manganese

Potassium (0.53 g; 0.014 g-atom) and 3-acetyl-2-methyl-pyrrole[3] (1.9 g; 15 mmole) were refluxed in tetrahydrofuran (25 ml) for 3 h. To the cooled solution of the potassium salt so formed, pentacarbonylbromomanganese (3.35 g; 12 mmole) in tetrahydrofuran (50 ml) was added and the mixture was refluxed for 5 h. Evaporation under reduced pressure followed by chromatography of the product on alumina gave first decacarbonyldimanganese (0.76 g), eluted with ligroin (b.p. 60–80°) and then tricarbonyl-π-(3-acetyl-2-methylpyrrolyl)-manganese (0.91 g; 50%), eluted with

* Part II see ref. 1.

TABLE 1

NMR PEAKS (τ) IN π-PYRROLYL COMPLEXES[a]

Compound	*Groups on pyrrole*											
	Unsubstituted		*2,4-Dimethyl*			*2,5-Dimethyl*		*2-Methyl-3-acetyl*			*2,4-Dimethyl-3-acetyl*	
(a) Ring hydrogens	*α-H*	*β-H*	*α-H*	*β-H*		*β-H*		*α-H*	*β-H*		*α-H*	
Free pyrrole	3.32dd ($CDCl_3$)	3.78dd	3.9m (CCl_4)	4.42m		4.37d (CCl_4)		3.45d ($CDCl_3$)			3.61 ($CDCl_3$)	
Tricarbonyl-manganese complex	3.9 (CCl_4)	4.8	4.33m (CCl_4)	5.13m		5.1 (CS_2)		4.1d (CS_2)	4.46d		4.28 (CS_2)	
Azaferrocene	4.73 (CCl_4)	5.56	4.87m (CCl_4)	5.63m		5.79 (CCl_4)					4.78 (CS_2)	
(b) Methyl hydrogens			*α-CH₃*	*β-CH₃*	*α-CH₃*		*α-CH₃*	*COCH₃*	*α-CH₃*	*β-CH₃*	*COCH₃*	
Free pyrrole				7.97m	7.93		7.45	7.58	7.52	7.72	7.58	
Tricarbonyl manganese complex[b]			7.85	8.03	7.86		7.72	7.59	7.63	7.85	7.63	
Azaferrocene			7.8	8.03	7.76				7.55	7.85	7.55	

[a] For each compound the peaks showed the expected relative intensities. All peaks are singlets except those marked d (doublets), dd (doubledoublet) or m (broad unresolved bands).

[b] Tricarbonyl-π-tetramethylpyrrolylmanganese shows peaks at τ = 7.93 (α-CH_3) and 8.1 (β-CH_3).

ligroin/benzene (1 : 1). It was further purified by sublimation at 40°/0.01 mm to give yellow crystals, m.p. 67.5–68°, ν_{max} (KCl disc) 2041, 1961 (MnC–O) and 1681 cm^{-1} (CH_3C–O). (Found: C, 46.4; H, 3.5; N, 5.4. $C_{10}H_8MnNO_4$ calcd.: C, 46.0; H, 3.1; N, 5.4%.)

Tricarbonyl-π-(3-acetyl-2,4-dimethylpyrrolyl)manganese

Potassium (0.54 g; 0.014 g-atom) and 3-acetyl-2,4-dimethylpyrrole (2.6 g; 9 mmole) were refluxed in tetrahydrofuran for 2 h. After cooling, pentacarbonylbromomanganese (3 g; 11 mmole) in tetrahydrofuran (50 ml) was added and the mixture refluxed for 5 h. Filtration through kieselguhr, evaporation under reduced pressure, followed by chromatography on alumina gave decacarbonyldimanganese (0.625 g) eluted with ligroin (b.p. 60–80°) and then tricarbonyl-(π-3-acetyl-2,4-dimethyl pyrrolyl)manganese (0.71 g; 45%) eluted with ligroin/benzene (1 : 1). After purification by distillation at 80–82.5°/0.02 mm and sublimation at room temperature/0.001 mm it formed yellow crystals, m.p. 44.5–45°, ν_{max} (KCl disc) 2041, 1961 (MnC–O) and 1681 cm^{-1} (CH_3C–O). (Found: N, 4.9, 5.0. $C_{11}H_{10}MnNO_4$ calcd.: N, 5.1%.)

π-(3-Acetyl-2,4-dimethylpyrrolyl)-π-cyclopentadienyliron

Potassium (0.51 g; 0.013 g-atom) and 3-acetyl-2,4-dimethylpyrrole (2.66 g; 19 mmole) were refluxed with stirring in tetrahydrofuran (10 ml) for 3 h. Most of the solvent was then evaporated by increasing the flow of nitrogen and, after cooling, dicarbonylcylopentadienyliodo-iron (4.6 g; 13 mmole) in benzene (75 ml) was added and the mixture refluxed for 5 h. After cooling and filtration (kieselguhr) the solution was evaporated *in vacuo* to small bulk and then chromatographed on alumina. Ligroin eluted a trace of ferrocene; ligroin/benzene (1 : 1) then eluted unreacted iodo compound (2.35 g) and ether eluted π-(3-acetyl-2,4-dimethylpyrrolyl)-π-cyclopentadienyliron (82 mg; 4%) a viscous red oil which was further purified by "sublimation" at 40°/0.01 mm. It was very sensitive to air and light and too unstable to be characterized by analysis. Its identity follows from its NMR spectrum (see Table 1 plus cyclopentadienyl peak at $\tau = 5.95$); ν_{max} (liquid film) 1667 cm^{-1} (CH_3C–O) and 1105, 1000 cm^{-1} (C_5H_5).

Tricarbonyl-π-(2-methylindolyl)manganese

Potassium (0.41 g; 0.01 g-atom) and 2-methylindole (2.0 g; 17.5 mmole) were refluxed in benzene (50 ml) for 2 h. After cooling, pentacarbonylbromomanganese (3.26 g; 12 mmole) in benzene (50 ml) was added and the mixture refluxed for 4 h. The cooled and filtered (kieselguhr) solution was evaporated to small bulk, under reduced pressure, and then chromatographed on alumina. Ligroin eluted decacarbonyldimanganese (0.84 g) and ligroin/benzene (7 : 3) eluted a mixture of the product and unreacted 2-methylindole. Removal of the latter by prolonged sublimation at room temp./0.01 mm left tricarbonyl-π-(2-methylindolyl)manganese (0.25 g; 16%) which formed orange crystals, m.p. 91.5–92°, ν_{max} (KCl disc) 2041 and 1961 cm^{-1} (CO); NMR peaks (CS_2) at $\tau = 2.65$ (multiplet; aromatic H); 4.5 (singlet; H at C_3); 7.78 (singlet; CH_3) of relative intensity 4 : 1 : 3. (Found: C, 53.1; H, 3.0; N, 5.3. $C_{12}H_8MnNO_3$ calcd.: C, 53.3; H, 3.0; N, 5.2%.)

Tricarbonyl-π-(1,2,3,4-tetrahydrocarbazolyl)manganese

Potassium (0.35 g; 0.009 g-atom) and 1,2,3,4-tetrahydrocarbazole (1.71 g; 10 mmole) were refluxed in tetrahydrofuran (30 ml) for 12 h. After cooling, pentacarbonylbromomanganese (2.48 g; 9 mmole) in the same solvent (30 ml) was added and the mixture refluxed for 3 h, cooled, filtered and the filtrate evaporated under reduced pressure. The residue was dissolved in ligroin (b.p. 60–80°) and chromatographed on neutralised alumina. Ligroin eluted decacarbonyldimanganese (0.54 g) and benzene/ligroin (1 : 9) eluted tricarbonyl-π-(1,2,3,4-tetrahydrocarbazolyl)manganese (0.88 g; 46%). Sublimation at 75°/0.1 mm gave yellow crystals, m.p. 105–106°, ν_{max} 2045, 1957 cm^{-1} (MnC–O); NMR peaks (CS_2) at $\tau = 2.65$ (multiplet; aromatic H), 7.3 (multiplet; H at C_1 and C_4) and 8.05 (multiplet; H at C_2 and C_3) of relative intensity 1 : 1 : 1. (Found: C, 58.9; H, 4.1; N, 4.5. $C_{15}H_{12}MnNO_3$ calcd.: C, 58.3; H, 3.9; N, 4.5%.)

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SUMMARY

Tricarbonylmanganese complexes of 3-acetyl-2-methylpyrrole, 3-acetyl-2,4-dimethylpyrrole, 2-methylindole and tetrahydrocarbazole and (3-acetyl-2,4-dimethylpyrrolyl)cyclopentadienyliron are described. The NMR spectra of these and other π-pyrrolyl complexes are discussed.

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