Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

METAL COMPLEXES OF HETEROCYCLES II*. N-PYRROLYL COMPLEXES OF IRON

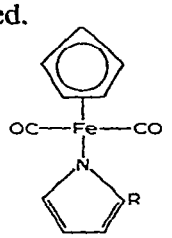
P. L. PAUSON AND A. R. QAZI
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow (Great Britain)

(Received May 26th, 1966)

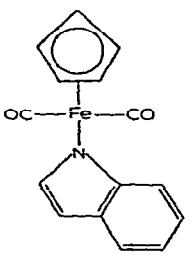
In the previous paper[1] we described the formation of π-pyrrolyl complexes of iron and manganese by the routes:

$$C_5H_5Fe(CO)_2I + C_4H_4NK \rightarrow 2\,CO + KI + C_5H_5FeC_4H_4N \quad (1)$$
$$Mn(CO)_5Br + C_4H_4NK \rightarrow 2\,CO + KBr + (CO)_3MnC_4H_4N \quad (2)$$

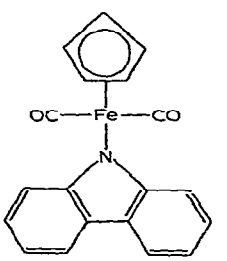
In each case, intermediate σ-pyrrolyl complexes may be postulated: $C_5H_5Fe(CO)_2$-σ-C_4H_4N and $(CO)_5Mn$-σ-C_4H_4N respectively, which would then lose carbon monoxide and change to the π-bonded end products. In the case of iron, an analogy is available from the reaction of the carbonyl halide with cyclopentadienylsodium[2] to give the dicarbonyl-π-cyclopentadienyl-σ- cyclopentadienyliron. We have now shown that the analogous σ-pyrrolyl complex (I; R = H) is indeed an intermediate which may be isolated by carrying out the above reaction (1) under mild conditions. Ready loss of carbon monoxide occurs on heating in refluxing benzene to give the π-complex. That the σ-complex is bonded through nitrogen as suggested by the mode of formation is clearly confirmed by the proton magnetic resonance spectrum and also by the absence of an N–H stretching frequency in the infrared.



I



II



III

Formation of stable N-pyrrolyl complexes appears to be favoured by certain substituents. Thus 2-acetylpyrrole and indole as well as tetrahydrocarbazole readily afford such compounds. At higher temperature the indoles also form π-complexes, but these less stable products have not yet been characterized fully. Carbazole gave only the N-carbazolyl complex (III).

In common with other carbonyl cyclopentadienyl derivatives the proton

* Part I see ref. 1.

resonance signal of the cyclopentadienyl group is found at lower frequency than in ferrocene or azaferrocene:

Compound:	$(C_5H_5)_2Fe$	$C_5H_5FeC_4H_4N$	$C_5H_5Fe(CO)_2$–σ–NC_4H_4	$C_5H_5Fe(CO)_2Br$
C_5H_5:	5.95	5.85	5.07	4.95

More remarkable is the change in the pattern observed for the hydrogens on the heterocyclic ring. The chemical shift difference between the α- ($\tau = 4.0$) and β- ($\tau = 4.15$) hydrogens is significantly reduced compared to pyrrole itself (α: $\tau = 3.3$; β: $\tau = 3.8$) and the splitting between them is more complex, whereas the opposite is true for the π-complex[3].

EXPERIMENTAL

All reactions were conducted under nitrogen.

Dicarbonyl-π-cyclopentadienyl-N-pyrrolyliron (I; R = H).

Pyrrolylpotassium was prepared by refluxing pyrrole (3.2 g; 48 mmole) and potassium metal (0.70 g; 0.017 g-atom) in benzene (50 ml) for 5–6 h. To the cooled solution, dicarbonylcyclopentadienyliodo-iron (6.6 g; 18 mmole) in benzene (50 ml) was added and the mixture was warmed to 50–60° for 2–3 h. The cooled mixture was filtered through kieselguhr, concentrated *in vacuo* and chromatographed on neutralized alumina. Ligroin eluted ferrocene (0.15 g); then benzene/ligroin (1 : 1) eluted unreacted iodo-compound (2.56 g) and ether eluted dicarbonyl-π-cyclopentadienyl-N-pyrrolyliron (0.6 g; 19%), further purified by low temperature crystallisation from ether and by sublimation at 60–70°/0.01 mm, to give brown crystals, m.p. 91°, ν_{max} 2020 and 1975 cm^{-1} in the carbonyl stretching region; NMR peaks (CS_2) at $\tau = 3.97$ (multiplet; α–H), 4.15 (doublet; β–H), 5.07 (singlet; C_5H_5) with relative intensities 2 : 2 : 5. (Found: N, 5.8, 5.6; $C_{11}H_9FeNO_2$ calcd.: N, 5.8%.) Finally ether eluted π-cyclopentadienyl-π-pyrrolyliron[1] (0.97 g; 35%).

A sample (0.12 g) of the N-pyrrolyl compound was refluxed in benzene (50 ml) with stirring for 1 h. Chromatography of the concentrated solution gave π-cyclopentadienyl-π-pyrrolyliron (56 mg; 60%); this was eluted with ether and was preceded on the column by bis(dicarbonylcyclopentadienyliron) (10 mg) which was eluted with ligroin/benzene (1 : 1). Both products were identified by mixed m.p. and infrared comparison with authentic samples.

Dicarbonyl-π-cyclopentadienyl(2-acetylpyrrol-1-yl)iron (I; R = $COCH_3$)

2-Acetylpyrrole (1.3 g; 12 mmole) was added to potassium metal (0.37 g; 0.1 g-atom) under benzene (30 ml) and the mixture refluxed for 5 h. After cooling, dicarbonylcyclopentadienyliodo-iron (3.22 g; 10 mmole) was added and the mixture warmed to 50–60° for 3 h. The product was worked up as in the preceding experiment. Chromatography yielded successively: ferrocene (0.15 g), unreacted iodocomplex (1.54 g), 2-acetylpyrrole (0.45 g) and dicarbonyl-π-cyclopentadienyl(2-acetylpyrrol-1-yl)iron (0.43 g; 28%), as yellow crystals, m.p. 110–111° after sublimation at 80–90°/0.01 mm; ν_{max} 2020, 1990 cm^{-1} (C≡O); NMR peaks (CS_2) at $\tau = 3.15$ (m; α–H); 3.45, 3.95 (m; β–H); 5.25 (s; C_5H_5) and 7.89 (s; CH_3CO) of relative intensity 1 : 1 : 1 : 4.9 : 3. (Found: C, 54.5; H, 4.0; N, 4.6. $C_{13}H_{11}FeNO_3$ calcd.: C, 54.8; H, 3.9; N, 4.9%.)

Dicarbonyl-π-cyclopentadienyl-1-indolyliron (II)

Indole (5.27 g; 45 mmole) and potassium (1.26 g; 0.04 g-atom) were refluxed in tetrahydrofuran (15 ml) until the formation of indolylpotassium was complete (3 h). Most of the solvent was then evaporated by increasing the flow of nitrogen and, after cooling, dicarbonylcyclopentadienyliodo-iron (8.0 g; 26 mmole) in benzene (175 ml) was added. The mixture was warmed to 60° for 5 h, then cooled, filtered, concentrated *in vacuo* and chromatographed on alumina. Ligroin (b.p. 60–80°) eluted ferrocene (0.25 g); benzene/ligroin (1 : 1) eluted unchanged iodo compound (3.87 g) and ether then eluted dicarbonyl-π-cyclopentadienyl-1-indolyliron (1.3 g; 31.5%). This formed red crystals, m.p. 114–114.5° by low temperature crystallisation from dichloromethane/ligroin; ν_{max} 2020 and 1975 cm^{-1} (C≡O); NMR peaks (CS_2) at $\tau = 3.3$ (broad multiplet; aromatic) and 5.06 (singlet; C_5H_5) of relative intensity 6 : 5. (Found : C, 61.1 ; H, 4.1 ; N, 4.75. $C_{15}H_{11}FeNO_2$ calcd. : C, 61.0 ; H, 3.8 ; N, 4.8%.) Further elution with ether gave an unidentified red oil (0.2 g); it had no carbonyl absorption in the IR and its NMR spectrum showed "aromatic" hydrogens, and a singlet at $\tau = 5.95$ attributable to a π-cyclopentadienyl group, but additional bands which were not readily identified.

Dicarbonyl-π-cyclopentadienyl(1,2,3,4-tetrahydrocarbazol-9-yl)iron

The reaction was conducted like the preceding one, substituting 1,2,3,4-tetrahydrocarbazole (3.42 g; 20 mmole) for indole, and using potassium (0.71 g; 0.018 g-atom) and dicarbonylcyclopentadienyliodo-iron (6.72 g; 22 mmole). Chromatography afforded ferrocene (0.25 g), unchanged iodo compound (4.32 g) and dicarbonyl-π-cyclopentadienyl(1,2,3,4-tetrahydrocarbazol-9-yl)iron (0.38 g; 15%); this was eluted with ligroin/benzene (1 : 1) and crystallised from ether on cooling, m.p. 150° (decomp.); ν_{max} 2020 and 1985 cm^{-1} (CO). (Found: C, 66.0; H, 5.3; N, 4.2. $C_{19}H_{17}FeNO_2$ calcd.: C, 65.7; H, 4.9; N, 4.0%.)

In a similar experiment conducted in refluxing benzene the product, eluted with ether and purified by sublimation at 80–90°/0.01 mm, was an unstable brown crystalline solid; possibly π-cyclopentadienyl-π-(1,2,3,4-tetrahydrocarbazolyl)iron; it showed the characteristic cyclopentadienyl bands at 1108 and 1005 cm^{-1} but no carbonyl peaks in the infrared spectrum.

Dicarbonyl-π-cyclopentadienyl-9-carbazolyliron (III)

The reaction was conducted as with indole, but substituting carbazole (3.05 g; 18 mmole) and using potassium (0.67 g; 0.017 g-atom) and the iodo-iron complex (4.88 g; 16 mmole). Chromatography of the product gave ferrocene (0.22 g), unchanged iodo compound (1.07 g) and dicarbonyl-π-cyclopentadienyl-9-carbazolyliron (1.08 g; 25%), eluted with ether from which it crystallised on cooling. It formed red crystals, m.p. 150–155° (decomp.); ν_{max} 2030, 1978 cm^{-1} (CO); NMR peaks (CS_2) at $\tau = 2.25$ (multiplet); 2.8 (multiplet; aromatic H); 4.95 (singlet; C_5H_5) (in $CDCl_3$ at $\tau = 1.9$, 2.7 and 4.9 respectively) in the ratio 2 : 6 : 5. (Found : C, 65.85 ; H, 3.9 ; N, 4.4. $C_{19}H_{13}FeNO_2$ calcd.: C, 66.3; H, 3.8; N, 4.1%.)

ACKNOWLEDGEMENTS

The authors thank Dr. P. BLADON for determination of the NMR spectra

and the U.S. Department of the Army for support of this work under Contract DA-91-591-EUC-3101.

SUMMARY

Dicarbonylcyclopentadienyliron complexes σ-bonded through nitrogen to pyrrolyl-, 2-acetylpyrrolyl-, indolyl-, 1,2,3,4-tetrahydrocarbazolyl- and carbazolyl-groups are described.

REFERENCES

1 K. K. JOSHI, P. L. PAUSON, A. R. QAZI AND W. H. STUBBS, *J. Organometal. Chem.*, 1 (1964) 471.
2 B. F. HALLAM AND P. L. PAUSON, *J. Chem. Soc.*, (1956) 3030.
3 P. L. PAUSON, A. R. QAZI AND B. W. ROCKETT, *J. Organometal. Chem.*, 7 (1967) 325.