ORGANOMETALLIC STUDIES

VIII[a]. AMINOCYCLOPENTADIENYLMANGANESE TRICARBONYL AND SOME RELATED COMPOUNDS[b]. APPLICATION OF THE SCHMIDT REACTION TO METALLOCENYL KETONES[c]

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Aminoferrocene has been prepared by several routes[2-5], one of which[2] is based on the Curtius degradation of ferrocenecarboxylic acid. Analogously to the latter method, Kozikowski and Cais[b] several years ago used chloroformylcyclopentadienylmanganese tricarbonyl to prepare azidoformylcyclopentadienylmanganese tricarbonyl and the latter was subjected to the Curtius degradation to yield aminocyclopentadienylmanganese tricarbonyl in 38 % yield. The relatively low yield obtained by the above method led us to seek an improved route to the synthesis of the amino derivative. A recent communication on this subject[d] prompts us to report the results of our work.

It was observed[b] that the major loss in yield, in the procedure described above, occurred during the rearrangement of azidoformylcyclopentadienylmanganese tricarbonyl, (I), to the isocyanate, (II). In addition to the toluene-soluble isocyanate, there was formed an insoluble, intractable material which weighed about one third of the starting material. To avoid this, we modified the procedure by heating the azidoformyl compound (I) in the presence of benzyl alcohol. The benzyloxycarbonyl derivative (III) was formed in yields of up to 88 % (after chromatographic purification). Treatment of (III) with hydrobromic acid/acetic acid solution[7] produced aminocyclopentadienylmanganese tricarbonyl, (IV), in yields of 40–60 %, based on the benzyloxycarbonyl derivative. In another modification, hydrogenolysis of (III) with Raney nickel catalyst[2] afforded the required amine in yields of about 57 %. The latter method appears to be preferable over the former for the preparation of aminocyclopentadienylmanganese tricarbonyl in larger than 1–2 g quantities.

Aminocyclopentadienylmanganese tricarbonyl is a volatile yellow solid, m.p.

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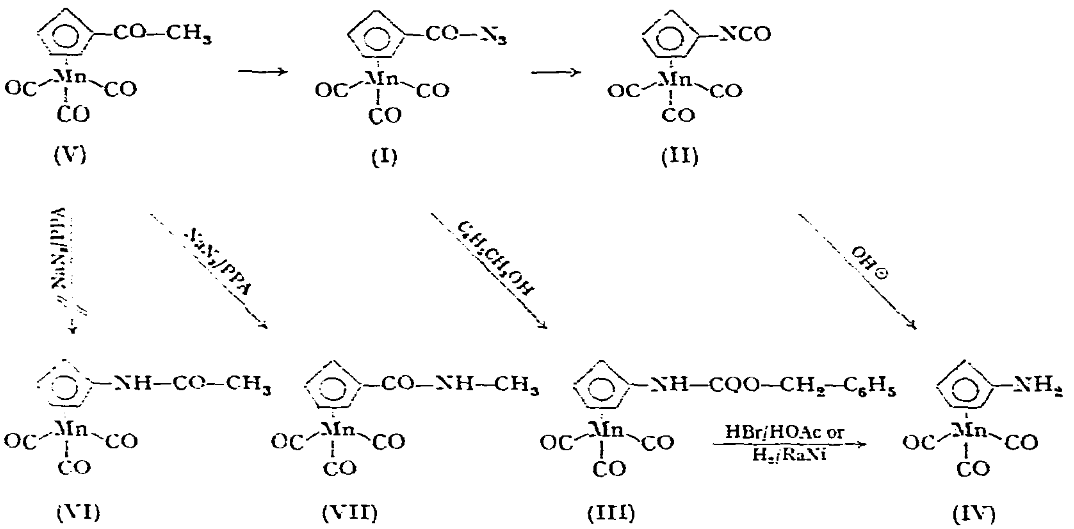
[a] Part VII, see ref. 1.

[b] First reported by J. KOZIKOWSKI, M. CAIS, R. E. MAGINN AND M. KLOVE at the *15th Southwest Regional Meeting of the American Chemical Society*, Baton Rouge, Louisiana, December 3–5, 1959.

[c] This work has been sponsored by Air Force Materials Laboratory, Research and Technology Division, AFSC, through the European Office of Aerospace Research, United States Air Force, Contract No. AF 61(052)-752.

[d] Cuingnet and Adalberon[6] have also reported the synthesis of aminocyclopentadienylmanganese tricarbonyl by a similar procedure.

REACTION SCHEME I



77°, and apparently quite stable at room temperature, in air. However, it appears to decompose in solutions of organic solvents, in particular under the influence of light. In this respect it behaves very similarly to the parent compound, cyclopentadienylmanganese tricarbonyl. A rather striking difference between aminocyclopentadienylmanganese tricarbonyl and aminoferrocene is found in the basicity of the two compounds. Whereas the latter has been found[4] to be 21 times *more* basic than aniline ($K_b^{20°}$ for aminoferrocene = 1.55×10^{-9} compared to $K_b^{20°} = 7.2 \times 10^{-11}$ for aniline), we have found aminocyclopentadienylmanganese tricarbonyl ($K_b^{25°} = 1.64 \times 10^{-12}$) to be about ten times *less* basic than aniline ($K_b^{25°} = 1.6 \times 10^{-11}$) under the same experimental conditions for the determination of K_b. This indication of the electron-withdrawing property of the $Mn(CO)_3$ moiety in cyclopentadienylmanganese tricarbonyl was not unexpected in view of the reported lower activity of the latter, compared to ferrocene, in electrophilic substitution reactions such as Friedel-Crafts acylations[8].

The very weak basicity of aminocyclopentadienylmanganese tricarbonyl is demonstrated also by the extremely rapid hydrolysis of the hydrochloride or hydrobromide salts and also by the reluctance of the amino derivative to enter into diazotization reactions. However, as expected, the diazonium derivative once formed, appears to be rather stable and it can be readily isolated as a solid salt[9]. This is in contrast to aminoferrocene which has been reported to be destroyed by nitrous acid, no diazonium salt being detectable[3].

The infrared carbonyl stretching frequencies of the Mn–CO groups (2018, 1928 cm^{-1}) are shifted to lower frequencies compared to the parent unsubstituted compound (2028, 1931 cm^{-1}). This can been ascribed to the greater charge-transfer to the manganese atom, and hence lowering of the carbonyl frequency, when a hydrogen atom of the cyclopentadienyl ring is replaced by the more electron-donating amino group. This effect is similar to that found[10] on comparing the carbonyl stretching frequencies of anilinechromium tricarbonyl (1965, 1884 cm^{-1}) with those of benzenechromium tricarbonyl (1977, 1900 cm^{-1}).

Although the above modifications for the preparation of aminocyclopentadienylmanganese tricarbonyl were an improvement over the original procedure*, they still used carboxycyclopentadienylmanganese tricarbonyl as starting material. Since rather numerous steps are necessary for the preparation of the latter compound* we deemed it desirable to find a shorter route to the required amine, (IV), by using as starting material the readily available[8,11,12] acetylcyclopentadienylmanganese tricarbonyl, (V).

Recently, Conley[13] has shown that the Schmidt reaction of ketones with sodium azide in polyphosphoric acid gives very high yields of the expected amides. Thus, acetophenone has been reported[13] to produce acetanilide in 98 % yields. It seemed reasonable to us to expect that the acetyl derivative (V) would react analogously to acetophenone to produce acetamidocyclopentadienylmanganese tricarbonyl, (VI), which upon hydrolysis should give the required amine (IV). Unfortunately, in our hands, (V) reacted with sodium azide in polyphosphoric acid to afford 50–70 % yields of the "wrong" amide, (VII), and none of the desired amide (VI).

At first sight it appeared that failure of the cyclopentadienylmanganese tricarbonyl moiety to migrate was analogous to the observations reported by Berger, McEwen and Kleinberg[14] on their investigations of the acid-catalyzed decomposition of ferrocenylphenylcarbinyl azide (VIII). The latter appears to be a complex reaction and in so far as the Schmidt rearrangement takes place, there is an apparently *exclusive migration of the phenyl group*. This result was contrary to that anticipated[14] since in the pinacol–pinacolone rearrangement of 1,2-diferrocenyl-1,2-diphenylethylene glycol the ferrocenyl group had been reported[15] to undergo exclusive migration.

In order to explain their apparently anomalous results, Berger *et al.*[14] envision that in strongly acidic conditions, (VIII) forms three conjugate acids: one in which the azido group is protonated, one in which the iron atom is protonated[16,17], and one in which both the azido group and the iron atom are protonated. Only the latter conjugate acid, the diprotonated species, is believed to undergo the Schmidt rearrangement. It is argued[14] that in the migration step the phenyl group, rather than the protonated ferrocenyl group, would be better able to migrate from carbon to cationoid nitrogen.

We felt that it might be useful to see whether the Schmidt reaction of metallocenyl ketones other than (V) would take place without migration of the metallocenyl moiety, for reasons based on the mechanism suggested by Berger *et al.*[14]. Consequently, a number of metallocenyl ketones were subjected to the Schmidt reaction in polyphosphoric acid[13] and the results obtained are tabulated in Table 1. The following two observations stand out from these data:

(*i*) The cyclopentadienylmanganese tricarbonyl moiety did not migrate under our reaction conditions.

(*ii*) The ferrocenyl moiety, contrary to the results of Berger *et al.*[14], did migrate in the Schmidt reaction, when carried out in polyphosphoric acid.

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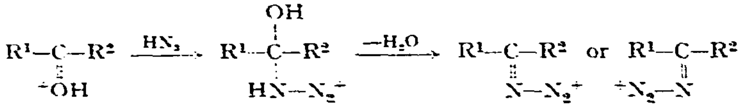
* First reported by J. Kozikowski, M. Cais, R. E. Maginn and M. Klove at the *15th Southwest Regional Meeting of the American Chemical Society*, Baton Rouge, Louisiana, December 3–5, 1959.

It seems rather difficult to reconcile our results with the mechanism favoured by McEwen, Kleinberg and co-workers[14,18].

The Schmidt reaction is usually envisaged* to proceed through combination of the conjugate acid of the ketone with molecular hydrogen azide to produce a protonated azidohydrin, (XX). The latter loses water to form an iminodiazonium ion, (XXI), which may or may not equilibrate between its two geometrically isomeric configurations, (XXIa) and (XXIb), when R¹ and R² are different. It is assumed that this geometrical isomerism governs the ratio of the amide isomers formed in the reaction, with steric factors influencing the course of the rearrangement of the iminodiazonium ion. However, the rule of thumb that the group which migrates preferentially is that which has the greatest bulk in the neighbourhood of the carbonyl group may have drastic exceptions where either conjugation or chelation factors come into play[19].



$$R^1-\underset{\overset{\vdots}{^+OH}}{C}-R^2 \xrightarrow{HN_3} R^1-\overset{OH}{\underset{HN-N_2^+}{C}}-R^2 \xrightarrow{-H_2O} R^1-\underset{N-N_2^+}{C}-R^2 \text{ or } R^1-\underset{^+N_2-N}{C}-R^2$$

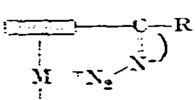
(XX) (XXIa) (XXIb)

It is at once obvious from the results reported herein that the rule of thumb concerning group bulkiness as a migration factor fails dismally in predicting the course of the Schmidt reaction for metallocenyl ketones.

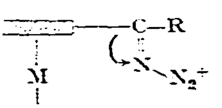
Mechanistic consideration involving reactions of metallocenes must take into account, in addition to the usual factors, two specific points.

(*i*) The role played by the metal atom.

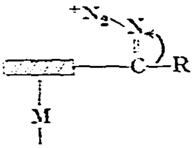
(*ii*) The possibility of additional stereoisomerism, due to the so-called "*ψ-endo*" and "*ψ-exo*" forms[20]. In the present case this would refer to whether the $=N-N_2^+$ group points in the same direction as, or opposite from, the second half of the "sandwich". Even though *a priori* one allows for free rotation round the bond between the ring and the carbinyl carbon atom, the possibility of interaction between the metal atom and the $=N-N_2^+$ grouping necessitates consideration of the "*endo–exo*" isomerism in addition to the two geometrical isomers of the iminodiazonium ion (XXI). The following four metallocenyliminodiazonium isomers may be considered: *ψ-endo-syn*, (XXII); *ψ-endo-anti*, (XXIII); *ψ-exo-syn*, (XXIV) and *ψ-exo-anti*, (XXV). The classification *syn* and *anti* refers to the relative positions of the metallocenyl and $-N_2^+$ groups with respect to the C=N bond.



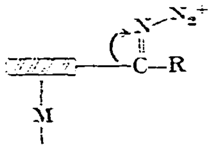
ψ-endo-syn
(XXII)



ψ-endo-anti
(XXIII)



ψ-exo-syn
(XXIV)



ψ-exo-anti
(XXV)

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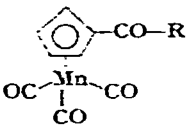
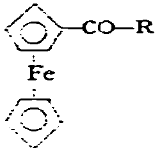
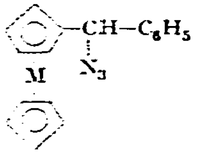
* For a critical examination of the evidence bearing on the mechanism of the Schmidt reaction see ref. 19.

TABLE 1

SCHMIDT REACTION PRODUCTS OF METALLOCENYL KETONES

Metallocenyl ketone		*R or M*	*Rearranged products*
	(V)	CH_3	$(CO)_3MnC_5H_4$–CO–NH–CH_3 (VII)
	(IX)	C_6H_5	$(CO)_3MnC_5H_4$–CO–NH–C_6H_5 (X)
	(XVIII)	$C_5H_4FeC_5H_5$	No amides
	(XXVIII)	$C_5H_4Mn(CO)_3$	Recovered starting material
	(XI)	CH_3	$C_5H_5FeC_5H_4$–CO–NH–CH_3 (XII) + $C_5H_5FeC_5H_4$–NH–CO–CH_3 (XIII)
	(XIV)	C_6H_5	$C_5H_5FeC_5H_4$–CO–NH–C_6H_5 (XV) + $C_5H_5FeC_5H_4$–NH–CO–C_6H_5 (XVI)
	(VIII)*	Fe	$C_5H_5FeC_5H_4$–CHO + $C_6H_5NH_2$
	(XXVI)*	Ru	$C_5H_5RuC_5H_4$–CHO + $C_6H_5NH_2$
	(XXVII)*	Os	No rearranged products

* See refs. 14 and 18.

If one tries to explain the course of the Schmidt rearrangement of metallocenyl derivatives on the basis of these four isomers, then, should structure (XXII) exist exclusively because of the strong possible interaction between the metal atom M and the N_2^+ group, one would expect exclusive migration of the R group. The same course, namely migration of the R group, would take place in the *exo-syn* structure (XXIV), although it is more difficult to argue as to why this structure should be the predominant or exclusive one, as would be necessary when considering the results involving the cyclopentadienylmanganese tricarbonyl derivatives. Migration of the metallocenyl moiety would be possible with any of the remaining two structures, (XXIII) and (XXV).

On the basis of the foregoing explanation one would be led to conclude that with cyclopentadienylmanganese tricarbonyl derivatives the iminodiazonium ion (XXII) is formed exclusively and once formed it does not equilibrate to either (XXIII) or (XXV) and hence the complete absence of metallocenyl migration. On the other hand with the ferrocene derivatives, either (XXII) or (XXIV) may be formed initially to be followed by equilibration with the respective forms (XXIII) or (XXV). One could suggest that a possible cause for the lack of equilibration in the case of the manganese compounds as opposed to the apparent equilibration in the case of the iron compounds might be due to the differences in the octahedral covalent radii of the two metal atoms. Manganese is reported[21] to have an octahedral covalent radius of 1.58 Å as compared to the Fe^{2+} radius of 1.23 Å. This may be responsible for a stronger interaction between the manganese *d*-electrons and the N_2^+ group with consequent greater stabilization of the *ψ-endo-syn* isomer (XXII). One may note that in the case of ruthenium and osmium atoms, both of which are reported[21] to have octahedral covalent radii of 1.33 Å, no migration of the metallocenyl group has been observed in the decomposition of the respective metallocenylphenylcarbinyl azides[14,18], (XXVI) and (XXVII) (Table 1).

In terms of simple M.O. theory, interaction may be expected between the π-electron orbitals of the diazonium group and the e_{2g} metal orbitals. Assuming the side chain lies in the xz plane of the molecule, where z is the five-fold symmetry axis of the metallocene, then the interaction is of the form:

$$3d_{x^2-y^2}:\pi_{x'},\pi^*_{x'}$$

$$3d_{xy}:\pi_y{}^i\ (i=1....4)$$

where $\pi_{x'}$ and $\pi^*_{x'}$ denote the π-orbitals of the N_2^+ group perpendicular to the N–N axis and lying in the xz plane; $\pi_y{}^i$ denotes the π-orbitals of the $C–N_1–N_2–N_3$ system. The interactions were estimated* from group overlap integrals calculated from standard overlap integrals[22] by normal methods[23]. The energies of interaction were also calculated according to previously described theory of organometallic compounds[23]. The net interaction was found to be about 2–6 kcal for the manganese compound to 0.8–2.4 kcal for the ferrocene derivative. We are offering the results of these rather crude calculations, as showing "order of magnitude" differences in the possible interactions of the manganese or iron atoms with suitably placed substituent groups in their metallocene derivatives.

It is interesting to note that in an experiment carried out for comparison purposes and in order to obtain some information on the Beckmann rearrangement involving the manganese compound, the only rearranged product isolated was the N-methylcarbamoylcyclopentadienylmanganese tricarbonyl, (VII).

The Beckmann rearrangement on acetylferrocene oxime under the usual conditions has been reported to have failed[2]; on the other hand, the Beckmann rearrangement of the N-tosyl derivative of benzoylferrocene oxime has been reported[15] to take place with migration of the phenyl group only. In view of the present results we are currently investigating the application of the chromatographic method[24] to the Beckmann rearrangement of metallocenyl ketones.

EXPERIMENTAL

The infrared spectra were measured in chloroform solution on a Perkin-Elmer Infracord Model 137 spectrophotometer. The ultraviolet spectra were measured in ethanol solution on a Carry Model 14 recording spectrophotometer. The NMR spectra were measured on Varian Model HR 60 spectrometer, with tetramethylsilane as internal standard. All melting points were determined on a Kofler block type instrument and are uncorrected.

1) *Aminocyclopentadienylmanganese tricarbonyl (IV)*

Sodium azide (0.97 g, 0.015 mole) was added in small amounts to a cooled solution (ice-bath) of chloroformylcyclopentadienylmanganese tricarbonyl (2.66 g, 0.01 mole) in acetone (35 ml). After stirring for 45 minutes, water (150 ml) was added,

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* The authors wish to thank Prof. D. A. BROWN, University College, Dublin, Eire, for the M.O. calculations.

stirring was continued for another 15 minutes and then the reaction mixture was extracted with ether (3 × 50 ml). After drying (Na_2SO_4), the ether extract was evaporated in vacuum and the residue taken up in petroleum ether (40–60°), filtered and concentrated to a very small volume to yield 2.6 g of azidoformylcyclopentadienylmanganese tricarbonyl, yellowish crystals, m.p. 41–42°. The latter (2.6 g), without further purification, was dissolved in benzene (80 ml) and refluxed for 2 h. The benzene solution was filtered to remove a yellow solid (~ 0.2 g) and then evaporated in vacuum to yield a yellow oil (2.4 g). The infrared spectrum of the oil showed, in addition to the metal carbonyl bands in the 2000 cm^{-1} region, a strong absorption band at 2300 cm^{-1}, typical of the isocyanate grouping (lit.[25] ~ 2270 cm^{-1}).

The isocyanate derivative in 20 % aqueous potassium hydroxide solution (70 ml) was refluxed for 1.5 h, cooled and extracted with ether (3 × 80 ml). After drying ($MgSO_4$) the ether solution was evaporated in vacuum to produce yellow crystals (1.4 g, 64 % based on the starting chloroformylcyclopentadienylmanganese tricarbonyl), m.p. 75–76°. Sublimation in high vacuum (30°/0.01 mm Hg) afforded the analytical sample of aminocyclopentadienylmanganese tricarbonyl, m.p. 77–77.5°. (Found: C, 43.99; H, 2.79; Mn, 24.9; N, 6.59. $C_8H_6O_3MnN$ calcd.: C, 43.80; H, 2.74; Mn, 25.1; N, 6.39 %.)

The major bands in the infrared spectrum: 3520(w), 3430(m), 2018(vs), 1928(vs), 1630(s), 1510(s), 1400(m) cm^{-1}. Ultraviolet spectrum: λ_{max} 205 mμ (log ε 4.51); λ_{max} 272 mμ (log ε 3.64); λ_{max} 324 mμ (log ε 3.06). NMR spectrum: NH_2 protons, wide band at τ 6.83 (relative intensity 2); cyclopentadienyl ring protons two triplets centred at τ 5.68 and 5.42 (relative intensity 4). The unsubstituted cyclopentadienylmanganese tricarbonyl shows a single proton absorption at τ 5.24.

The basicity of aminocyclopentadienylmanganese tricarbonyl was determined in methanol/water (80:20 v/v) solution using a Beckmann pH meter Model 72. The calculations, carried out as for aminoferrocene[4], gave $K_b^{25} = 1.64 \times 10^{-12}$. Under the same conditions, aniline was found to have $K_b^{25} = 1.6 \times 10^{-11}$.

2a) Benzyloxycarbonylaminocyclopentadienylmanganese tricarbonyl (III)

Azidoformylcyclopentadienylmanganese tricarbonyl (15.5 g, 0.56 mole) in benzyl alcohol (100 ml) was heated for 3 h in an oil bath at 140°. After removal of the solvent in vacuum, the residue was extracted with 100 ml of hot benzene/chloroform (1:1). After heating the extract solution with carbon black, filtration and evaporation of the solvent there was obtained a residue which was chromatographed over basic alumina (500 g). Elution with benzene/chloroform (1:1) (750 ml) yielded 17.5 g (88 %) of yellow needles, m.p. 115–116°. Recrystallization from petroleum ether (40–60°) produced the analytical sample of benzyloxycarbonylaminocyclopentadienylmanganese tricarbonyl, m.p. 115–116°. (Found: C, 54.29; H, 3.19; Mn, 15.48; N, 3.80. $C_{16}H_{12}MnNO_5$ calcd.: C, 54.41; H, 3.39; Mn, 15.55; N, 3.96 %.)

The more important bands in the infrared spectrum: 3500(m), 3100(w), 3000(vw), 2040(vs), 1940(vs), 1754(s), 1538(s), 1470(w), 1400(m), 1365(m), 1280 (broad) cm^{-1}.

In one experiment, chromatography of the reaction mixture over alumina and elution with benzene produced first a crystalline material (~ 0.1 %), m.p. 42–45°. Recrystallization from hexane gave yellow crystals, m.p. 45.5–46.0°. (Found: C, 57.02; H, 3.45; Mn, 16.06. $C_{16}H_{11}MnO_5$ calcd.: C, 56.80; H, 3.28; Mn, 16.24 %.)

The infrared spectrum and melting point of this compound were identical with those of the benzyl ester of carboxycyclopentadienylmanganese tricarbonyl, prepared directly by refluxing carboxycyclopentadienylmanganese tricarbonyl with benzyl alcohol in the presence of a catalytic amount of *p*-toluenesulfonic acid.

2b) *Aminocyclopentadienylmanganese tricarbonyl from benzyloxycarbonyl derivative* (*2a*)

Decomposition of the benzyloxycarbonyl derivative (17.5 g) with 38 g hydrobromic acid/acetic acid solution (30 %) as described in the literature[7] yielded the hydrobromide of aminocyclopentadienylmanganese tricarbonyl. The latter was stirred with a saturated solution of sodium bicarbonate and extracted with methylene chloride. After drying (Na_2SO_4) the methylene chloride solution was evaporated to dryness to yield 6.6 g (~ 61 %) of aminocyclopentadienylmanganese tricarbonyl whose melting point and infrared spectrum were identical with those of the amine prepared in (*1*).

Hydrogenolysis of the benzyloxycarbonyl derivative (12 g) in methanol (100 ml) with Raney Nickel catalyst in the Paar hydrogenation apparatus for 20 h at 70–80° and pressure of 5 atm yielded 4.9 g of crude aminocyclopentadienylmanganese tricarbonyl. Thin-layer chromatography showed this to contain only traces of the starting benzyloxycarbonyl derivative. Chromatography over basic alumina and elution with benzene (1.5 l) yielded 4.21 g (~ 51 %) of pure amine.

3) *N-Methylcarbamoylcyclopentadienylmanganese tricarbonyl* (*VII*) (*by Schmidt reaction*)

Acetylcyclopentadienylmanganese tricarbonyl (2.96 g, 0.012 mole) was added, with stirring and cooling (ice-bath) to polyphosphoric acid (prepared by dissolving 41.2 g of phosphorus pentoxide in 25 ml of 85 % orthophosphoric acid solution). This was followed by the addition, in small amounts, of sodium azide (0.86 g, 0.013 mole). Stirring was continued at room temperature for 30 min, then at 50° for 22 h and finally at 68° for 2 h. The addition of iced water (100 ml) to the cooled reaction mixture resulted in the formation of a yellow precipitate (1.47 g), m.p. 135–147°. Extraction of the aqueous filtrate with methylene chloride (3 × 100 ml), and evaporation of the extracts yielded a brown-yellow oil (0.96 g) which was shown by thin-layer chromatography to contain starting material, in addition to a compound identical with the precipitated material. Crystallization of the yellow precipitate from benzene yielded *N*-methylcarbamoylcyclopentadienylmanganese tricarbonyl as yellow crystals, m.p. 165–167°. (Found: C, 46.21; H, 3.30; Mn, 20.72; N, 5.45. $C_{10}H_8MnNO_4$ calcd.: C, 46.00; H, 3.09; Mn, 21.04; N, 5.37 %.)

The major bands in the infrared spectrum 3500 (m), 3400 (m), 3030 (m), 2040 (vs), 1940 (vs), 1665 (vs), 1540 (s), 1460 (w), 1420 (m), 1380 (m), 1290 (s), 1180 (w), 1155 (w), 1010 (w) cm^{-1}.

The oil was chromatographed over basic silica (50 g) (prepared by mixing 100 g silica with a solution of 5.6 g potassium hydroxide in 130 ml water, evaporation under vacuum and heating in vacuum oven to 120° for 5 h). Elution with petroleum ether/benzene (1:1) (1200 ml) produced 380 mg of yellow crystals, m.p. 159–160°, whose infrared spectrum was identical with that described in the previous paragraph.

4) *Direct synthesis of* (*a*) *N-methylcarbamoylcyclopentadienylmanganese tricarbonyl* (*VII*) *and* (*b*) *acetamidocyclopentadienylmanganese tricarbonyl* (*VI*)

a) On passing dry methylamine for 10 min through a solution of chloroformylcyclopentadienylmanganese tricarbonyl (2.0 g) in dry diethyl ether (10 ml) there was an immediate precipitation of yellow crystals. After removal of the solvent the residue was taken up in methylene chloride (50 ml) and the solution washed with water, dilute hydrochloric acid solution and then again with water. After drying (Na_2SO_4) and evaporation of the solvent there were obtained yellow crystals (1.64 g), m.p. 167–168°. (Found: C, 46.04; H, 3.18; Mn, 20.81; N, 5.42.) The m.p. was undepressed on admixture with N-methylcarbamoylcyclopentadienylmanganese tricarbonyl obtained form the Schmidt reaction and had identical infrared absorption spectrum with the latter.

b) Acetyl chloride (0.13 g) was added dropwise to a cooled (ice-bath) solution of aminocyclopentadienylmanganese tricarbonyl (0.20 g) in dry diethyl ether (10 ml). After stirring for 10 min, water (10 ml) was added, extracted with methylene chloride (3 × 25 ml) and the organic layer was washed first with a saturated aqueous solution of sodium bicarbonate and then with water. After drying (Na_2SO_4) and evaporation of the solvent there were obtained yellow crystals (0.19 g), m.p. 132–138°. Recrystallization from benzene yielded the analytical sample of acetamidocyclopentadienylmanganese tricarbonyl, m.p. 144.5–145°. (Found: C, 46.14; H, 3.09; Mn, 20.71; N, 5.17. $C_{10}H_8MnNO_4$ calcd.: C, 46.00; H, 3.09; Mn, 21.04; N, 5.37 %.)

The infrared spectrum was different in many respects from that of the Schmidt reaction product. The major bands: 3480 (m), 3390 (m), 2040 (vs), 1940 (vs), 1710 (vs), 1525 (s), 1485 (m), 1425 (m), 1400 (m), 1260–1190 (broad band) cm^{-1}.

5) *N-Phenylcarbamoylcyclopentadienylmanganese tricarbonyl (by Schmidt reaction)*

The experimental procedure followed was identical with that described for the N-methyl compound (reaction 3). From 3.1 g (0.01 mole) of benzoylcyclopentadienylmanganese tricarbonyl there was obtained (in addition to 0.43 g of starting material) N-phenylcarbamoylcyclopentadienylmanganese tricarbonyl as yellow crystals (1.49 g), m.p. 173–175° (from benzene). (Found: C, 55.77; H, 3.29; Mn, 16.98. $C_{15}H_{10}MnNO_4$ calcd.: C, 55.74; H, 3.12; Mn, 17.00; N, 4.33 %.)

The infrared spectrum: 3500 (m), 3400 (w), 2040 (vs), 1950 (vs), 1675 (vs), 1600 (s), 1520 (s), 1470 (m), 1440 (s), 1375 (m), 1320 (s), 1270 (m), 1250–1190 (broad band) cm^{-1}.

6) *Direct synthesis of (a) N-phenylcarbamoylcyclopentadienylmanganese tricarbonyl, (X), and (b) benzamidocyclopentadienylmanganese tricarbonyl*

a) Aniline (1.29 g) was added to a cooled (ice-bath) ether solution of chloroformylcyclopentadienylmanganese tricarbonyl (0.3 g) and after stirring for 10 min the reaction product was worked up as in (*4a*) to produce yellow crystals (0.32 g) whose m.p., mixed m.p. and infrared spectrum were identical with those of N-phenylcarbamoylcyclopentadienylmanganese tricarbonyl obtained in the Schmidt reaction (5).

b) Benzoyl chloride (1.5 g) was added dropwise to a cooled (ice-bath) ether solution of aminocyclopentadienylmanganese tricarbonyl (0.22 g). Stirring was continued for 10 min at 0°, then for 10 min at room temperature followed by another 10 min at 50° (water-bath). After cooling to room temperature, water (20 ml) was added and the mixture extracted with chloroform (3 × 25 ml). The chloroform extract was washed with saturated sodium bicarbonate solution, then with water and dried (Na_2SO_4). Removal of solvent and application of high vacuum (oil pump) to the residue to remove traces of benzoyl chloride, followed by crystallization from benzene, yielded yellow crystals, of benzamidocyclopentadienylmanganese tricarbonyl (0.28 g), m.p. 151–152°. (Found: C, 55.54; H, 3.29; N, 4.49. $C_{15}H_{10}MnNO_4$ calcd.: C, 55.74; H, 3.12; N, 4.33 %.)

The infrared spectrum: 3500 (w), 3370 (vw), 2040 (vs), 1950 (vs), 1700 (s), 1620 (w), 1535 (s), 1460 (w), 1360 (s), 1265 (s) cm^{-1}.

7) The Schmidt reaction on acetylferrocene

Acetylferrocene (4.56 g, 0.02 mole) was added with stirring and cooling (ice-bath) to polyphosphoric acid (prepared from 58 g phosphorus pentoxide and 35 ml 85 % orthophosphoric acid). After adding, in small amounts, sodium azide (1.6 g), the reaction mixture was heated to 50° for 3 h and then at 60° for 25 h. After cooling to room temperature, iced water (100 ml) was added and the mixture extracted with chloroform (3 × 150 ml). After drying (Na_2SO_4) and evaporation of the solvent there was obtained a yellow-brown precipitate (1.5 g). This was chromatographed over basic silica (75 g) (see reaction *3*). Elution with benzene (1300 ml) produced 0.75 g of crystalline material which, after crystallization from chloroform/carbon tetrachloride had m.p. 172–173°. (Found: C, 59.18; H, 5.50; N, 5.98. $C_{12}H_{13}FeNO$ calcd.: C, 59.28; H, 5.39; N, 5.76 %.) Acetamidoferrocene (XIII) has been reported[2] to have m.p. 170.5–172°.

Infrared spectrum: 3500 (w), 3050 (m), 1685 (vs), 1530 (s), 1290 (vw), 1110 (m), 1010 (m) cm^{-1}.

Further elution of the column with benzene chloroform (1:1) (700 ml) yielded 0.44 g of material which crystallized from benzene, m.p. 194–195°. (Found: C, 59.19; H, 5.36; $C_{12}H_{13}FeNO$ calcd.: C, 59.28; H, 5.39 %.) This was shown to be identical (infrared spectrum, mixed m.p.) with *N*-methylcarbamoylferrocene, (XII), synthesized directly from chloroformylferrocene and methylamine, under the same conditions as described in (*4a*).

Infrared spectrum: 3550 (w), 3050 (m), 1665 (vs), 1535 (s), 1420 (m), 1380 (w), 1290 (s), 1190 (w), 1120 (m), 1055 (w), 1035 (m), 1010 (m) cm^{-1}.

8) The Schmidt reaction on benzoylferrocene

This reaction was carried out under the same conditions as for reaction (*7*). From 3.48 g (0.012 mole) benzoylferrocene there were obtained, after chromatography on basic silica (elution with benzene) 0.39 g of benzamidoferrocene, (XVI), m.p. 184–185° (lit.[3,4] m.p. 177–178°) and 0.12 g of *N*-phenylcarbamoylferrocene, (XV), m.p. 216–217° (lit.[2] m.p. 208–210°). (Found: C, 66.74; H, 5.02. $C_{17}H_{15}FeNO$ calcd.: C, 66.89; H, 4.96 %.)

9) The Schmidt reaction on ferrocenoylcyclopentadienylmanganese tricarbonyl, (XVIII)

Ferrocenoylcyclopentadienylmanganese tricarbonyl[26] (0.35 g) was subjected to the Schmidt reaction under the same conditions as for reaction (*7*). After work up, there was obtained a yellow oil (0.18 g, crude) whose infrared spectrum was quite different from that of the starting ketone and moreover it did not show any of the absorption bands typical of the amide grouping.

Infrared spectrum: 3000 (s), 2060 (s), 1950 (s), 1730 (s), 1625 (w), 1470 (m), 1385 (m), 1265 (s), 1165 (s), 1135 (s), 1110 (s), 1075 (s), 1020 (s) cm^{-1}.

In all the Schmidt reactions involving ferrocenyl ketones chromatography of the crude products yielded as the first fractions on elution with hexane minute amounts (~ 3%) of material whose infrared absorption spectra showed the absence of the characteristic amide bands, and instead they had a strong band at about 1730 cm^{-1}, which might be due to the presence of an ester carbonyl grouping.

The structure of these compounds is currently under investigation.

10) The Schmidt reaction on bis(cyclopentadienylenemanganese tricarbonyl) ketone (XXVIII)

When the above ketone[26] (0.49 g) was subjected to the Schmidt reaction under the same conditions as for 7), starting material (0.32 g) was the only product isolated from the reaction mixture.

11) Beckmann rearrangement of the oxime of acetylcyclopentadienylmanganese tricarbonyl

The oxime of acetylcyclopentadienylmanganese tricarbonyl (1.3 g) in acetone (10 ml) was treated with an 8% aqueous sodium hydroxide solution (3 ml) and *p*-toluenesulfonyl chloride (0.95 g) at 0° and allowed to stand for 10 min. After removal of the solvent in vacuum (water pump) the oily residue was extracted with benzene. The organic extracts were dried (Na_2SO_4) and concentrated to a small volume (~ 5 ml). This solution which contained the N-tosyl oxime of acetylcyclopentadienylmanganese tricarbonyl was chromatographed over basic alumina (80 g). Elution with benzene (15 ml) yielded a yellow oil (0.2 g) which crystallized on standing. The infrared spectrum of this material indicates it to be the N-tosyl oxime of acetylcyclopentadienylmanganese tricarbonyl. Further elution with benzene (25 ml) yielded 0.3 g of acetylcyclopentadienylmanganese tricarbonyl. This was followed by elution with benzene/chloroform (1:1) (350 ml) to produce 0.3 g of material whose infrared spectrum showed it to be mainly N-methylcarbamoylcyclopentadienylmanganese tricarbonyl, (VII).

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SUMMARY

Aminocyclopentadienylmanganese tricarbonyl, prepared by the Curtius degradation of azidoformylcyclopentadienylmanganese tricarbonyl as well as by hydrolysis or hydrogenolysis of the benzyloxycarbonyl derivative, has been found to be ten times less basic than aniline.

The results of the Schmidt reaction carried out on several metallocenyl ketones indicate that the metal atom may play an important role in determining migratory aptitudes of the metallocenyl moiety in rearrangement reactions involving metallocenes.

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