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Ferrocene derivatives

XXVIII *. The metallation of phenylazoferrocene and the synthesis of phenylazocyclopentadienyl derivatives of other metals

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Abstract

Phenylazoferrocene undergoes nickelation and palladation exclusively on the phenyl group. Lithium phenylazocyclopentadienide has been converted into derivatives of Mo, Mn, Fe, Ru and Rh.

1. Introduction

Cyclometallation, or intramolecular oxidative addition of a metal across a C–H bond, is a ubiquitous reaction encompassing alkynes, amines, anils, azoarenes, ethers, hydrazones, phosphines and phosphites and favours aromatic C–H bonds (orthometallation) [2]. Although in some cases the reaction products appear to be consistent with the metallating agent acting as an electrophilic species it is generally assumed that more than one mechanism may be involved [3]. This paper describes some experiments designed to gain further insight into the mechanism of cyclometallation of azo-compounds.

2. Discussion

Ferrocene and its derivatives are more reactive than benzene towards electrophiles and metallating agents such as butyllithium and phenylsodium. It appeared possible that phenylazoferrocene **1** might undergo preferential metallation at the substituted cyclopentadienyl ring, **3**, (Scheme 1) and thus provide a new route, after suitable functional group elaboration, to inherently chiral 1,2-disubstituted ferrocenes.

The first example of orthometallation was the discovery by Kleiman and Dubeck [4] that azobenzene could displace a cyclopentadienyl ligand from nickelocene. The reaction between phenylazoferrocene and nickelocene gave a low yield of a blue crystalline solid **2a**, m.p. 184°C, which was very difficult to separate from **1**. ^{1}H NMR spectroscopy indicated that this product was substituted on the phenyl ring and not on the ferrocenyl group; apart from singlets at δ 4.22 (Cp-Fe) and δ 5.62 (Cp-Ni), the spectrum exhibited the usual A_2B_2 pattern (δ 4.39 m, 4.95 m) of a monosubstituted cyclopentadienyl ring and the characteristic two double doublets and two apparent triplets (δ 7.00–δ 8.05) for an *ortho* disubstituted benzene ring.

Palladation of azobenzene was first demonstrated by Cope and Sieckman [5]; modifications [6,7] to the original experimental procedure have allowed shorter reaction times and improved yields. Reaction between phenylazoferrocene and either palladium(II) chloride or potassium tetrachloropalladate(II) yielded a green solid which showed a number of spots on TLC. Whilst chromatography on neutral alumina (ethyl acetate neutralised) allowed the separation of unchanged **1**, the number of products increased, probably due to chloride–acetate–ethoxide metathesis and the formation of monomers **4** and *cis–trans* dimers *e.g.*, **5** and **6** (Scheme 2). This mixture was therefore treated with thallium cyclopentadienide to give a low yield of the blue crys-

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* For part XXVII see Ref. 1.

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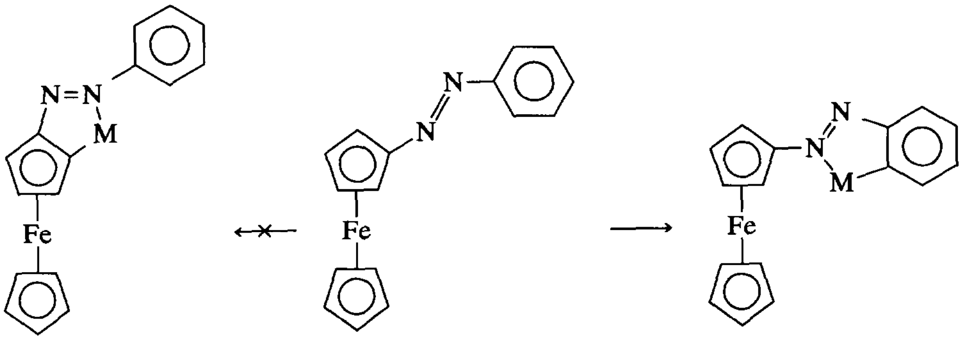


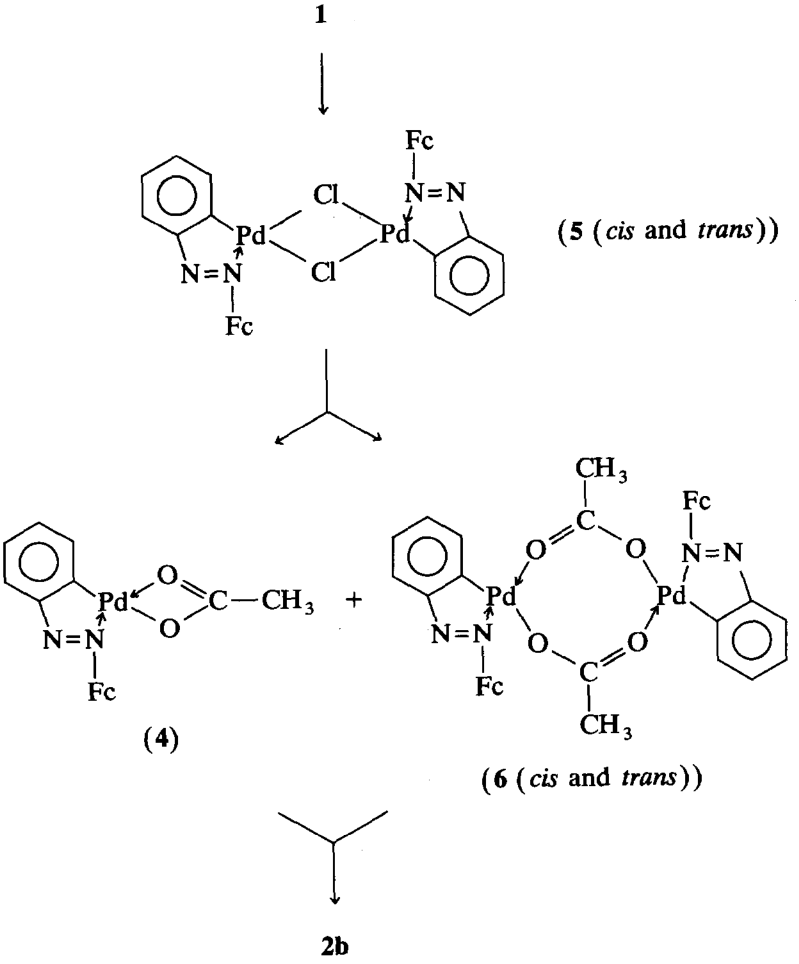
(3) (1) (2)

(a, M = NiC_5H_5;
b, M = PdC_5H_5)

Scheme 1.

talline palladium complex **2b**. The ^1H NMR spectrum of this complex showed good agreement with that of **2a** and again indicated substitution on the phenyl group.

We had previously shown that azobenzene underwent an *ortho*-semidine rearrangement on photolysis with pentacarbonyliron [8], but under similar condi-



(5 (*cis* and *trans*))

(4)

(6 (*cis* and *trans*))

Scheme 2.

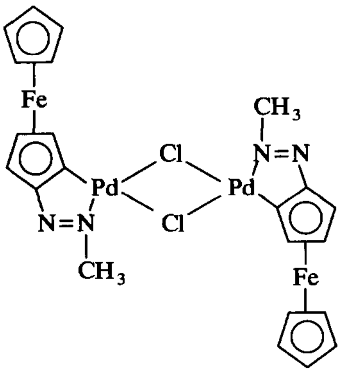
tions the azo-compound **1** was unreactive. Again, no significant reaction was observed between this compound and $[CpFe(CO)_2]_2$ under the conditions for reaction of the latter with azobenzene [9].

It is clear that the products of metallation do not arise from a simple competition between two aromatic systems, although it may be that the strongly electron-donating ferrocenyl group causes inductive activation of the phenyl group. It is likely that differences between the cyclopentadienyl C–H and phenyl C–H bond reactivity are significant together with the disfavoured enthalpy requirements of forming a fused 5–5 ring system, **3**, *versus* the 5–6 ring system, **2**.

Because the successful metallations each involved the phenyl group rather than the ferrocenyl group, we synthesised methylazoferrocene **7**. This volatile red solid, m.p. 55–56°C, was obtained by co-reaction of methylazocyclopentadienyllithium, cyclopentadienyllithium and anhydrous ferrous chloride, following the procedure for synthesising **1** [10]. Complex **7** reacted with palladium(II) chloride to give a low yield of a purple solid which analysed correctly for **8**. However, due to the insolubility of this compound we were unable to prove unambiguously by NMR spectroscopy that substitution had occurred on the cyclopentadienyl ring and the material may be polymeric. Attempts to replace the palladium atom by other groups, *eg*., acetyl [11], were unsuccesful. We also investigated alternative methods of synthesising **1**, modelled on the synthesis of benzylferrocene [12]. However, the σ-phenylazocyclopentadienyl complex **9** proved to be relatively resistant to controlled decomposition (thermal, photolytic, chemical) and the yield of **1** was inferior to the known method.

In an attempt to gain access to a variety of aminocyclopentadienylmetal derivatives, several other phenylazocyclopentadienylmetal complexes were prepared using lithium phenylazocyclopentadienide, although this salt appears to be rather unreactive. Furthermore the electron-withdrawing phenylazo group appears to destabilise the cyclopentadienylmetalcarbonyl derivatives.

Bromopentacarbonylmanganese gave a very low yield of **10a** but the yield improved to 45% with $BrMn(CO)_3(CH_3CN)_2$. Unlike the ferrocene analogue, **10a** proved to be resistant to hydrogenolysis to the known [13] (aminocyclopentadienyl)tricarbonylmanganese, **10b**, and whilst it absorbed one mole of hydrogen (Adam's catalyst, acetic acid), the product, presumably **10c**, was rapidly re-oxidised to **10a** on exposure to air. A low yield of the molybdenum complex **11a**, contaminated by **11b**, was also obtained by reacting lithium phenylazocyclopentadienide with $Mo(CO)_6$, whilst the dicarbonylrhodium complex **12**, was extremely unstable and also obtained in low yield. Finally the bright red bis-substituted ruthenocene derivative **13** was formed in yields sufficient only for characterisation, but not enough for reactivity studies. Although spectroscopic evidence suggested that the mono-substituted phenylazoruthenocene was also formed, we were unable to isolate enough for characterisation.



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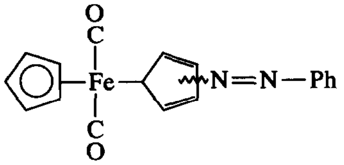

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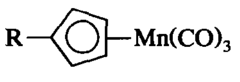
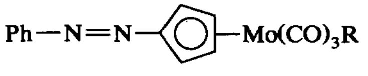


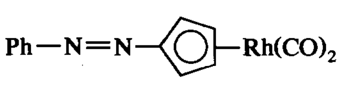
(**a**, R = -N=NPh;
b, R = -NH$_2$;
c, R = -NH-NHPh)

(10)



(**a**, R = CH$_3$;
b, R = COCH$_3$)

(11)



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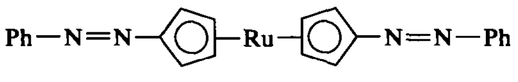

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3. Experimental details

3.1. General information

NMR spectra were recorded on Perkin–Elmer R32 (90 MHz), Bruker WP (250 MHz) or Bruker AMX (400 MHz) spectrometers using TMS as internal standard for deuteriochloroform solutions. The designations Ha, Hb are used for the monosubstituted cyclopentadienyl ring. IR spectra were recorded on a Perkin–Elmer 397 spectrometer. Mass spectra were recorded on an AEI (Kratos) MS9 mass spectrometer. Melting points are uncorrected. TLC was performed with precoated Polygram silica gel or aluminium oxide plates (Macherey, Nagel and Co). Column chromatography was performed with alumina that had been neutralised by being kept under ethyl acetate for at least 7 days, filtering off, washing (ethanol, water), and re-activating at 160°C for 12 h. All solvents were purified and dried by standard methods. Petrol refers to the fraction of b.p. 40–60°C. Unless otherwise stated all reactions were performed under nitrogen.

3.2. Reagents

4-Toluenesulphonyl azide [14], diazocyclopentadiene [15], phenylazoferrocene [10], bis(acetonitrile)bromotricarbonylmanganese [16], thallium cyclopentadienide [17], bromodicarbonyl(η^5-cyclopentadienyl)iron [12] and nickelocene [18] were obtained by literature procedures.

3.3. Phenylazoferrocene (1)

Lithium cyclopentadienide was prepared by adding freshly distilled cyclopentadiene (7.65 g, 8.3 mmol) in anhydrous ether (30 ml), with stirring, to phenyllithium (42.25 ml, 2.0 M solution in cyclohexane). In a separate flask lithium phenylazocyclopentadienide was prepared by adding diazocyclopentadiene (5.48 g, 8.3 mmol) in anhydrous ether (30 ml), with stirring, to phenyllithium (42.25 ml, 2.0 M solution in cyclohexane) at 0°C. The two product solutions were stirred separately for 30 min and then the lithium cyclopentadienide suspension was added to the other flask and stirring continued for a further 30 min at room temperature. Ferrous chloride [19] (which had been previously prepared by heating anhydrous ferric chloride (35 g, 21.5 mmol) in freshly distilled chlorobenzene (250 ml) to 160°C for ~ 6 h until the red/brown precipitate of ferrous chloride had formed. The product was filtered, washed well with ether and used immediately), in dry THF (50 ml) was then added and stirring continued for 14 h. The mixture was then added to an ice/water mixture (500 ml). The ether layer was removed and the aqueous layer extracted with ether. The combined extracts were dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was chromatographed on alumina deactivated by exposure to air for 6 h. There were ten bands seen on the column, but only two were large enough to be of interest. The first was identified as ferrocene (6.64 g) and the fourth as phenylazoferrocene **1** (5.43 g) which was recrystallised from an ether/petrol mixture to give violet needles.

Yield: 4.28 g (18%) (Lit. [10] 5.5%), m.p. 101°C (Lit [10] m.p. 109–110°C). ^{1}H NMR: δ 4.26 (s, 5H, unsubstituted ring); 4.58 (m, 2H, Hb); 5.09 (m, 2H, Ha); 7.25 (m, 1H, aryl-H); 7.46 (m, 2H, aryl-H); 7.75 (m, 2H, aryl-H *ortho* to N). MS: m/z 290.0515 (M^+), m/z 185.0050 ($M^+ - C_6H_5N_2$); $C_{16}H_{14}FeN_2$ calc.: m/z 290.0506.

3.4. (η^5-2,4-Cyclopentadien-1-yl)(C^2,N′-phenylazoferrocenyl)nickel (2a)

Phenylazoferrocene (**1**) (1.5 g, 5.17 mmol) and nickelocene (0.98 g, 5.17 mmol) were heated at 135°C for 4 h. The resulting mixture was purified by chromatography. Unchanged nickelocene (0.42 g) was eluted with petrol, and unchanged phenylazoferrocene and a blue product were eluted together with 20% ether/petrol. After repeated chromatography phenylazoferrocene (0.84 g) was recovered and product **2a** (0.145 g, 15%) obtained as blue microcrystals, m.p. 184°C, after recrystallisation from ether/petrol.

^{1}H NMR: δ 4.22 (s, 5H, C_5H_5Fe); 4.39 (m, 2H, Hb); 4.95 (m, 2H, Ha); 5.62 (s, 5H, C_5H_5Ni); 7.00 (m, 2H, aryl-H); 7.70 (m, 1H, aryl-H adj. to C bonded to N); 8.05 (m, 1H, aryl-H adj. to C bonded to Ni).

Found: C, 61.3; H, 4.7; N, 6.2; $C_{21}H_{18}FeN_2Ni$ calc.: C, 61.1; H, 4.4; N, 6.8%.

3.5. trans-μ-Dichlorobis(C^2,N′-phenylazoferrocenyl)dipalladium (5)

3.5.1. Method 1

Phenylazoferrocene (1.6 g, 5.5 mmol), palladium(II) chloride (0.19 g, 1.1 mmol), dioxane (50 ml) and water (25 ml) were heated to 85°C for 1 h. The reaction mixture was cooled and filtered to give a black precipitate (0.21 g) which showed no peaks in the IR. The solvent was removed *in vacuo* from the filtrate and the residue obtained was redissolved in ether. The ether solution was dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by chromatography. Only starting material **1** (1.3 g) was eluted, but a green band remained at the top of the column. This was recovered by extracting the top portion of the column with methanol. The green solid (**4**, **5**, **6**) collected (68 mg) was recrystallised from methylene chloride/petrol.

Yield: 31 mg, m.p. 170–180°C. Found: C, 48.4; H, 3.4; N, 4.8; $C_{32}H_{26}Cl_2Fe_2N_4Pd_2$ calc.: C, 44.6; H, 3.0; N, 6.5%.

3.5.2. Method 2

Phenylazoferrocene (**1**) (1.5 g, 5.17 mmol), potassium tetrachloropalladate(II) (1.63 g, 5.68 mmol) and ethanol (40 ml) were stirred together at room temperature for 24 h after which time the mixture was examined by TLC. Only starting material was present, and so the mixture was heated at reflux for 16 h. TLC showed a number of slow running green spots. The solvent was removed *in vacuo* and residue chromatographed on silica gel. Unreacted phenylazoferrocene (**1**) (0.11 g) was recovered, but there was no separation of the green bands (1.04 g).

*3.6. (η^5-2,4-Cyclopentadien-1-yl)(C^2,N-phenylazoferrocenyl)palladium (**2b**)*

The mixture obtained from the attempted preparation of *trans*-μ-dichlorobis-(C^2,N'-phenylazoferrocenyl)dipalladium (**5**) (1.16 g, 1.69 mmol (based on chloride complex)) was dissolved in THF (20 ml) and mixed with thallium(I) cyclopentadienide (0.50 g, 1.86 mmol) in THF (15 ml). The mixture was stirred at room temperature for 18 h after which time the solvent was removed *in vacuo*. The residue was purified by silica gel chromatography.

Phenylazoferrocene (0.176 g) was eluted initially followed by a blue solid (90 mg, 14%) and finally a mixture of the unreacted green starting material(s) **4**, **5**, **6** (0.253 g). The blue product **2b**, m.p. 186–188°C, was recrystallised from petrol.

^{1}H NMR: δ 4.25 (s, 5H, C_5H_5Fe); 4.53 (m, 2H, Hb); 5.06 (m, 2H, Ha); 5.96 (s, 5H, C_5H_5Pd); 6.92–8.04 (m, 4H, aryl-H).

Found: C, 54.3; H, 3.8; N, 5.7; $C_{21}H_{18}FeN_2Pd$ calc.: C, 54.8; H, 3.9; N, 6.1%.

3.7. Methylazoferrocene (7)

Lithium cyclopentadienide was prepared by adding freshly distilled cyclopentadiene (1.42 g, 22.5 mmol) in anhydrous ether (30 ml) with stirring, to methyllithium (15 ml, 1.5 M solution in cyclohexane) at 0°C. In a separate flask lithium methylazocyclopentadienide was prepared by adding diazocyclopentadiene (6.23 g, 67.6 mmol) in anhydrous ether (30 ml), with stirring, to methyllithium (45 ml, 1.5 M solution in cyclohexane) at 0°C. The two product solutions were stirred separately for 30 min and then the lithium cyclopentadienide suspension was added to the other flask and stirring continued for a further 30 min at room temperature. Ferrous chloride (prepared [19] from ferric chloride (26.53 g, 0.163 mol)) in dry THF (50 ml) was then added and stirring continued for 14 h. The mixture was then added to ice/water (400 ml), the ether layer removed and the aqueous layer extracted with ether. The combined extracts were dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was chromatographed on alumina deactivated by exposure to air for 6 h. Three fractions were eluted from the column. The first orange band was ferrocene (1.1 g), the second was the monosubstituted product **7** (1.68 g, 20%) and the third was the disubstituted product 1,1′-bis(methylazo)ferrocene [10] (0.7 g).

3.7.1. Spectra and analysis for methylazoferrocene (7)

M.p. 55–56°C. ^{1}H NMR: δ 3.72 (s, 3H, CH_3); 4.20 (s, 5H, C_5H_5); 4.39 (t, 2H, Hb); 4.84 (t, 2H, Ha). ^{13}C NMR: δ 56.93 (q, CH_3, ^1J(CH) = 135.65 Hz), 64.21 (dq, C_3, ^1J(CH) = 178.9 Hz), 69.12 (dq, C_2, ^1J(CH) = 177.6 Hz), 69.54 (d quintets, C_5H_5, ^1J(CH) = 175.7 Hz), 105.93 (s, C_1). MS: m/z 228.0287 (M^+), m/z 185.0027 ($M^+ - N_2CH_3$), m/z 162.9978 ($C_5H_4N_2$-CH_3Fe); $C_{11}H_{12}FeN_2$ calc: m/z 228.0349.

Found: C, 58.0; H, 5.2; N, 12.3; $C_{11}H_{12}FeN_2$ calc.: C, 57.9; H, 5.3; N, 12.3%.

3.7.2. Spectra and analysis for 1,1′-bis(methylazo)ferrocene

1,1′-Bis(methylazo)ferrocene sublimed at 64°C/0.001 torr. (Lit. [10] 50°C/0.005 torr), m.p. 98°C (Lit. [10] m.p. 101–103°C). ^{1}H NMR: δ 3.72 (s, 6H, 2x-CH_3); 4.40 (t, 4H, Hb); 4.89 (t, 4H, Ha). ^{13}C NMR: δ 57.14 (q, 2x-CH_3, ^1J(CH) = 135.65Hz), 65.38 (dq, C_3, ^1J(CH) = 179.8 Hz), 70.40 (dq, (with further fine splitting) C_2, ^1J(CH) = 175.2 Hz); 107.01 (s, C_1). MS: m/z 270.0500 (M^+), m/z 228.0315 ($M^+ - N_2CH_2$), m/z 227.0256 ($M^+ - N_2CH_3$), m/z 185.0029 ($C_{10}H_9Fe$); $C_{12}H_{11}FeN_4$ calc.: m/z 270.0567.

Found: C, 53.1; H, 5.7; N, 20.8; $C_{12}H_{14}FeN_4$ calc.: C, 53.4; H, 5.2; N, 20.7%.

3.8. Reaction of methylazoferrocene (7) with palladium(II) chloride

Methylazoferrocene (**7**) (100 mg, 0.44 mmol), palladium(II) chloride (77.7 mg, 0.45 mmol), dioxane (4 ml) and water (2 ml) were stirred together at room temperature for 5 h until the colour of the solution had changed from the original pink/red to purple. The mixture was filtered and the purple solid, **8**, (0.152 g) collected was washed well with ether. This solid (m.p. 234°C) gave positive tests for iron and chlorine.

^{1}H NMR: This product had very low solubility in most common solvents, but appeared to dissolve in dimethyl sulphoxide. The spectrum, however, showed only paramagnetic material. Found: C, 35.7; H, 3.2; N, 7.35; $C_{22}H_{22}Cl_2Fe_2N_4Pd_2$ calc.: C, 35.8; H, 3.0; N, 7.6%.

3.9. Dicarbonyl(η^5-2,4-cyclopentadien-1-yl)[η^1-(phenylazo)-2,4-cyclopentadien-1-yl]iron (9)

Diazocyclopentadiene (1 g, 10.8 mmol) in anhydrous ether (20 ml) was added dropwise, with stirring, to phenyllithium (6.59 ml, 1.7 M solution in hexane/ether) at 0°C. This mixture was stirred for 10 min. Bromodicarbonyl(η^5-2,4-cyclopentadien-1-yl)iron (2.78 g, 10.8 mmol) was then added in portions, followed by the dropwise addition of dry THF (10 ml) in anhydrous ether (15 ml). Stirring was continued for a further 2 h. After this time the solvent was removed *in vacuo* and the residue chromatographed with ether as eluent to give the desired product as a brown oil/semi-solid.

Yield: 1.9 g (51 %). IR (petrol) ν(CO): 1967s, 2000s, 2040w cm^{-1}.

3.10. Decomposition of dicarbonyl(η^5-2,4-cyclopentadien-1-yl)[η^1-(phenylazo)-2,4-cyclopentadien-1-yl]iron (9)

3.10.1. By heat

The reaction was repeated four times. The dicarbonyl **9** (100 mg per 15 ml of solvent), prepared as above, was heated at reflux in toluene for 16 h. The mixture was then cooled, filtered, and the solvent removed *in vacuo*. The residue was purified by chromatography. Ferrocene, biphenyl and azobenzene were all formed in these reactions as well as phenylazoferrocene (**1**). The yield of phenylazoferrocene varied from 2 to 25% with the highest yields occurring only in small scale reactions.

3.10.2. By air

This reaction was repeated twice. The dicarbonyl **9** (100 mg per 15 ml of solvent) was dissolved in benzene. Air was then bubbled through the solution for 16 h. The mixture was filtered and the solvent removed *in vacuo*. The residue was purified by chromatography. All four of the products mentioned above were isolated, the yield of phenylazoferrocene **1** varying from 5 to 28%, with the highest yield again occurring only in the small scale reactions.

3.10.3. By Me_3NO

(a) This reaction was repeated twice. The dicarbonyl **9** (100 mg) was dissolved in benzene (15 ml) and trimethylamine-*N*-oxide dihydrate (2 molar equivalents) was added. The mixture was stirred for 18 h at room temperature then worked-up in the usual way to yield the four products described previously. The yield of phenylazoferrocene (**1**) in both reactions was 9%.

(b) The above reaction was repeated on a large scale (2 g of the dicarbonyl) and anhydrous trimethylamine-*N*-oxide (2 molar equivalents) used instead of the dihydrate. Again all four products were formed with the yield of phenylazoferrocene (**1**) being 9.5%.

3.10.4. By irradiation

This reaction was repeated twice. An amount of the dicarbonyl (100 mg per 10 ml of solvent) was dissolved in dry THF and irradiated with UV light for 16 h. Work-up was in the usual way to yield all four previous products. The yield of phenylazoferrocene (**1**) in both cases was 10%.

All of the products from the above reactions were combined for further purification and during this process a small amount of another product was discovered and identified as dicarbonyl(η^5-2,4-cyclopentadien-1-yl)(η^1-phenyl)iron.

IR (CCl_4) ν(CO): 1962, 2003 cm^{-1}. Lit. [21] IR (CCl_4): 1965, 2011 cm^{-1}. ^{1}H NMR: δ 4.84 (s, 5H, C_5H_5); 6.95 (m, 3H, aryl-H), 7.43 (m, 2H, aryl-H *ortho* to Fe).

3.11. Tricarbonyl[η^5-(1-phenylazo)-2,4-cyclopentadien-1-yl]manganese (10a)

Diazocyclopentadiene (0.66 g, 7.28 mmol) in anhydrous ether (10 ml) was added dropwise, with stirring, to phenyllithium (4.44 ml, 1.7 M solution in hexane/ether) at 0°C. The mixture was stirred for 10 min. Bis(acetonitrile)bromotricarbonylmanganese (1.096 g, 3.64 mmol) in dry THF was then added and stirring continued for 1 h at room temperature in the absence of light. The mixture was then filtered and the solvent removed *in vacuo*. The residue was chromatographed using 30% ether/petrol as the eluent. Biphenyl (70 mg) was first eluted, followed by the desired product **10a** (0.57 g, 50%) as a yellow crystalline solid, m.p. 73°C. The product was sublimed 84°C/0.001 torr.

IR (petrol) ν(CO): 1953, 2028 cm^{-1}. ^{1}H NMR: δ 4.82 (m, 2H, Hb); 5.59 (m, 2H, Ha); 7.45 (m, 3H, aryl-H); 7.76 (m, 2H, aryl-H *ortho* to N). ^{13}C NMR: δ 80.21 (dm, C_3, ^1J(CH) = 150.4 Hz); 81.25 (dm, C_2, ^1J(CH) = 150.4 Hz); 119.15 (s, C_1); 122.66 (d, C_b); 129.14 (d, C_c); 131.38 (d, C_d); 152.38 (s, C_a); 223.64 (s, CO). MS: *m/z* 309.0011 ($M^+ + 1$), *m/z* 307.9983 (M^+), *m/z* 252.0087 ($M^+ - 2CO$), *m/z* 224.0145 ($M^+ - 3CO$). $C_{14}H_9MnN_2O_3$ calc. *m/z* 307.9993.

Found: C, 54.45; H, 2.9; N, 8.8; $C_{14}H_9MnN_2O_3$ calc.: C, 54.2; H, 3.6; N, 9.0%.

3.12. Tricarbonylmethyl[η^5-(1-phenylazo)-2,4-cyclopentadien-1-yl]molybdenum (11a)

Diazocyclopentadiene (2 g, 21.5 mmol) in anhydrous ether (20 ml) was added dropwise, with stirring, to phenyllithium (13.45 ml, 1.7 M solution in hexane/ether) at 0°C. The mixture was stirred for 10 min. Hexacarbonylmolybdenum (2.84 g, 10.75 mmol) was washed into the mixture with dry THF (30 ml) and the whole was heated to 80°C in the absence of light for 14 h. The mixture was then cooled and iodomethane (9.16 g, 64.5 mmol) in dry THF (30 ml) was added dropwise. Stirring was continued for a further 18 h at room temperature. The mixture was filtered and evaporated.

Chromatography gave three fractions, the first, biphenyl (0.10 g), and the second being the desired product **11a**. The product was recrystallised from petrol to give orange-red crystals. Yield: 0.437 g (11%), m.p. 84°C. IR (petrol) ν(CO): 1945, 2025 cm^{-1}. ^{1}H NMR: δ 0.49 (s, 3H, CH_3); 5.40 (m, 2H, Hb); 6.01 (m, 2H, Ha); 7.55–7.85 (m, 5H, aryl-H). ^{13}C NMR: δ 1.03 (q, CH_3, ^1J(CH) = 68.4 Hz); 88.11 (dm, C_3, ^1J(CH) = 150.4 Hz); 90.91 (dm, C_2, ^1J(CH) = 164.1 Hz); 122.66 (m, C_b); 129.145 (m, C_c); 131.365 (m, C_d); 152.42 (s, C_a); 225.31 (s, CO). MS: m/z 365.9903 (M^+), m/z 337.9940 (M^+ – CO), m/z 309.9981 (M^+ – 2CO), m/z 281.9999 (M^+ – 3CO), m/z 266.9828 (M^+ – 3CO – CH_3); $C_{15}H_{12}{}^{98}MoN_2O_3$ calc. m/z 365.9910.

Found: C, 49.3; H, 3.5; N, 7.5; $C_{15}H_{12}MoN_2O_3$ calc.: C, 49.4; H, 3.3; N, 7.65%.

3.13. Dicarbonyl[η^5-(1-phenylazo)-2,4-cyclopentadien-1-yl]rhodium, (12)

Diazocyclopentadiene (0.372 g, 4 mmol) in anhydrous ether (15 ml) was added dropwise, with stirring, to phenyllithium, which had been prepared from bromobenzene (0.65 g, 4.14 mmol) and lithium (0.06 g, 8.57 mg atoms) in anhydrous ether (30 ml). The suspension was stirred for 10 min. Dichlorotetracarbonyldirhodium [20] (0.39 g, 1 mmol) in anhydrous ether (15 ml) was then added dropwise under an atmosphere of carbon monoxide. The mixture was stirred for 1 h and then filtered, and the solvent was removed *in vacuo*. The residue was purified by chromatography. One orange fraction was collected (89 mg, 30%) and this was recrystallised from petrol to give crystals of m.p. 50°C.

IR (petrol) ν(CO): 1988, 1994, 2050 cm^{-1}, *cf.* $CpRh(CO)_2$, 1987, 2051 cm^{-1}. ^{1}H NMR: δ 5.38 (m, 2H, Hb); 5.78 (m, 2H, Ha); 7.30–7.70 (m, 5H, aryl-H).

Due to instability it was not possible to obtain satisfactory microanalyses or mass spectra of this complex.

3.14. Preparation of 1,1'-bis(phenylazo)ruthenocene (13)

Lithium cyclopentadienide was prepared by adding freshly distilled cyclopentadiene (0.64 g, 9.64 mmol) with stirring, to phenyllithium, which had been prepared from bromobenzene (1.57 g, 9.98 mmol) and lithium (0.14 g, 20.66 mg atoms) in anhydrous ether (30 ml). The suspension was stirred for 10 min. In a separate flask lithium phenylazocyclopentadienide was prepared by adding diazocyclopentadiene (0.90 g, 9.64 mmol) in anhydrous ether (20 ml) with stirring, to phenyllithium at 0°C which had been prepared from bromobenzene (1.57 g, 9.98 mmol) and lithium (0.14 g, 20.66 mg atoms) in anhydrous ether (30 ml). The suspension was stirred for 30 min.

The two suspensions were then mixed and stirred for 30 min, and then ruthenium(III) chloride (1 g, 4.82 mmol) was washed into the flask with a little anhydrous ether (10 ml) and the mixture was stirred at room temperature, in the absence of light, for 18 h. After this time the mixture had become dark brown, and TLC showed three major spots. Zinc dust (1.55 g, 24.1 mg atoms) was added and stirring continued for a further 10 min, after which time TLC showed no change in the reaction mixture. The mixture was filtered through kieselguhr and the solvent removed *in vacuo*. The residue was chromatographed and yielded two main bands. Spectral data showed the first band, an orange powder, to be 1,1'-bis(phenylazo)ruthenocene (110 mg, 2.4%), although contaminated with biphenyl. Recrystallisation from petrol/ether did not achieve complete purification as the material appeared to be unstable. Spectral data suggested that the second band, a red oil (32 mg), was a mixture of mono- and di-substituted products.

3.14.1. Data on 1,1'-bis(phenylazo)ruthenocene (13)

M.p. 195°C. ^{1}H NMR: δ 4.85 (m, 4H, Hb); 5.47 (m, 4H, Ha); 7.2–7.6 (m, 10H, aryl-H).

Found: C, 59.45; H, 3.8; N, 12.7; $C_{22}H_{18}N_4Ru$ calc.: C, 60.1; H, 4.1; N, 12.7%.

3.14.2. Spectrum for second fraction

^{1}H NMR: δ 4.92 (m), 5.48 (m) (due to disubstituted product); 4.60 (s), 4.80 (m), 5.40 (m) (due to monosubstituted product), 7.3–7.8 (m, C_6H_5).

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