Notes

The Reaction of Arenediazonium Ions with Cycloheptatriene (cht) and with $[Fe(CO)_3(\eta^4\text{-cht})]$: Azo-coupling *versus* Hydrazone Formation

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The complex $[Fe(CO)_3(\eta^4\text{-cht})]$ (cht = cycloheptatriene) and $[N_2C_6H_4NO_2\text{-}p][BF_4]$ give $[Fe(CO)_3\{\eta^5\text{-}C_7H_8N_2C_6H_4NO_2\text{-}p\}][BF_4]$ (1) which is deprotonated on alumina to give *syn*- and *anti*-isomers of the hydrazone complex $[Fe(CO)_3\{\eta^4\text{-}C_7H_6NN(H)C_6H_4NO_2\text{-}p\}]$ (2); the $C_7H_6NN(H)C_6H_4NO_2\text{-}p$ is detached from the metal on reaction with $N(O)Me_3{\cdot}2H_2O$. By contrast, free cycloheptatriene and $[N_2C_6H_4NO_2\text{-}p][BF_4]$ in water yield 4-hydroxy-5-*p*-nitrophenylazobicyclo[4.1.0]hept-2-ene.

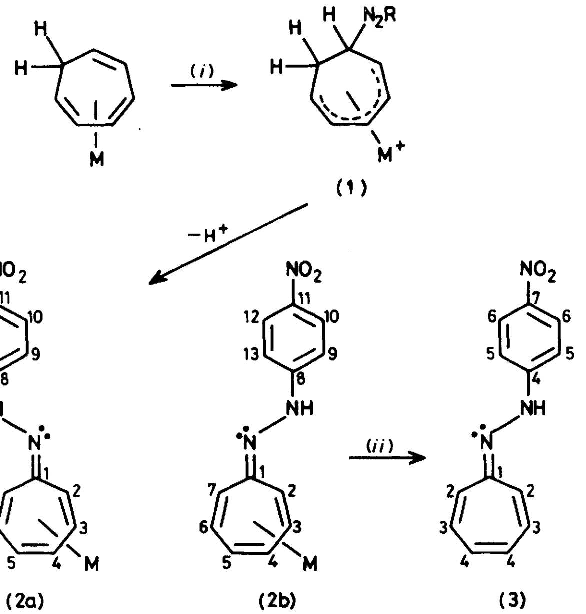
We have shown recently[1] that arenediazonium ions undergo arylation and azo-coupling reactions with $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4\text{-cot})]$ (n = 0—2; cot = cyclo-octatetraene). We now report that the cycloheptatriene (cht) analogue, $[Fe(CO)_3(\eta^4\text{-cht})]$, also forms a C–N bond with $[N_2C_6H_4R'\text{-}p]^+$ (R′ = OMe, NO_2, or F) but that deprotonation of the unstable product gives the hydrazone derivative $[Fe(CO)_3\{\eta^4\text{-}C_7H_6NN(H)C_6H_4R'\text{-}p\}]$ (R′ = NO_2). By contrast, the reaction between free cht and $[N_2C_6H_4NO_2\text{-}p][BF_4]$ in water gives the azo-compound 4-hydroxy-5-*p*-nitrophenylazobicyclo[4.1.0]hept-2-ene.

Results and Discussion

The reactions of $[Fe(CO)_2L(\eta^4\text{-cht})]$ [L = CO, PPh_3, or $P(OPh)_3$] with $[N_2C_6H_4R'\text{-}p][BF_4]$ (R′ = OMe, NO_2, or F) in acetone (−23 °C) give yellow solutions from which unstable yellow solids are isolable on addition of diethyl ether. The complexes, formulated as $[Fe(CO)_2L(\eta^5\text{-}C_7H_8N_2C_6H_4R'\text{-}p)][BF_4]$ (1), have not been fully characterised, loss of N_2 precluding good elemental analyses. However, their salt-like nature is established by the presence of $\tilde{\nu}$(BF) in the Nujol mull i.r. spectra, and by high-energy carbonyl stretching absorptions in CH_2Cl_2 [1; L = CO, R′ = NO_2-*p*, $\tilde{\nu}$(CO) = 2 117s and 2 076s,br; L = PPh_3, R′ = NO_2-*p*, $\tilde{\nu}$(CO) = 2 050s and 2 009s cm^{-1}] very similar to those of the cycloheptadienyl cations $[Fe(CO)_2L(\eta^5\text{-}C_7H_9)]^+$ [L = CO, $\tilde{\nu}$(CO) = 2 115, 2 072, and 2 059 cm^{-1}; L = PPh_3, $\tilde{\nu}$(CO) 2 048s and 2 007s cm^{-1}]. That C–N bond formation has occurred was established by deprotonation of (1; L = CO, R′ = NO_2-*p*).

Column chromatography of freshly prepared $[Fe(CO)_3(\eta^5\text{-}C_7H_8N_2C_6H_4NO_2\text{-}p)][BF_4]$ on Brockman Alumina (Activity II) led to the isolation of a bright red, light sensitive solid (2) which is formulated, on the basis of elemental analysis (C, H, and N) and the i.r. carbonyl spectrum [$\tilde{\nu}$(CO) (n-hexane) = 2 059, 1 999, and 1 987 cm^{-1}], as $[Fe(CO)_3(C_7H_7N_2C_6H_4NO_2\text{-}p)]$. Proton n.m.r. spectroscopy (Table) showed that (2) is a mixture of two isomers of the hydrazone complex $[Fe(CO)_3\{\eta^4\text{-}C_7H_6NN(H)C_6H_4NO_2\text{-}p\}]$ (Scheme), which we have also prepared from $[Fe(CO)_3(2\text{—}5\text{-}\eta\text{-tropone})]$ (tropone = cyclohepta-2,4,6-trien-1-one) and $NH_2N(H)C_6H_4NO_2\text{-}p$ by the previously published method.[2]

The ligand $C_7H_7N_2C_6H_4NO_2\text{-}p$ can exist in five tautomeric forms (Figure 1). That the two isomers of (2) are not tautomers is revealed by the observation that both show NH proton resonances in the ^1H n.m.r. spectrum (Table); forms (*b*)—(*e*) (Figure 1) do not contain an NH group.



Scheme. M = $Fe(CO)_3$, R = $C_6H_4NO_2$-*p*; (*i*) N_2R^+; (*ii*) $N(O)Me_3{\cdot}2H_2O$

In [$^2H_6$]acetone the two isomers occur in approximately equal concentrations as shown by the ^1H (Figure 2) and ^{13}C n.m.r. spectra (Table). In [$^2H_6$]benzene, however, the isomer ratio is 2 : 1 and this, together with ^1H-{^1H} decoupling experiments, has allowed a partial assignment of the n.m.r. spectra (Table). The hydrazone structure for (2) (Scheme) is also supported by the large downfield shifts of the NH proton resonances, from δ 7.37 and 7.08 in [$^2H_6$]benzene to 10.04 and 9.84 in [$^2H_6$]acetone. Such shifts, also found for the NH protons of free hydrazones,[3] may be attributable to hydrogen bonding as may the variation in isomer ratio. Polar solvents are known, for example, to stabilise the less hindered *syn* isomers of aldehyde 2,4-dinitrophenylhydrazones.[4]

The equilibrium between (2a) and (2b) (Scheme) is apparently similar to that between the separable isomers $[Fe(CO)_3(2\text{—}5\text{-}\eta\text{-}2,4,6\text{-triphenyltropone})]$ and $[Fe(CO)_3(4\text{—}7\text{-}\eta\text{-}2,4,6\text{-triphenyltropone})]$ which equilibrate[5] in boiling benzene over a period of 4 h. Unfortunately sample decomposition precluded a high temperature n.m.r. study of the isomerisation mechanism.

Table. Proton and ^{13}C N.m.r. data at room temperature

Compound	$\delta(^1H)$ [a]/p.p.m.	$\delta(^{13}C)$ [a]/p.p.m.
(2)	3.16 (1 H, m, H^5 or $H^{5'}$), 3.35 (1 H, m, H^5 or $H^{5'}$), 4.03 (2 H, m, H^2 and $H^{2'}$), [5.59 (1 H, m), 6.03 (6 H, m,), 6.32 (1 H, m); H^3,$H^{3'}$,H^4,$H^{4'}$,H^6,$H^{6'}$,H^7,$H^{7'}$], 7.27 (4 H, t, H^{10},$H^{10'}$,H^{12},$H^{12'}$), 8.13 (4 H, d, H^9,$H^{9'}$,H^{13},$H^{13'}$), 9.84 (1 H, s br, NH), 10.04 (1 H, s br, NH) [b–d]	49.0, 57.8 (C^2,C^5), 89.0, 95.0 (C^3,C^4), 113.0 (C^{10},C^{12}), 126.5 (C^9,C^{13}), 125.1, 133.1 (C^6,C^7), 149.0, 151.1 (C^8,C^{11}), 211 (CO) 55.6, 65.5 ($C^{2'}$,$C^{5'}$), 89.2, 95.6 ($C^{3'}$,$C^{4'}$), 110.4, 140.8 ($C^{7'}$,$C^{6'}$), 112.7 ($C^{10'}$,$C^{12'}$), 126.5 ($C^{9'}$,$C^{13'}$), 148.1, 151.3 ($C^{8'}$,$C^{11'}$), 211 (CO) [b–d]
	2.45 (1 H, m, H^5), 2.88 (1 H, m, H^2), 5.56 (4 H, m, H^3,H^4,H^6,H^7), 6.54 [2 H, d, $J(H^9H^{10},H^{12}H^{13})$ 9 Hz; H^9,H^{13}], 7.37 (1 H, s, NH), 8.00 [2 H, d, $J(H^9H^{10},H^{12}H^{13})$ 9 Hz; H^{10},H^{12}]	46.3, 57.8 (C^2,C^5), 87.3, 93.3 (C^3,C^4), 112.6 (C^{10},C^{12}), 141.1 (C^1), 146.9, 149.3 (C^8,C^{11})
	2.25 (1 H, m, $H^{5'}$), 3.75 (1 H, m, $H^{2'}$), 4.86 (4 H, m, $H^{3'}$,$H^{4'}$,$H^{6'}$,$H^{7'}$), 6.53 [2 H, d, $J(H^{9'}H^{10'},H^{12'}H^{13'})$ 9 Hz; $H^{9'}$,$H^{13'}$], 7.08 (1 H, s, NH), 8.03 [2 H, d, $J(H^{9'}H^{10'},H^{12'}H^{13'})$ 9 Hz; $H^{10'}$,$H^{12'}$] [b,c,e]	53.9, 64.5 ($C^{2'}$,$C^{5'}$), 87.5, 93.9 ($C^{3'}$,$C^{4'}$), 112.1 ($C^{10'}$,$C^{12'}$), 108.0, 139.9 ($C^{6'}$,$C^{7'}$), 141.1 ($C^{1'}$), 146.4, 148.9 ($C^{8'}$,$C^{11'}$), 210.1 (CO) [b,c,e,f]
(3)	6.0—6.7 (6 H, m, H^2–H^4), 7.0 [2 H, d, $J(H^5H^6)$ 9 Hz; H^6], 8.05 [2 H, d, $J(H^5H^6)$ 9 Hz; H^5], 9.5 (1 H, s, NH) [b,d]	
(4)	0.80 (2 H, m, H^7,$H^{7'}$), 1.56 (1 H, m, H^1), 1.80 (1 H, m, H^6), 2.00 (1 H, s, br, OH), 4.65 [1 H, m, $J(H^3H^4)$ 5.8 Hz, $J(H^4H^5)$ 0.0 Hz; H^4], 4.85 [1 H, m, $J(H^4H^5)$ 0.0 Hz; H^5], 5.50 [1 H, m, $J(H^2H^3)$ 10.5 Hz, $J(H^3H^4)$ 5.8 Hz; H^3], 5.90 [1 H, m, $J(H^2H^3)$ 10.5 Hz; H^2], [7.80 (2 H, d), 8.30 (2 H, d); H^9,H^{10}] [g]	3.4 (t, C^7), [14.2, d, 17.6, d; C^1,C^6], [65.1, d, 73.1 d; C^4,C^5], [121.5, d, 134.0, d; C^2,C^3], [123.0, d, 124.6, d; C^9,C^{10}], [139.4, s, 155.1, s; C^8,C^{11}] [g,h]

[a] Downfield from $SiMe_4$; s = singlet, d = doublet, t = triplet. [b] Numbering as in Scheme. [c] H′ and C′ refer to the less abundant isomer in $[^2H_6]$acetone. [d] In $[^2H_6]$acetone. [e] In $[^2H_6]$benzene. [f] C^6,C^7,C^9,$C^{9'}$,C^{13},$C^{13'}$ signals obscured by solvent. [g] In $CDCl_3$. Numbering as in Figure 3. [h] Partially proton-decoupled spectrum.

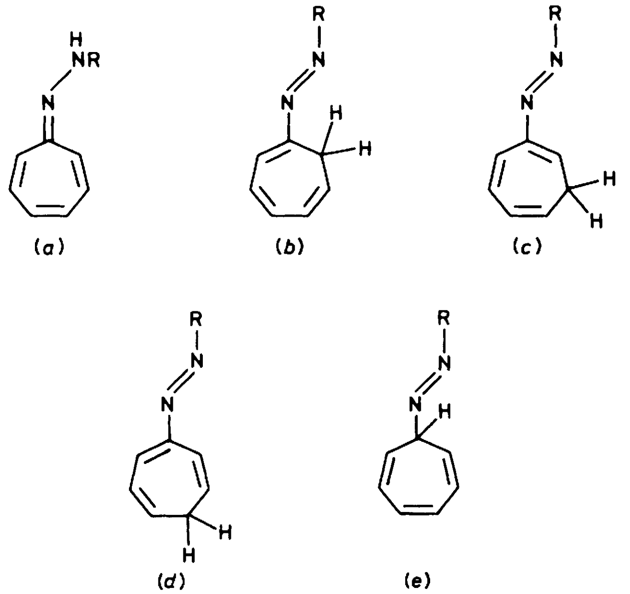


Figure 1. The tautomers of $C_7H_7N_2R$ ($R = C_6H_4NO_2$-*p*)

The low-temperature ^1H n.m.r. spectra of (2) in $[^2H_6]$-acetone are more informative. As the temperature is lowered rotation of the *p*-nitrophenyl group about the C^8–N bond slows so that at −90 °C protons H^9 and H^{13}, and protons H^{10} and H^{12} (Scheme) are no longer equivalent. The ^1H n.m.r. signals at δ 8.13 and 7.27 (Table) are replaced by doublets (J = 9—10 Hz) at δ 8.33, 8.20, 7.65, and 7.55 and a triplet at δ 7.08. During the changes associated with the aryl group the remaining part of the spectrum is invariant.

The free hydrazone ligand, $C_7H_6NN(H)C_6H_4NO_2$-*p* (3), which can be made directly from tropone and the appropriate hydrazine,[6] is readily displaced from (2) on reaction with $N(O)Me_3\cdot 2H_2O$ in acetone. The ^1H n.m.r. spectrum (Table) shows no evidence for tautomerism.

The Reaction of Cycloheptatriene with $[N_2C_6H_4NO_2$-*p*$][BF_4]$.—In contrast to the reaction between diazonium ions and the tricarbonyliron complex, free cht and $[N_2C_6H_4NO_2$-*p*$][BF_4]$ in water yield a disubstituted derivative of bicyclo[4.1.0]hept-2-ene; the orange precipitate is crystallised from n-hexane to give orange-yellow, air-stable $C_7H_8(OH)(N_2C_6H_4NO_2$-*p*) (4; Figure 3). The compound was characterised by elemental analysis (C, H, and N) and by the mass spectrum which showed a parent ion at *m/e* 259 and an ion at *m/e* 241 corresponding to the loss of water.

The ^1H n.m.r. spectrum of (4) (Table) confirmed the presence of the substituents OH and $N_2C_6H_4NO_2$-*p*, and ^1H-{^1H} decoupling, together with the proton-decoupled ^{13}C n.m.r. spectrum, revealed the bicyclo[4.1.0]hept-2-ene skeleton. Partial proton-decoupling of the ^{13}C n.m.r. spectrum (Table) also verified that C^7, the apical carbon atom of the cyclopropane ring, bears two hydrogen atoms (Figure 3).

A comparison of the ^1H n.m.r. spectrum of (4) with those of a series of norcarenes[7] shows that the former adopts a pseudo-boat conformation as shown in Figure 3. With the aid of molecular models to determine bond angles, and with the coupling constants determined from the ^1H-{^1H} decoupled spectra, the relative orientations of the substituents at C^4 and C^5 were assigned. However, which substituent (OH or $N_2C_6H_4NO_2$-*p*) is bonded to which carbon atom (C^4 or C^5) cannot be established by spectroscopic methods alone.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. All solvents were dried, distilled, and deoxygenated before use. The compounds $[Fe(CO)_2L(\eta^4\text{-cht})]$ [L = CO,[8] PPh_3, or $P(OPh)_3$ [9]] and $[N_2C_6H_4R'$-*p*$][BF_4]$ (R′ = NO_2, F, or OMe)[10] were prepared by published methods. Infrared spectra were recorded on a Perkin-Elmer PE 257 spectro-

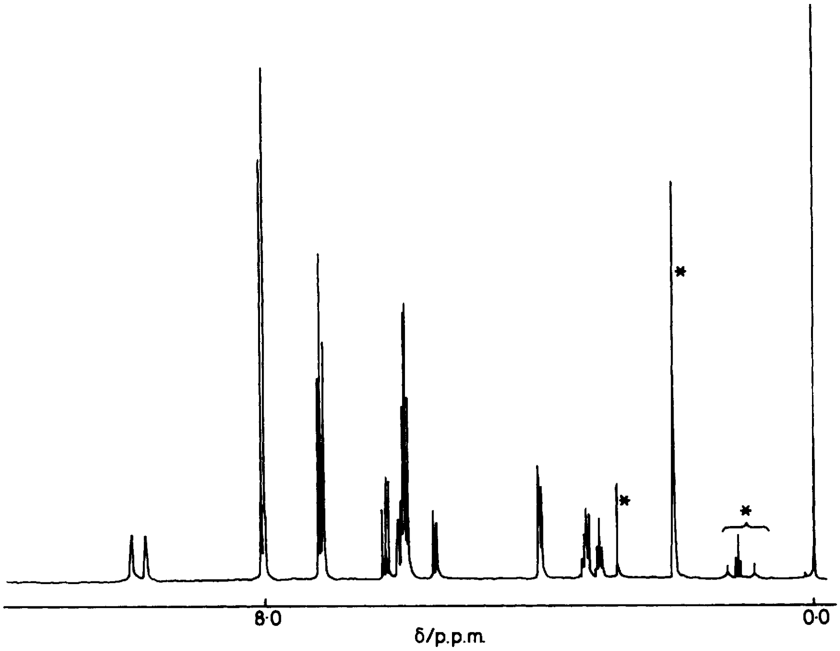
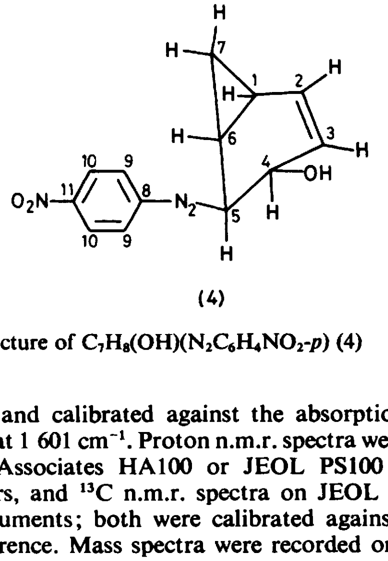


Figure 2. The room temperature ^1H n.m.r. spectrum of $[Fe(CO)_3\{\eta^4\text{-}C_7H_6NN(H)C_6H_4NO_2\text{-}p\}]$ (2) in $[^2H_6]$acetone. Impurities are marked with an asterisk



(4)

Figure 3. Structure of $C_7H_8(OH)(N_2C_6H_4NO_2\text{-}p)$ (4)

photometer and calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Proton n.m.r. spectra were recorded on Varian Associates HA100 or JEOL PS100 or FX200 spectrometers, and ^{13}C n.m.r. spectra on JEOL PFT100 or FX200 instruments; both were calibrated against $SiMe_4$ as internal reference. Mass spectra were recorded on an A.E.I. MS 902 instrument. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

The Reaction of $[Fe(CO)_3(\eta^4\text{-cht})]$ *with* $[N_2C_6H_4NO_2\text{-}p][BF_4]$.—To a cold (−23 °C) solution of $[Fe(CO)_3(\eta^4\text{-cht})]$ (0.74 g, 3.19 mmol) in acetone (10 cm^3) was added a cold (−23 °C) solution of $[N_2C_6H_4NO_2\text{-}p][BF_4]$ (0.70 g, 2.95 mmol) in acetone (50 cm^3). The mixture was allowed to warm to 20 °C during 30 min and then diethyl ether was added to precipitate $[Fe(CO)_3(\eta^5\text{-}C_7H_8N_2C_6H_4NO_2\text{-}p)][BF_4]$ (1) as a pale yellow powder, yield 0.44 g (32%). The complex is air-sensitive in the solid state, partially soluble in CH_2Cl_2, and very soluble in acetone to give yellow, air-sensitive solutions.

Tricarbonyl(2—5-η-*cycloheptatrienone* 1-p-*nitrophenylhydrazone*)*iron*, $[Fe(CO)_3\{\eta^4\text{-}C_7H_6NN(H)C_6H_4NO_2\text{-}p\}]$ (2).—To a solution of $[Fe(CO)_3(\eta^4\text{-cht})]$ (1.32 g, 5.69 mmol) in acetone (5 cm^3) was added a solution of $[N_2C_6H_4NO_2\text{-}p][BF_4]$ (1.20 g, 5.06 mmol) in acetone (75 cm^3). After 5 min the solvent was removed *in vacuo* and the residue extracted with boiling $CHCl_3$ (70 cm^3) to give an orange solution. The solvent was removed *in vacuo* and the red residue dissolved in a minimum of acetone and chromatographed on a hexane–alumina column. Elution with acetone–diethyl ether (1 : 9) gave a red product contaminated with diacetone alcohol. Recrystallisation from diethyl ether–hexane gave the *complex* as a red, light-sensitive solid, yield 0.37 g (17%). The complex is slightly soluble in hexane but very soluble in polar solvents such as acetone to give deep orange solutions.

Cycloheptatrienone 1-p-*Nitrophenylhydrazone*, $C_7H_6\text{-}NN(H)C_6H_4NO_2\text{-}p$ (3).—To a solution of $[Fe(CO)_3\{\eta^4\text{-}C_7H_6NN(H)C_6H_4NO_2\text{-}p\}]$ (0.053 g, 0.138 mmol) in acetone (50 cm^3) was added $N(O)Me_3\cdot 2H_2O$ (0.12 g, 0.77 mmol). A green colouration formed rapidly but after stirring for 2 h the solution was red. The solvent was then removed under vacuum and the residue extracted with diethyl ether (25 cm^3). Addition of hexane gave the *product* as a yellow-green solid, yield 0.029 g (87%). The product is insoluble in hexane but soluble in polar solvents such as diethyl ether and acetone giving red solutions.

4-*Hydroxy*-5-p-*nitrophenylazobicyclo*[4.1.0]*hept*-2-*ene*, $C_7H_8(OH)(N_2C_6H_4NO_2\text{-}p)$ (4).—To a solution of $[N_2C_6H_4NO_2\text{-}p][BF_4]$ (0.98 g, 4.13 mmol) in water (50 cm^3) was added cycloheptatriene (0.42 g, 4.57 mmol). After 3 h the orange precipitate was removed by filtration, and recrystallised from hexane to give the *product* as bright yellow-orange crystals, yield 0.89 g (83%) [Found: C, 59.7; H, 5.4; N, 15.9. $C_{13}H_{13}N_3O_3$ requires C, 60.2; H, 5.0; N, 16.2%], m/e = 259, m.p. = 125—126 °C. The product is soluble in polar solvents such as diethyl ether and acetone to give intensely coloured, yellow, air-stable solutions.

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