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Complexation of 1,4,5,8,9,10-Hexahydroanthracene (HHA) to Iron or Ruthenium: A Bis(diene)diiron HHA Geometry, Hydroaromatic Ruthenium Compounds Related to $Ru(\eta^6\text{-THA})Cl_2(DMSO)$ (THA = 1,4,9,10-Tetrahydroanthracene; DMSO = Dimethyl Sulfoxide), and $Ru_3(CO)_{12}$-Catalyzed HHA Rearrangements

Timothy J. Beasley, Ron D. Brost, Chit Kay Chu, Stephen L. Grundy, and Stephen R. Stobart*

Department of Chemistry, University of Victoria,
Victoria, British Columbia, Canada V8W 2Y2

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The nonconjugated tetraene 1,4,5,8,9,10-hexahydroanthracene (HHA; **I**) reacts with $Fe(CO)_5$ to afford mono- and bis(tricarbonyliron) derivatives **1** and **2**, in which the hydrocarbon fragment is bound to iron as a η^4-diene (respectively tricarbonyl((1,10,11,12-η^4)-tricyclo[4.4.0.0^{3,8}]tetradeca-1(10),3(8),5,11-tetraene)iron (**1**) and *anti*-hexacarbonyl((8,3,4,5-η^4:1,10,11,12-η^4)-tricyclo-[8.4.0.0.^{3,8}]tetradeca-1(10),3(8),4,11-tetraene)diiron (**2**)). Complex **2**, which crystallizes in the space group $P2_1/c$ (a = 11.0617(7) Å, b = 12.239(2) Å, c = 6.9928(5) Å, β = 105.82(6)°, V = 910.9(9) Å^3, Z = 2), has been characterized by using X-ray diffraction, establishing the anti disposition of the two $Fe(CO)_3$ groups. Compounds **1** and **2** have been further characterized by using ^{13}C NMR spectroscopy. In the presence of $Ru_3(CO)_{12}$, HHA is converted catalytically to other anthracenes, mainly by isomerization. With hydrated ruthenium(III) chloride, HHA binds to Ru as a η^6-arene (*i.e.* 1,4,9,10-tetrahydroanthracene (THA; **II**), *via* aromatization in one terminal ring), as is illustrated in the crystal structure of the product $Ru(\eta^6\text{-THA})Cl_2(L)$ (**4**, L = DMSO; space group $P2_1/n$, a = 10.821(3) Å, b = 12.472(4) Å, c = 12.738(4) Å, β = 107.63(7)°, V = 1638(2) Å^3, Z = 4), from which facile displacement of DMSO may be accomplished to give **6** (L = Me_2pzH, pzH = pyrazole), **7** (L = PPh_3), **8** (L = $P(OEt)_3$), **9** (L = $PMePh_2$), and **10** (L = PCy_3, Cy = cyclohexyl). The ^1H and ^{13}C NMR spectra of compounds **7**–**10** show differential shielding of $H^{6,7}$ of the THA ligand attributable to ring current effects due to the proximity of the PPh_3 ligand and identify selective coupling of $C^{8a,10a}$ to the ^{31}P nucleus in **7**, *i.e.* consistent with the existence of an energy minimum during η^6-THA rotation.

Introduction

Cyclic as well as acyclic dienes readily attach to iron in a η^4-bonding mode *via* ligand displacement reactions of the metal in its formally zerovalent state.[1] The extensive family of compounds so derived includes the prototypal analogues[2] in which either buta-1,3-diene or cyclohexa-1,3-diene is bound to a tricarbonyliron unit to complete an 18-electron count. A parallel route does not exist, however, for the synthesis of η^6-arene complexes of iron, which are typically prepared by methods that lead the products to be regarded[3,4] as derivatives of Fe^{II}. In contrast and in a manner closely linked to its prominence in hydrogenation, dehydrogenation, and catalysis, ruthenium behaves more ambiguously:[5] thus, although diene complexes do exist, they are less stable than the iron congeners;[6,7] while the reaction of $RuCl_3$ with cyclohexadienes offers[8,9] the simplest way of making η^6-arene complexes of Ru^{II}. Organoruthenium compounds belonging to this latter category are thus almost all derivatives of monocyclic aromatic molecules.[10]

The commercial availability of 1,4,5,8,9,10-hexahydroanthracene (HHA; **I**) has led us to investigate its coordination behavior toward iron and ruthenium. This compound has further highlighted characteristic differences in the organic chemistry of the two metals, and it has yielded a ruthenium complex of a polycyclic η^6-arene,

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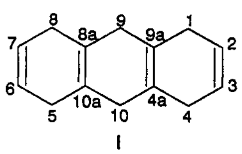

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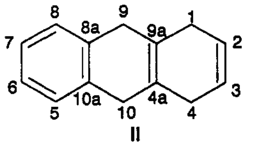

II

1,4,9,10-tetrahydroanthracene (**II**; THA), which has been crystallographically characterized and contains a labile dimethyl sulfoxide (DMSO) ligand. Replacement of the latter affords a series of analogues in which the extended hydrocarbon framework of **II** remains bound to Ru; at elevated temperature **II** is displaced from Ru in DMSO solution to give the known[11,12] *cis*-$RuCl_2(DMSO)_4$. This suggests that catalytic conversion of **I** to **II** may be possible, although appropriate conditions remain to be discovered; we are interested in such a transformation of **I**, to a single functionalized hydroaromatic isomer that can be adapted by iron-mediated steps[4] toward high-value targets. In the presence of $Ru_3(CO)_{12}$, reorganization of the tetraene **I** is catalytic but is not specific, giving a mixture of five hydrogenated anthracenes.

Experimental Section

Synthetic operations were carried out under an atmosphere of dinitrogen gas, and solvents were dried and purified by using conventional methods. 1,4,5,8,9,10-Hexahydroanthracene (HHA) and $Fe(CO)_5$ were supplied by Aldrich; $Ru_3(CO)_{12}$ was obtained from hydrated ruthenium(III) chloride by using published procedures. Analytical data were determined by Canadian Microanalytical Services Ltd., New Westminster, BC, Canada. NMR data were measured on a Bruker WM250 Fourier transform spectrometer (250, 62.8, or 101.3 MHz, respectively, for ^1H, ^{13}C, or ^{31}P); the GC/MS results were obtained using a Varian 3700–Finnigan 3300 combination.

Reactions of HHA. (a) With $Fe(CO)_5$. A mixture of HHA (0.92 g, 5.0 mmol) and $Fe(CO)_5$ (1.0 g, 5.1 mmol) dissolved in benzene (35 mL) in a quartz reaction tube was irradiated (medium-pressure Hg lamp) for 40 h. The solvent was then removed *in vacuo*, leaving an orange-brown residue; this was extracted with methanol (3 × 20 mL), which yielded a clear orange solution (**A**) and a yellow-brown insoluble solid (**B**). Evaporation of solution **A** resulted in recovery of a bright orange oil that was purified by vacuum distillation (100 °C/10^{-1} mmHg), the IR data of which agreed with those reported by Birch *et al.*[13] for (η^4-3,4,5,8,9,10-hexahydroanthracene)tricarbonyliron, *i.e.* tricarbonyl((1,10,11,12-η^4)-tricyclo[4.4.0.0.^{3,8}]tetradeca-1(10),3(8),5,11-tetraene)iron (**1**; 60%). Anal. Calcd for $C_{17}H_{16}FeO_3$: C, 62.64; H, 4.89; Fe, 17.2. Found: C, 62.97; H, 4.97; Fe, 17.1. ^1H NMR ($CDCl_3$): δ 5.70 (s, 3H), 5.15 (d, 1H), 3.07 (m, 4H), 2.64 (m, 4H), 1.68 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 23.9, 24.5, 30.7, 34.5, 39.0, 56.7, 59.5, 79.6, 80.2, 102.2, 103.7, 124.0, 124.2, 124.3, 212.2. Soxhlet extraction of the solid **B** with CH_2Cl_2 afforded a yellow solution which upon cooling yielded a further bright yellow product, shown by X-ray crystallography to be *anti*-(3,4,7,8,9,-10-hexahydroanthracene)bis(tricarbonyliron), *i.e.* *anti*-hexacarbonyl((8,3,4,5-η^4:1,10,11,12-η^4)-tricyclo[8.4.0.$0^{3,8}$]tetradeca-1(10),3-(8),4,11-tetraene)diiron (**2**; 20%). Anal. Calcd for $C_{20}H_{16}Fe_2O_6$: C, 51.59; H, 3.45; Fe, 24.1. Found: C, 51.77; H, 3.45; Fe, 24.8. IR (CH_2Cl_2): 2040, 1970 cm^{-1}. UV/vis: λ_{max} 300 nm, ϵ 4.9 × 10^3 L mol^{-1} cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.8 (m, 8 H), 2.91 (d, 2 H), 3.03 (m, 2 H), 3.73 (d, 2 H), 5.20 (d, 2 H). ^{13}C NMR ($CDCl_3$): δ 23.9, 32.0, 38.9, 58.5, 77.0, 80.2, 102.3, 212.2. Subsequent reactions afforded a methylene chloride extract of **B** that failed to yield crystalline **2** and instead gave the product as a yellow powder. Anal. Found: C, 51.82; H, 3.55. The ^{13}C NMR spectrum of this material showed in addition to the spectrum of complex **2** a further set of signals as follows ($CDCl_3$): δ 31.6, 34.9, 42.9, 58.3, 78.9, 80.4, 100.5. These are attributed to an isomer of **2**, **2a**, the identity of which is discussed below. The ^1H NMR spectrum ($CDCl_3$) of the **2**/**2a** mixture consisted of overlapping multiplets, but with the doublets at δ 2.91, 3.73 of **2** clearly distinguishable from corresponding singlets at δ 2.79, 3.92 due to **2a**; relative intensities of these peaks indicated that the two constituents were present in *ca.* 1:1 ratio with one another. Prolonged irradiaton failed to alter the **2**:**2a** ratio. No reaction was observed when pure **2** was stirred (24 h) with PPh_3 (1 mol equiv) or when Me_3NO (1 mol equiv) was added to the same mixture.

(b) With $Ru_3(CO)_{12}$. A mixture of HHA (0.23 g, 1.26 mmol) and $Ru_3(CO)_{12}$ (0.10 g, 0.16 mmol) dissolved in cyclohexane (100 mL) was heated to reflux for 48 h. Filtration and then evaporation of solvent yielded a brown oil; heating this oil *in vacuo* afforded a white sublimate, which was collected on a cooled probe, leaving a black nonvolatile residue. The white solid was shown by GC/MS to consist almost entirely of five distinguishable hydrogenated anthracenes with M = *m*/*e* 182 (two isomers, 20% and 6%), 184 (two isomers, 46% and 11%), or 186 (11%). The same product distribution was observed with typical conversion of 60% in 60 h when the proportion of HHA was increased to 10 or 30 mol equiv *vs* $Ru_3(CO)_{12}$; in contrast, the black reaction residue had no effect on HHA in refluxing cyclohexane. In the presence of the known[7] (η^4-cyclohexa-1,3-diene)tricarbonylruthenium(0) (IR: 2057, 1991, 1985 cm^{-1}) in refluxing cyclohexane, less than 5% of HHA (20 mol equiv) was converted in 60 h, mainly (78%) to one product with M = *m*/*e* 182 (M = *m*/*e* 184 (6%), 186 (9%), others (7%)). After stirring at 20 °C in solution in heptane, the IR spectrum of a mixture of HHA (0.0 g, 0.48 mmol) with $Ru_3(CO)_{12}$ (0.10 g, 0.16 mmol) contained carbonyl absorptions due only to the latter; however, on heating to reflux, additional IR bands at 2054 s, 1986 vs, and 1981 sh cm^{-1} slowly accumulated. After 60 h, repeated cycles of chilling at −78 °C and then filtration were used to remove most of the HHA; separation by elution with pentane down a short Florisil column gave a fraction shown by IR spectroscopy to contain the new carbonyl complex free of any $Ru_3(CO)_{12}$. Introduction of this material into a refluxing solution in cyclohexane of HHA (*ca.* 20 mol equiv) led after 60 h to less than 5% conversion, mainly (73%) to a product with M = *m*/*e* 182 (second M = *m*/*e* 182 (7%), 184 (16%), 186 (4%)).

(c) With Hydrated $RuCl_3$. After a solution in ethanol (50 mL) of $RuCl_3{\cdot}3H_2O$ (0.50 g, 1.9 mmol) together with HHA (0.70 g, 3.8 mmol) was refluxed for 48 h, filtration of the warm reaction mixture left a yellow-brown solid which was washed thoroughly with diethyl ether (3 × 20 mL). The product was formulated[8,9] as the chloro-bridged ruthenium arene $[Ru(\eta^6\text{-}C_{14}H_{14})RuCl(\mu\text{-}Cl)]_x$ (**3**). Anal. Calcd for $C_{14}H_{14}Cl_2Ru$: C, 47.47; H, 3.98; Cl, 20.02. Found: C, 46.89; H, 3.80; Cl, 20.42. Dissolution of complex **3** (0.1 g, 0.28 mmol) in dimethyl sulfoxide (5 mL) yielded a deep red solution, into which slow diffusion of diethyl ether resulted in the formation of brilliant red crystals suitable for X-ray diffraction, whereby the product was identified as the 1,4,9,10-tetrahydroanthracene complex $Ru(\eta^6\text{-}C_{14}H_{14})Cl_2(DMSO)$ (**4**), in which the DMSO ligand is S-bound at Ru. Compound **4** was isolated as a red solid (65%) after adding diethyl ether (20 mL) and washing with the same solvent (3 × 20 mL). Anal. Calcd for $C_{16}H_{20}Cl_2ORuS$: C, 44.42; H, 4.67; Cl, 16.41. Found: C, 44.12; H, 4.58; Cl, 16.54. Prolonged heating above 70 °C of the red solution of **3** in DMSO afforded both yellow and orange crystals of $Ru(DMSO)_4Cl_2$. Anal. Calcd for $C_8H_{24}Cl_2O_4RuS_4$: C, 19.79; H, 4.95; Cl, 14.65. Found: C, 19.81; H, 5.22; Cl, 14.60.

Reactions of Compound 3 with Pyrazole (pzH) and 3,5-Dimethylpyrazole (Me_2pzH). A mixture of compound **3** (100 mg, 0.28 mmol) and pyrazole (40 mg, 0.56 mmol) was stirred (20 h) in dichloromethane (40 mL). Filtration yielded a yellow solution which after reduction to one-tenth volume and then addition of hexane (20 mL) afforded the yellow bis(pyrazole) adduct $[Ru(\eta_6\text{-}C_{14}H_{14})Ru(pzH)_2Cl]Cl$ (**5**; 80%). Anal. Calcd for

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$C_{20}H_{22}N_4Cl_2Ru$: C, 48.98; H, 4.33; N, 11.43. Found: C, 48.81; H, 4.44; N, 11.50. Only the same product (5) could be detected by ^1H NMR spectroscopy after repetition of this reaction using an equimolar ratio of 3 and pzH. Compound 3 (50 mg, 0.14 mmol) was slurried in dichloro (10 mL), and then a solution of 3,5-dimethylpyrazole (14 mg, 0.14 mmol) in the same solvent (10 mL) was added over 2 h. The resulting orange mixture was stirred (14 h); then solid material was removed by filtration, after which the solution was reduced in volume and hexane (20 mL) was added to precipitate the orange product $Ru(\eta^6\text{-}C_{14}H_{14})(Me_2pzH)Cl_2$ (6; 50%). Anal. Calcd for $C_{19}H_{22}N_2Cl_2Ru$: C, 50.67; H, 4.89; N, 6.22. Found: C, 50.42; H, 4.85; N, 6.21.

Ligand Substitution Reactions of Complex 4. Displacement of DMSO. (a) By 3,5-Dimethylpyrazole. Complex 4 (86 mg, 0.20 mmol) and Me_2pzH (20 mg, 0.20 mmol) were stirred together (2 h) in dichloromethane (20 mL). Reduction in volume followed by addition of hexane (20 mL) afforded complex 6 (80%), which was also the only product of a similar reaction in which Me_2pzH was used in 20-fold molar excess.

(b) By Triphenylphosphine. Compound 4 (80 mg, 0.18 mmol) was dissolved in dichloromethane (10 mL); then PPh_3 (96 mg, 0.36 mmol) was added, and the resulting orange solution was stirred (30 min). Reduction to one-fifth volume and then addition of hexane (15 mL) precipitated the product as a salmon pink solid (85%), which was recrystallized from chloroform/hexane as the $CHCl_3$ monosolvate (7). Anal. Calcd for $C_{33}H_{30}Cl_5PRu$: C, 53.80; H, 4.10. Found: C, 53.75; H, 4.14.

(c) By Triethyl Phosphite. To compound 4 (80 mg, 0.18 mmol) in dichloromethane (10 mL) was added $P(OEt)_3$ (31 mg, 0.18 mmol) dissolved in the same solvent (1 mL). After this mixture was stirred for 5 min and then reduced in volume as before, the pink product 8 was precipitated (90%) by addition of hexane (15 mL). Anal. Calcd for $C_{20}H_{29}Cl_2O_3PRu$: C, 46.13; H, 5.61. Found: C, 45.75; H, 5.52.

(d) By Methyldiphenylphosphine. Approximately 2 mol equiv of $PMePh_2$ was added to a solution in dichloromethane (10 mL) of compound 4 (80 mg, 0.18 mmol). The mixture lightened from deep orange to yellow as it was stirred. After 30 min solvent was removed; then the residual yellow solid was slurried (12 h) with hexane (15 mL). The sandy colored product (78%) was recrystallized as a $CHCl_3$ solvate (9) from chloroform/hexane. Anal. Calcd for $C_{28}H_{28}Cl_5PRu$: C, 49.89; H, 4.18. Found: C, 50.39, H, 4.35.

(e) By Tricyclohexylphosphine. To complex 4 (80 mg, 0.18 mmol) in dichloromethane (15 mL) was added PCy_3 (65 mg, 0.23 mmol). The orange mixture became red on stirring. After 10 min solvent was removed to leave an orange residue, which was dissolved in chloroform (2 mL). Filtration and then addition of hexane (10 mL) precipitated the red product 10 (85%). Anal. Calcd for $C_{32}H_{47}Cl_2PRu$: C, 60.54; H, 7.47. Found: C, 59.33; H, 7.11.

X-ray Data Collection and Structure Refinement. Bright yellow crystals of compound 2 were grown by vacuum sublimation (200 °C/10^{-1} mmHg); the bright red crystals of compound 4 were deposited during slow diffusion of diethyl ether into a solution in DMSO of complex 3. Crystal data are listed in Table I. Both data sets were collected with an Enraf-Nonius CAD-4 automatic diffractometer using Mo Kα radiation (λ = 0.710 69 Å). The intensities were corrected for Lorentz and polarization effects and for absorption using EMPABS.[14] The structures were solved through the use of standard Patterson and Fourier techniques and the SHELX series of computer programs.[15] Atomic scattering factors and anomolous dispersion terms were taken from the usual tabulations.[16,17] For each crystal the lattice parameters were determined from a least-squares refinement of 15 reflections ($2\theta > 30°$), and data were collected by using the ω–2θ method for the range $1.0 < 2\theta < 45°$. At the end of either refinement, the largest parameter shifts in the final cycle were less than 0.002 of the estimated standard deviations.

Table I. Crystallographic Data for Compounds 2 and 4

compd	2	4
formula	$Fe_2C_{20}O_6H_{16}$	$RuCl_2SOC_{16}H_{20}$
fw	464.037	432.37
temp, K	295	295
a, Å	11.0617(7)	10.821(3)
b, Å	12.239(2)	12.472(4)
c, Å	6.9928(5)	12.738(4)
β, deg	105.82(6)	107.63(7)
V, Å^3	910.9(9)	1638(2)
space group	$P2_1/c$	$P2_1/n$
Z	2	4
ρ_{calc}, g cm^{-3}	1.69	1.75
μ, cm^{-1}	16.14	13.86
$R(F_o)^a$	0.0474	0.0773
$R_w(F_o^2)^b$	0.0524	0.0864
λ, Å	0.710 69	0.710 69

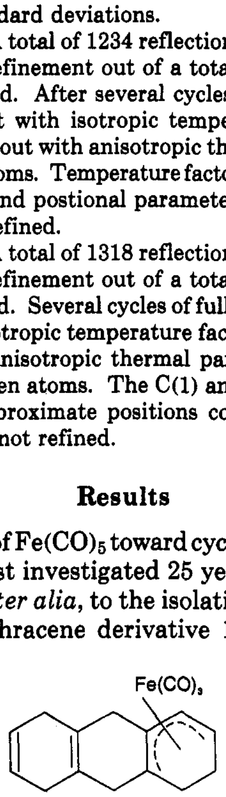
^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(F_o^2)]^{1/2}$.

Compound 2. A total of 1234 reflections with $I > 8\sigma(I)$ were used in the final refinement out of a total of 1264 which were considered observed. After several cycles of full-matrix least-squares refinement with isotropic temperature factors, more cycles were carried out with anisotropic thermal parameters for all non-hydrogen atoms. Temperature factors for hydrogen atoms were not refined, and postional parameters for H(2) and H(3) were set and not refined.

Compound 4. A total of 1318 reflections with $I > 5\sigma(I)$ were used in the final refinement out of a total of 1621 which were considered observed. Several cycles of full-matrix least-squares refinement with isotropic temperature factors were followed by more cycles with anisotropic thermal parameters for all non-carbon and hydrogen atoms. The C(1) and C(10)–C(14) atoms were placed at approximate positions converted to a regular hexagon and were not refined.

Results

The reactivity of $Fe(CO)_5$ toward cyclic dienes, including HHA (I), was first investigated 25 years ago by Birch *et al.*[13] This led, *inter alia*, to the isolation of the 3,4,5,8,9,10-hexahydroanthracene derivative 1 as an orange oil,



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which was, however, identified only on the basis of microanalysis and its IR spectrum. We have used NMR spectroscopy to confirm the identity of 1: the low-field ^1H resonance (δ 5.70) due to three olefinic hydrogens is accompanied by a sharp doublet (δ 5.15), which may be assigned to the unique diene proton attached at C^1, and the lack of molecular symmetry results in differentiation of all 14 carbon atoms of the ligand tricycle in the ^{13}C spectrum.

We find also that a second product is formed with complex 1 during UV irradiation of HHA and $Fe(CO)_5$; this bright yellow compound, which was initially fortuitously recovered as crystals suitable for X-ray diffraction, has been characterized crystallographically as a bis(tricarbonyliron) derivative 2 of 3,4,7,8,9,10-hexahydroanthracene (**III**), in which iron centers are bound in an η^4 fashion to each of the isolated conjugated diene units on opposite faces of the tricyclic hydrocarbon skeleton (*i.e.*

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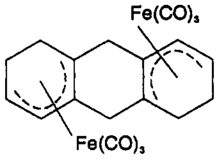

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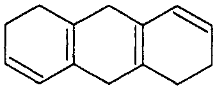
anti to one another across the latter). The ^{1}H NMR spectrum of pure **2** consists of a doublet (δ 5.20) and multiplet (δ 3.03) pattern, attributable to protons attached respectively at the 1,5- and 2,6-carbons of the coordinated diene, a multiplet to high field accounting for the eight methylene protons at the 3-, 4-, 7-, and 8-positions, and a conspicuous AB pattern (δ 3.73 and 2.91) due to the 9,9′- and 10,10′-hydrogens, which show a geminal coupling J_{AB} = 19 Hz. In accordance with the centrosymmetric structure (molecular point group C_i), the 14 carbon atoms of the organic framework give rise to 7 signals in the ^{13}C NMR spectrum of pure **2**, accompanied by a high-frequency resonance (δ 212 ppm) due to Fe(CO)$_3$ carbons (as is also the case for compound **1**).



III

Structurally significant coordination shifts are obvious in the ^{13}C NMR spectra of complexes **1** and **2**. Of four weak signals attributable to ring-junction carbon atoms in **1** (*i.e.* showing little NOE: those at δ 124.2, 103.7, 102.2, and 80.2 ppm), the two at lowest frequency (highest field) are assigned to C^{4a,9a} of the Fe-bound diene (shifted from δ 123.3 ppm in HHA), with those at δ 79.6 and 59.5 arising from the other diene pair C^{1,2}. This analysis, which is supported by unambiguous interpretation of the simpler spectrum of compound **2** (see below), leaves C^{6,7} (δ 124.0 and 124.3) unperturbed from δ 124.3 ppm in uncomplexed HHA, together with a set of methylene resonances (C^{3,4,5,8,9,10}) between 56.7 and 23.9 ppm. For **2**, feeble NOE again identifies lines due to quaternary carbons C^{9a,10a}, C^{4a,8a} (at δ 102.2 and 80.2), while resonances at δ 77.0 and 59.5 are due to coordinated C^1 and C^2; three signals at 38.9, 32.0, and 23.9 ppm account for the remaining (methylene) C$^{3/7,4/8,9/10}$. Within the diene–iron assembly there is thus a 20 ppm separation between inner and outer carbons, with the latter more shielded, as is expected.[18]

Further reactions afforded the yellow product only as a powder, which although microanalytically indistinguishable from complex **2** was shown by NMR spectroscopy to be a mixture. Thus, seven additional signals were superimposed on the characteristic ^{13}C spectrum of compound **2**, while in the ^{1}H NMR spectrum a window between overlapping multiplets clearly showed two singlets (δ 3.92 and 2.79) flanking the AB pattern due to **2** roughly equal in intensity with the latter, as is shown in Figure 1. We identify these extra features with the presence of an isomer **2a** of **2**, in which pairs of carbon atoms are again symmetry related in the tricyclic unit. The syn isomer of **2**, *i.e.* both Fe(CO)$_3$ groups on the same face of the ring system (see Chart I), has idealized C_2 symmetry (with a 2-fold axis perpendicular to the tricycle, relating seven pairs of carbon atoms) under which the H^9 methylene hydrogens are anisochronous (*i.e.* nonequivalent, although each is equivalent to a H^{10}). In contrast the idealized geometries of anti and syn isomers arising from localization of diene units on the same edge of the tricyclic framework (*i.e.* complexes of 3,4,5,6,9,10-hexahydroanthracene (**IV**) in Chart I, belonging to point groups C_2 and C_s, respectively) each possess eight distinguishable carbon environments (six equivalent pairs with C^9, C^{10} unrelated); moreover, in the anti arrangement, 2-fold rotation (*i.e.* about the C^9–C^{10} direction) generates equivalent pairs of methylene hydrogens at these two centers, although this is not true for the planar symmetry of the syn analogue. What this boils down to is that either **2a** is the syn isomer of **2**, in which J_{AB} between the methylene hydrogens is reduced to *ca.* zero through conformational changes (perhaps widening of the H$_A$–C–H$_B$ angle through buckling of the central ring to relieve interactions between Fe(CO)$_3$ units), or (less likely) an eighth ^{13}C resonance has gone undetected and **2a** is the alternate anti isomer with isochronous 9,9′- and 10,10′-proton pairs. Our efforts to separate **2** from **2a**, or to interconvert the two, were not successful.

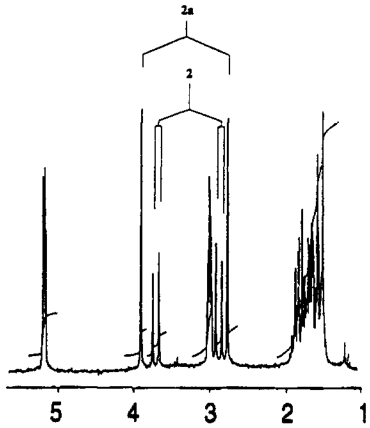
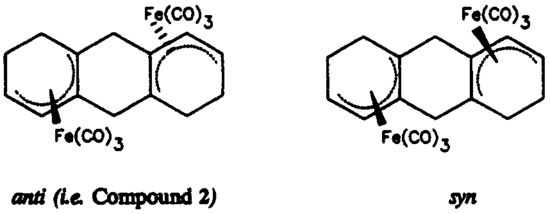
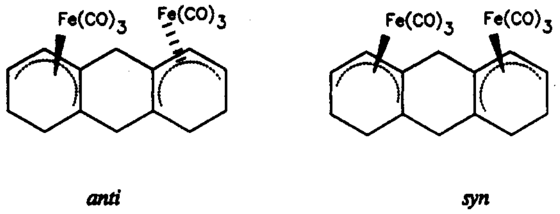


Figure 1. ^{1}H NMR spectrum of a mixture (*ca.* 1:1 ratio) of compounds **2** and **2a** in the δ 0–5 ppm range.

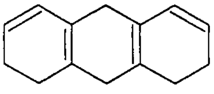
Chart I



Complexation of 3,4,7,8,9,10-hexahydroanthracene (*i.e.* III)



Complexation of 3,4,5,6,9,10-hexahydroanthracene (*i.e.* IV)



IV

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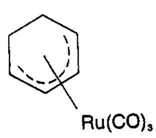
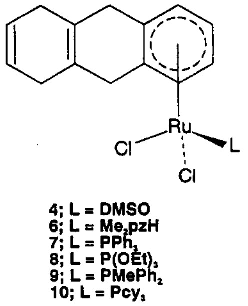
[18] Retcofsky, H. L.; Frankel, E. N. Gutowsky, H. S. *J. Am. Chem. Soc.* **1966**, *88*, 2710. Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135.

In an attempt to synthesize ruthenium analogues of 1 and 2, the reaction of HHA with $Ru_3(CO)_{12}$ was investigated. Attempts to isolate a product afforded white, volatile, solid material shown by ^{13}C NMR spectroscopy to be a mixture of hydrocarbons. This was resolved by GC/MS into unchanged HHA accompanied by five further constituents having M = *m/e* 182, 184, or 186 (*vs m/e* 184 for HHA). Comparable distributions were obtained for conversion of about 60% (60 h, in refluxing cyclohexane) when the proportion of HHA was increased to 10 and then 30 mol equiv *vs* $Ru_3(CO)_{12}$. These results are consistent with catalytic isomerization *vs* disproportionation (or unconcerted hydrogenative and dehydrogenative aromatization) of HHA in a roughly 3:2 ratio (see Experimental Section). Monitoring the reaction profile by using IR spectroscopy (1900–2200 cm^{-1} range) established (a) that $Ru_3(CO)_{12}$ remained throughout, (b) that a second species with a spectrum virtually identical with that[7] of the cyclohexa-1,3-diene complex $(\eta^4\text{-}C_6H_8)Ru(CO)_3$ (11) slowly increased in concentration, and (c) that no other carbonyl complexes were detectable in solution. Attempted recovery of the carbonyl product formed during the reaction (see (b) above) yielded it as a colorless solid that could not however be freed from HHA, precluding its definitive characterization. It was found in experiments using this material or authentic[7] $(\eta^4\text{-}C_6H_8)Ru(CO)_3$ (11) instead of $Ru_3(CO)_{12}$ that only very slow transformation of HHA was evident with conversion estimated by GC/MS at <100% (*i.e.* noncatalytic), mainly to a dehydrogenated analogue with M = *m/e* 182.



11

Reaction between HHA and hydrated $RuCl_3$ in refluxing ethanol afforded a yellow-brown compound which possessed very limited solubility in a wide range of common solvents. On the basis of microanalysis and indifferent NMR data this material was tentatively formulated as $[Ru(\eta^6\text{-}C_{14}H_{14})Cl_2]_x$ (3), a member of the well-known chloro-bridged polyruthenium family; while there has been discussion concerning the nuclearity of such species,[5,8] we anticipated that the extended hydrocarbon framework in 3 would restrict $x = 2$, with the HHA skeleton aromatized in one end ring and bound to Ru as a π-arene. Support for these expectations was provided when, after dissolution of complex 3 in DMSO, the red crystalline product 4 was recovered, which was shown by X-ray diffraction to be the mononuclear adduct $Ru(\eta^6\text{-}C_{14}H_{14})Cl_2(DMSO)$, in which the tricyclic system is indeed attached at Ru as the η^6 hydroaromatic ligand 1,4,9,10-tetrahydroanthracene (*i.e* II). Like related complexes of Ru^{II}, 4 readily undergoes ligand displacement of DMSO: on reaction with pyrazole (*i.e.* pzH), the yellow cation $[Ru(\eta^6\text{-}C_{14}H_{14})Cl(pzH)_2]^+$ was obtained, as its chloride salt (5), and a series of neutral adducts $Ru(\eta^6\text{-}C_{14}H_{14})Cl_2(L)$ analogous to 4 were isolated similarly, as orange or pink solids, where L = Me_2pzH (6), PPh_3 (7), $P(OEt)_3$ (8), $PMePh_2$ (9), and PCy_3 (tricyclohexylphosphine; 10).



4; L = DMSO
6; L = Me2pzH
7; L = PPh3
8; L = P(OEt)3
9; L = PMePh2
10; L = Pcy3

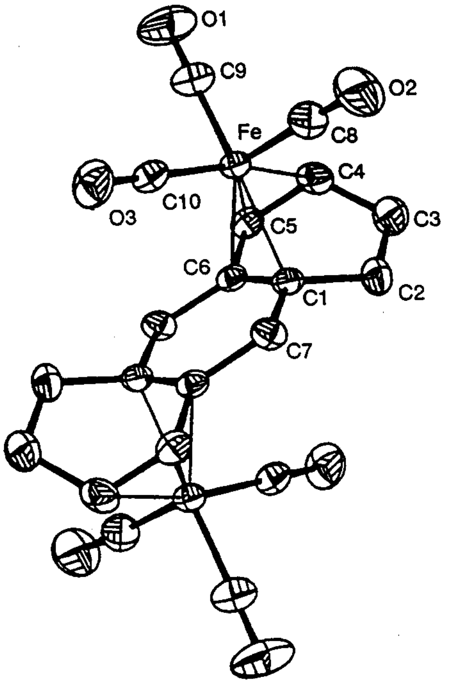


Figure 2. Molecular geometry of compound 2. Important bond distances (Å) and angles (deg): Fe–C(1) = 2.140(4), Fe–C(4) = 2.106(4), Fe–C(5) = 2.039(4), Fe–C(6) = 2.075(3), Fe–C(8) = 1.782(5), Fe–C(9) = 1.785(4), Fe–C(10) = 1.778(4), C(2)–C(1) = 1.502(5), C(6)–C(1) = 1.426(5), C(3)–C(2) = 1.546(5), C(4)–C(3) = 1.494(6), C(5)–C(4) = 1.427(6), C(6)–C(5) = 1.403(5); C(4)–Fe–C(1) = 76.4(1), C(9)–Fe–C(8) = 100.9(2), C(10)–Fe–C(9) = 91.8(2), C(6)–Fe–C(5) = 39.9(1), C(10)–Fe–C(8) = 101.2(2).

X-ray Crystal and Molecular Structures of Complexes 2 and 4. Crystallographic data for both the diiron complex 2 and the Ru^{II} arene (4) are collected in Table I; the molecular geometries are illustrated in Figures 2 and 3, respectively, the captions for which also list some important bond distances and angles. Positional parameters are listed in Tables II and III. The two metal atoms in compound 2 are isolated from one another (anti) on opposite faces of the tricyclic hydrocarbon skeleton, occupying positions related by inversion in which each is coordinated at a diene fragment that includes a ring-junction double bond. Thus, isomerization of the totally nonconjugated duplex 1,4-diene system in HHA has led to a pair of independent 1,3-diene units, in which the short–long–short relationship of carbon–carbon distances is characteristically[1,2] reversed through synergic bonding to the iron atom, so that the central C(5)–C(6) bond at 1.403 (5) Å is measurably shorter than C(1)–C(6) and C(4)–C(5) (1.426 and 1.427 Å). Much of the carbocyclic framework lies very close to coplanarity, with only the outermost atoms, *i.e.* in C(2) and C(3) positions, twisted away from this.

The structure of compound 4 confirms that reaction with $RuCl_3$ effects dehydrogenation of HHA in one outer

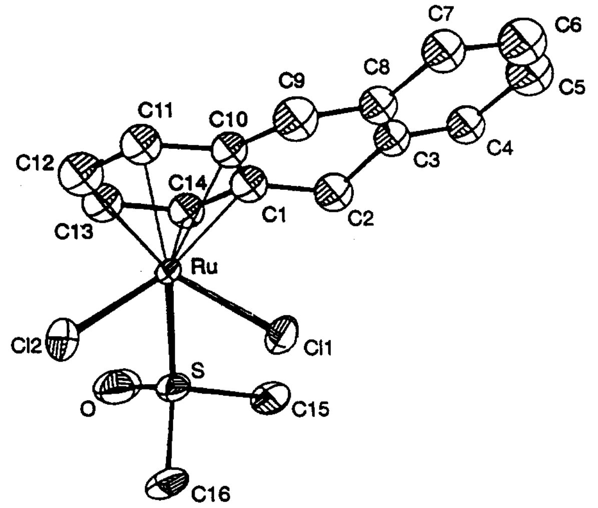


Figure 3. Molecular geometry of compound 4. Important bond distances (Å) and angles (deg): Ru–C(10) = 2.202(1), Ru–C(12) = 2.167(1), Ru–C(14) = 2.176(2), Ru–C(1) = 2.196(2), Ru–C(11) = 2.187(1), Ru–C(13) = 2.161(2), C(15)–S = 1.783(21), C(3)–C(2) = 1.530(29), C(4)–C(3) = 1.507(28), C(5)–C(4) = 1.520(33), O–S = 1.482(16), C(16)–S = 1.796(22), C(1)–C(2) = 1.556(21) C(8)–C(3) = 1.261(25), C(6)–C(5) = 1.282(30); Cl(2)–Ru–Cl(1) = 89.1(2), S–Ru–Cl(2) = 86.4(2), O–S–Ru = 114.7(6), C(15)–S–O = 108.5(11), C(16)–S–O = 109.9(10), S–Ru–Cl(1) = 85.4(2), C(15)–S–Ru = 108.8(7), C(16)–S–Ru = 114.2(8).

Table II. Fractional Atomic Coordinates and Temperature Parameters for Compound 2[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}, Å^2
Fe	24752(4)	–6240(4)	–7147(7)	264(3)
C(1)	3964(4)	443(3)	789(6)	26(1)
C(2)	3403(4)	1382(3)	1634(6)	37(1)
C(3)	2090(4)	1690(3)	290(7)	44(1)
C(4)	1723(4)	948(3)	–1471(7)	37(1)
C(5)	2633(4)	659(3)	–2490(6)	29(1)
C(6)	3835(3)	392(3)	–1295(5)	25(1)
C(7)	5166(4)	–24(4)	2243(6)	29(1)
C(8)	1932(5)	–721(3)	1455(8)	42(2)
C(9)	1203(4)	–1249(3)	–2516(7)	43(1)
C(10)	3404(3)	–1827(3)	–500(5)	33(1)
O(1)	–388(3)	1638(3)	–6338(5)	79(1)
O(2)	1591(4)	–740(3)	2849(6)	67(2)
O(3)	4007(3)	–2603(3)	–345(5)	55(1)
H(2)	337(0)	124(0)	312(0)	20(0)*
H(3)	134(0)	160(0)	112(0)	20(0)*
H(4)	95(4)	98(3)	–236(5)	20(0)*
H(5)	246(3)	58(2)	–399(6)	20(0)*
H(7)	542(3)	58(2)	341(6)	20(0)*
H(7′)	494(3)	–62(3)	309(6)	20(0)*

[a] Estimated standard deviations are given in parentheses. Coordinates are ×10^n, where n = 5, 4, 4, and 3 for Fe, O, C, and H. Temperature parameters ×10^n, where n = 4, 3, 3, and 3 for Fe, O, C, and H. $U_{e1} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*(\mathbf{a}_i\text{-}\mathbf{a}_j)$. Starred values indicate that U_{iso} is given. $T = \exp(8\pi^2U_{iso}(\sin^2\theta)/\lambda^2)$.

Table III. Fractional Atomic Coordinates and Temperature Parameters for Compound 4[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}, Å^2
Ru	31135(13)	17949(12)	38388(14)	311(7)
Cl(1)	1447(4)	2451(4)	2274(5)	45(2)
Cl(2)	3414(5)	303(4)	2751(5)	53(2)
S	1471(5)	783(4)	4194(5)	39(2)
O	1904(14)	84(12)	5178(14)	61(7)
Me(1)	256(19)	1671(16)	4367(20)	51(10)
Me(2)	516(19)	22(18)	3036(19)	54(9)
C(2)	2327(20)	4164(17)	4799(17)	44(6)*
C(3)	2506(19)	5210(16)	4233(16)	38(5)*
C(4)	1837(19)	6141(17)	4586(17)	42(5)*
C(5)	1975(23)	7157(20)	3972(20)	61(7)*
C(6)	2556(24)	7196(19)	3233(20)	59(7)*
C(7)	3270(20)	6275(18)	2875(17)	45(6)*
C(8)	3158(18)	5269(18)	3566(16)	40(6)*
C(9)	3842(21)	4307(17)	3187(17)	49(6)*
C(1)	3346(0)	3284(0)	4800(0)	39(0)*
C(10)	4019(0)	3393(0)	4029(0)	35(0)*
C(11)	4935(0)	2625(0)	3972(0)	42(0)*
C(12)	5177(0)	1749(0)	4686(0)	54(0)*
C(13)	4504(0)	1640(0)	5457(0)	46(0)*
C(14)	3588(0)	2408(0)	5514(0)	39(0)*

[a] Estimated standard deviations are given in parentheses. Coordinates are ×10^n, where n = 5, 4, 4, 4, and 4 for Ru, Cl, S, O, and C. Temperature parameters are ×10^n, where n = 4, 3, 3, 3, and 3 for Ru, Cl, S, O, and C. $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*{}_a a^*{}_j(\mathbf{a}_i\text{-}\mathbf{a}_j)$. Starred values indicate that U_{i}3o is given. $T = \exp(8\pi^2U_{iso}(\sin^2\theta)/\lambda^2)$.

ring, which complexes at the metal center through a η^6-arene interaction, while the third ring retains nonconjugated diene character with C(3)–C(8) and C(5)-C(6) distances short at 1.26(3) and 1.28(3) Å (see Figure 3). The product is therefore a η^6-1,4,9,10-tetrahydroanthracene complex (*i.e.* of THA, **II**) in which the ring system is dished away from the Ru center about C(2)–C(9) at an angle of 157°. The Ru–C(arene) distances, in the range 2.161(2)–2.202(1) Å, are normal;[19] the ring-junction carbons lie slightly farther from the metal center than C(12) and C(13), amounting to a marginal ring tilt. The DMSO ligand is bound through sulfur at Ru–S = 2.333(5) Å; the two Cl atoms are equidistant within error from Ru (2.39 and 2.40 Å). Coordination of DMSO to platinum-group metals has been observed through either O or S; in particular, in[12] *cis*-$RuCl_2(DMSO)_4$ a single sulfoxide is bound at Ru through O, with the other three attached by bonds to S that are about 0.05 Å shorter than that distinguished here in complex 4. The trigonal $RuCl_2$(DMSO) group is rotated by about 10° out of eclipse with arene carbon atoms, in a manner that places one Cl below the central ring of the polycyclic ligand and projects the DMSO molecule across the direction of the latter, while the roughly tetrahedral arrangement about S points the S=O bond under Ru. These relationships are clarified by reference to Figure 3.

NMR Spectra of the Tetrahydroanthracene (THA) Ruthenium(II) Complexes 4–10. The ^1H NMR data for the (arene)ruthenium derivatives Ru(η^6-$C_{14}H_{14}$)Cl_2(L) (4 and 6–10) are listed in Table IV. A singlet resonance consistently near δ 5.7 for all these species is due to protons $H^{2,3}$ at the uncomplexed olefinic bond. Also to low field is an AA′BB′ pattern, arising from coupling among the $H^{5,8}$ and $H^{6,7}$ pairs, while methylene protons appear as two AB arrays above δ 4.0 that are clearly distinguishable in terms of chemical shift difference. Thus, half of one multiplet is found near δ 2.9 with it complement as much as 0.7 ppm to low field varying in position with L, while in the other the wings overlap with one another in the vicinity of δ 2.6. The latter may then be assigned to $H^{1,4}$ protons, which are more distant from the metal center: the differential influences on exo *vs* endo faces will be felt more strongly in the central ring by $H^{9,10}$ hydrogens, of which the endo pair will be more sensitive to the nature of L. Pyrazole complexation gave products (compounds 5 and 6) in which H or Me at heterocycle C^3, C^5 (Table IV) are nonequivalent, *i.e.* metal N–N site-exchange is not occurring on the NMR time scale.

The NMR properties of the triphenylphosphine adduct 7 were further investigated by using homonuclear decou-

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(19) Moriarity, R. M.; Ku, Y.; Gill, U. S.; Culardi, R.; Perrier, R. E.; McGlinchey, M. J. *Organometallics* **1989**, *8*, 960.

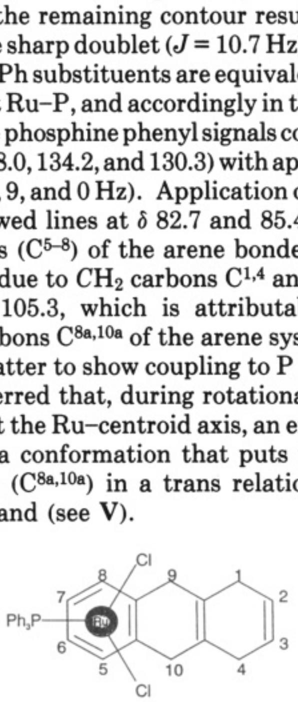
Table IV. ^1H NMR Data for $Ru(\eta^6\text{-}C_{14}H_{14})Cl_2(L)$, Compounds 4 and 6–10[a]

compd	L	$H^{6,7}$	$H^{5,8}$	$H^{2,3}$	$H^{9,10}$	$H^{1,4}$	L
4	DMSO	5.50 (m, 2H), 5.66 (m, 2H)		5.71 (s, 2H)	3.00 (m, 2H), 3.47 (m, 2H)	2.65 (m, 4H)	3.13 (s, 6H)
6	Me_2pzH	5.45 (m, 2H), 5.66 (m, 2H)		5.72 (s, 2H)	2.91 (m, 4H)	2.54 (m, 4H)	2.17 (s, 3H), 2.49 (s, 3H), 5.92 (d, 1H), 10.80 (s, 1H)
7	PPh_3[b]	4.30 (m, 2H)	4.95 (m, 2H)	5.70 (s, 2H)	2.93 (m, 2H), 3.65 (m, 2H)	2.66 (m, 4H)	7.3–7.8 (m, 15H)
8	$P(OEt)_3$[c]	5.30 (m, 2H)	4.95 (m, 2H)	5.67 (s, 2H)	2.90 (m, 2H), 3.46 (m, 2H)	2.60 (m, 4H)	1.25 (t, 3H),[d] 4.11 (m, 2H)[e]
9	$PMePh_2$[f]	4.55 (m, 2H)	4.89 (m, 2H)	5.70 (s, 2H)	2.93 (m, 2H), 3.52 (m, 2H)	2.65 (m, 4H)	1.98 (d, 3H),[g] 7.3–7.8 (m, 5H)
10	PCy_3[h]	5.32 (m, 2H)	4.83 (m, 2H)	5.68 (s, 2H)	2.90 (m, 2H), 3.61 (m, 2H)	2.60 (m, 4H)	1.1–2.2 (m, 33H)

[a] $CDCl_3$ solution; all values in δ. [b] $\delta(^{31}P) = 30.5$ (s). [c] $\delta(^{31}P) = 118.1$ (s). [d] $^3J_{HH} = 7$ Hz. [e] $^3J_{PH} = 3$ Hz. [f] $\delta(^{31}P) = 26.6$ (s). [g] $^2J_{PH} = 12$ Hz. [h] $\delta(^{31}P) = 35.2$ (s).

pling, spectral simulation, and ^{13}C NMR spectroscopy. Irradiation within the AA′BB′ envelope at the frequency of the δ 4.30 signal led to collapse of its counterpart (δ 4.95) to a singlet, with no effect on the remainder of the spectrum; in reverse, however (*i.e.* irradiation at frequency equivalent of δ 4.95), the δ 4.30 resonance simplified to a doublet attributable only to coupling with P (*i.e.* the latter is X in an AA′BB′X spin system), with $^3J_{PH} = 3.0$ Hz. A similar effect was observed for complex **8**, where the δ 5.3 signal took on a doublet structure (J again 3.0 Hz) on irradiation into the δ 4.95 component. An accurate line-shape fit of both multiplets for compound **7** was possible by spectral simulation using the following coupling constants: $J_{AA'} = 4.99$, $J_{AB} = 5.61$, $J_{AB'} = 0.80$, $J_{AX} = 2.56$, $J_{BB'} = -0.03$, $J_{BX} = 0.00$ Hz. It may be concluded that the protons showing coupling to P are those which couple more strongly to one another, *i.e.* the adjacent $H^{6,7}$ pair rather than $H^{5,8}$, a distinction that is required in further discussion below.

Decoupling from one another of phosphine ^1H resonances led to the trivial observation that, for $P(OEt)_3$ in complex **8**, $^3J_{PH} = 7.0$ Hz with $^4J_{PH} = 0$; more significantly, however, in **7** one clearly resolved part of the PPh_3 envelope could be assigned to ortho protons, since irradiation at the center of the remaining contour resulted in collapse to only a single sharp doublet ($J = 10.7$ Hz). This suggests that the three Ph substituents are equivalent through free rotation about Ru–P, and accordingly in the ^{13}C spectrum of adduct **7** the phosphine phenyl signals constitute a single set (δ 133.7, 128.0, 134.2, and 130.3) with appropriate values for J_{PC} (20, 10, 9, and 0 Hz). Application of a DEPT pulse sequence allowed lines at δ 82.7 and 85.4 to be assigned to CH carbons (C^{5-8}) of the arene bonded to Ru, with δ 30.5 and 30.7 due to CH_2 carbons $C^{1,4}$ and $C^{9,10}$. A weak feature at δ 105.3, which is attributable to the two remaining carbons $C^{8a,10a}$ of the arene system, is the only signal of the latter to show coupling to P ($^2J_{PC} = 9.5$ Hz). It may be inferred that, during rotational motion of the η^6-arene about the Ru–centroid axis, an energy minimum may exist at a conformation that puts these same two carbon atoms ($C^{8a,10a}$) in a trans relationship with the phosphine ligand (see **V**).



V

The observation that phosphorus is coupled to the $H^{6,7}$ pair ($J = 3$ Hz, see above) but not to $H^{5,8}$ in compound **7** may also be explained in terms of conformation (**V**), as a "through-space" interaction. Furthermore, there is a striking shift in the position of $H^{6,7}$ when PPh_3 is replaced by $P(OEt)_3$ (by 1 ppm, compound **8** *vs* **7**; Table IV), a change that suggested shielding effects due to Ph ring current in a conformation such as **V** for **7**. In accordance with this idea, a rather smaller downfield shift was observed (0.75 ppm; Table IV) in the PPh_2Me analogue **9** while the PCy_3 complex **10** exhibited no shift *vs* compound **8**. In contrast, the $H^{5,8}$ resonance is essentially invariant over the series (*i.e.* **7–10**; Table IV).

Discussion

The tricyclic nonconjugated tetraene HHA (**I**) forms complexes with Fe or Ru in a manner that reaffirms characteristic differences in organometallic chemistry between the two elements. Thus, with iron, isomerization accompanying C substitution that yields the known[13] 1,3-diene complex **1** repeats itself to give the corresponding bis(tricarbonyliron) compound **2**: in this molecule (and possibly also in its isomer **2a**), the two metal centers are remote from one another on opposite faces of the hydrocarbon. A curious feature of the molecular geometry of **2** (see Figure 2) is the degree to which the ring system is planar, especially since the C(1)–C(6) and C(4)–C(5) bonds clearly show loss of double-bond character due to back-donation from the iron atoms. In contrast, while ruthenium analogues of **1** and **2** do not appear to be directly accessible, $RuCl_3$ behaves typically by effecting dehydrogenation at one 1,4-diene nucleus of HHA to bind it as a η^6-arene (**II**). The resulting polycyclic arene–ruthenium arrangement, as is exhibited in compound **4** (see Figure 3), is of a type not previously characterized crystallographically.[19]

The conversion of HHA by $RuCl_3$ to **II**, which can subsequently be displaced from Ru on heating in DMSO, constitutes a potentially useful specific transformation if conditions that cycle it catalytically could be found. Reorganization of HHA is catalytic in the presence of $Ru_3(CO)_{12}$ but occurs predominantly by isomerization to give a mixture of anthracene derivatives. A new carbonyl complex is formed concurrently, which on the basis of its IR spectrum may be the ruthenium analogue of compound **1**: however, when this species or the cyclohexa-1,3-diene complex[7] $(\eta^4\text{-}C_6H_8)Ru(CO)_3$ (**11**) is introduced instead of $Ru_3(CO)_{12}$, conversion of HHA is very slow (mainly by dehydrogenation) and indeed may not be catalytic. This is in conflict with an earlier claim that complex **11** is an active catalyst for inter- or intramolecular hydrogen-transfer reactions.[20] No other ruthenium complexes could be detected by IR or NMR spectroscopy, suggesting that isomerization of HHA may be mediated by the Ru_3 center. The ^{13}C NMR spectra of product mixtures were compli-

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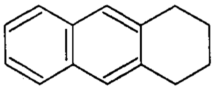
(20) Whitesides, T. H.; Budrick, R. A. *J. Chem. Soc., Chem. Commun.* **1973**, 87.

cated and could not be used to identify every component detected by GC/MS. It was clear, however, that the dominant dehydrogenation product (M = *m/e* 182) was (^{13}C NMR[21])1,2,3,4-tetrahydroanthracene (VI) and not



VI

II and that none of the more stable 9,10-dihydroanthracene or anthracene itself (M = *m/e* 180 and 178, respectively) was formed. Selectivity for VI has also been observed in the catalytic hydrogenation of anthracene by anionic Ru^{III} systems.[22] The relative thermodynamic stability of hydrogenated anthracenes has been quantified in a discussion[23] of possible products from coal liquefaction; ^{13}C NMR spectra for I, VI, and some octahydroanthracene isomers (M = *m/e* 186) are illustrated in ref 21.

The NMR properties of the PPh_3 adduct 7 establish that in solution the phosphine rotates freely about the Ru–P bond but that an energy minimum may exist during rotation of the η^6-bound hydrocarbon (II). Thus, selective coupling of P to $C^{8a,10a}$ and to $H^{6,7}$ can be accounted for in terms of a conformation such as V, which is also the most likely for enhanced shielding of $H^{6,7}$ by Ph ring current effects associated with the PPh_3 ligand. Existence of the latter in a comparable but unrelated system has been highlighted very recently.[24] The unsymmetrical nature of ligand II with respect to the Ru–arene axis in 7 precludes[25] any estimate by NMR spectroscopy of the relative stability of conformation V.

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Supplementary Material Available: Tables giving anisotropic thermal parameters and bond distances and angles for 2 and 4 (6 pages). Ordering information is given on any current masthead page.

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