

PROPELLANES. PART XCVII. MIXED COMPLEXES OF COBALT AND IRON WITH A
TETRAENIC [4.4.3]PROPELLANES IMIDE **

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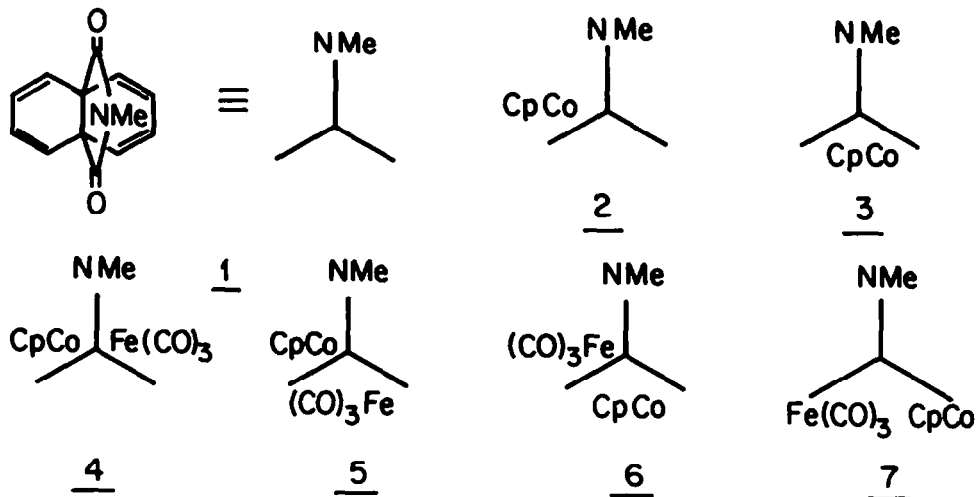
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(Received in UK 20 June 1988)

Abstract. - Cyclopentadienyl-cobalt complexes of 12-methyl-12-aza[4.4.3] propella-2,4,7,9-tetraene **1** have been used to prepare mixed complexes with $\text{Fe}(\text{CO})_3$. Their structures have been established and competitive oxidation experiments have been conducted.

Introduction. - Various complexes have been reported with organic substrates, in which two different metal atoms are present.¹ Various mono and bis syn and anti cyclopentadienyl cobalt complexes of tetraene propellane imides have been prepared² and separated from the reaction mixture.³ Further, many $\text{Fe}(\text{CO})_3$ complexes of various tetraenic propellanes have also been prepared⁴ and their structures established.⁵

Thus it appeared of interest to treat CpCo complexes of **1** with $\text{Fe}_2(\text{CO})_9$ in order to obtain mixed iron, cobalt complexes. Since we had available both mono CpCo complexes of **1**, syn, **2**, and anti, **3** it should, in principle, be possible to obtain a total of four mixed complexes **4-7**. The last of the foursome, **7**, ought to be the most interesting structurally, if indeed it could be

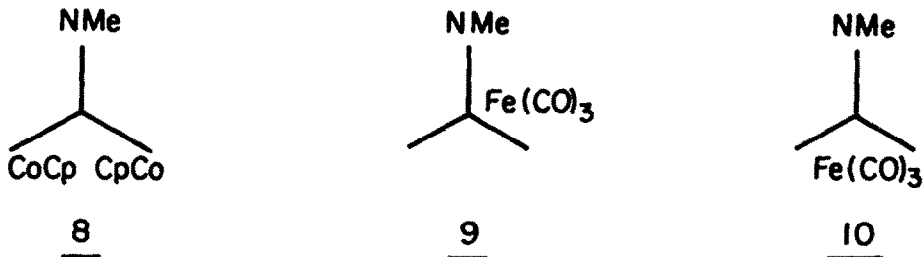


** Dedicated in friendship to Professor Alan R. Battersby in honor of his seminal contributions to the biosynthesis of natural products containing iron and cobalt.

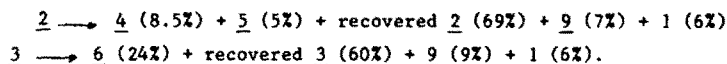
Part XCVI. Y. Klopstock, P. Ashkenazi, A. Mandelbaum, D. Muller, W.J. Richter, and D. Ginsburg, *Tetrahedron*, in press.

prepared despite the necessary steric accommodation of the neighboring Fe and CO functions. We already know that the isomer 8 is missing in the product mixture obtained from 1 with CpCo diethene.¹

Alternatively, since we have the Fe(CO)₃ complexes 9 and 10 at our disposal^{5c} it may be possible to obtain by interaction with CpCo(CO)₂ the same foursome: 4 and 6 from 8, and 5 and 7 from 9, respectively.

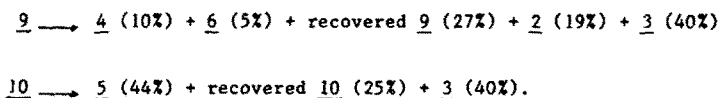


Scheme 1 summarizes the results of treatment of the syn CpCo complex 2, and of its anti CpCo isomer 3.



Scheme 1

Scheme 2 summarizes the results of the "reverse" reaction, i.e. introduction of CpCo into the syn and anti Fe(CO)₃ complexes, 9 and 10 respectively. The Vollhardt procedure, using CpCo(CO)₂ was used.⁶ (Thus, a solution of 9 or 10 was irradiated in boiling *o*-xylene).

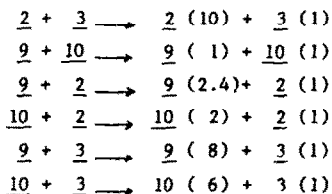


Scheme 2

Evidently irradiation of 9 and of 10 removes some of the Fe(CO)₃ and iron-free, mono CpCo complexes are also isolated.

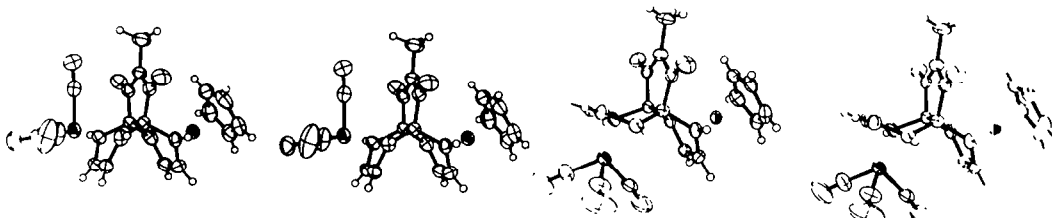
One would predict that CpCo is more weakly bound to a diene than Fe(CO)₃. We conducted several competition experiments with Ce^{IV}. We oxidized separately a synthetic mixture of the syn and anti mono CpCo and mono Fe(CO)₃ complexes shown in Scheme 3 and used ¹H-NMR as the criterion. We indeed found that CpCo is more loosely bound than Fe(CO)₃.

A 1:1 molar mixture of the substrates shown was allowed to stand overnight at r.t. with 0.5 mol Ce^{IV} in MeOH-EtOAc. After workup (see experimental section) the ¹H-NMR spectrum of the resulting product mixture showed the ratios given in the parentheses in Scheme 3.



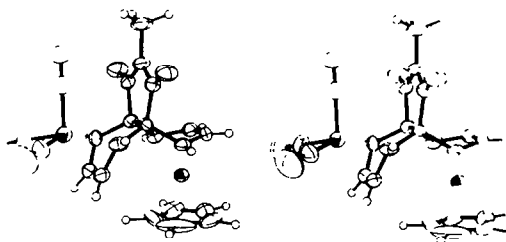
Scheme 3

As shown, 9 and/or 10 (containing $\text{Fe}(\text{CO})_3$) survive 2 and/or 3 (containing CpCo). As expected, the organo-cobalt bond is the weaker. It is true that we compare apples to pears, a 1,3-dienic system attached to two different groups, CpCo and $\text{Fe}(\text{CO})_3$, but this cannot be helped. Extended-Huckel calculations germane to such comparisons have been made.⁷



ORTEP 4

ORTEP 5



ORTEP 6

All of the ^1H - and ^{13}C -NMR data appears in the experimental section. Inspection of values between the central protons and the central carbon atoms in the 1,3-diene system complexed by a metal, and the terminal protons and terminal carbons of the system for syn and anti mono-complexes and syn-anti bis-complexes shows that they are always higher for the anti complexes. But the relationship is reversed for the mixed complexes of $\text{Fe}(\text{CO})_3$ and CpCo ; of the syn is higher than that of the anti-complexes. Numerical data for other systems may be found in the literature.⁸

Particularly interesting mass spectral fragmentations of 5, 6, and 7 will be reported separately.^{9,10}

Presumably no 7 nor 8³ could be isolated because of the steric requirements of 2 anti groups.

Experimental. - IR spectra were all measured in CHCl_3 using a Perkin-Elmer 298 spectrophotometer. NMR spectra were measured in CDCl_3 on a 400 MHz Bruker spectrometer. Mass spectra were measured using a Varian MAT 711 instrument.

All m.p.'s are uncorrected.

Reactions with $\text{Fe}_2(\text{CO})_9$. - a) Complex 2 (89 mg) and $\text{Fe}_2(\text{CO})_9$; (960 mg) in benzene (50 ml) were heated under reflux for 6 days. After evaporation of solvent and separation of the product mixture on prep. silica plates using EtOAc (15); hexane (85) afforded the products shown in Scheme 1, inter alia 4 and 5.

4: Red prismatic needles, m.p. 156-158°C (ethyl acetate). IR: 2056, 1993, 1777, 1701, 1435, 1385, 1295, 1010 cm^{-1} . ^1H -NMR: 5.17 (dd, 2H, $J_{3,4}=4.8$, $J_{2,3}=2.7$, Fe-vinylic), 5.08 (dd, 2H, $J_{3,4}=4.3$, $J_{2,3}=2.3$, Co-vinylic), 4.56 (s, 5H, Cp), 3.23 (s, 3H, NCH_3), 2.91 (m, 4H, Fe-vinylic, Co-vinylic). ^{13}C -NMR: 200.29, 83.10, 79.89, 75.96, 60.15, 53.17, 24.50. MS: 477(M^+ , 60); 420 (100); 394 (31); 391 (21); 337 (55.5); 335 (4); 324 (47); 308 (89); 297 (60); 252 (33); 213 (3); 211 (4); 186 (11); 184 (39); 179 (22); 128 (75); 124 (94).

MW: Found 476.9682. $\text{C}_{21}\text{H}_{16}\text{NO}_5\text{CoFe}$ requires 476.9710.

5: Red plates, m.p. 166°C (EtOAc). IR: 2059, 1998, 1763, 1700, 1430, 1380, 1290, 1010 cm^{-1} . $^1\text{H-NMR}$: 5.24 (dd, 2H, $J_{3,4}=4.6$, $J_{2,3}=2.3$, Fe-vinyl), 5.05 (dd, 2H, $J_{3,4}=4.9$, $J_{2,3}=2.9$, Co-vinyl), 4.59 (s, 5H, Cp), 3.05 (s, 3H, NCH_3), 3.04 (dd, 2H, $J_{3,4}=4.6$, $J_{2,3}=2.3$, Fe-vinyl), 2.96 (dd, 2H, $J_{3,4}=4.9$, $J_{2,3}=2.9$, Co-vinyl). $^{13}\text{C-NMR}$: 199.87, 84.62, 79.82, 77.00, 65.87, 52.77, 24.65. MS: 477 (M^+ , 43); 448 (2); 420 (100); 394 (41); 392 (7); 390 (41); 337 (67); 335 (6); 325 (16); 308 (28); 297 (33); 279 (5); 252 (29); 186 (13); 184 (42); 179 (23); 128 (58); 124 (81).

MW: Found 476.9718.

b) 3 (129 mg), $\text{Fe}_2(\text{CO})_9$ (275 mg), benzene (50 ml) heated under reflux for 24h. Workup as in a) but EtOAc (10): hexane (90) gave the products shown in Scheme 1, *inter alia* 6.

6: Red plates m.p. 230-234°C (EtOAc). IR: 2058, 1990, 1768, 1698, 1430, 1370, 1285, 1005 cm^{-1} . $^1\text{H-NMR}$: 5.66 (m, 2H, Fe-vinyl), 4.99 (m, 2H, Co-vinyl), 4.82 (s, 5H, Cp), 3.28 (m, 2H, Fe-vinyl), 3.06 (m, 2H, Co-vinyl), 2.7 (s, 3H, NCH_3). $^{13}\text{C-NMR}$: 200.11, 83.73, 80.85, 76.48, 62.71, 59.35, 24.17. MS: 477 (M^+ , 28); 448 (2); 420 (30); 394 (12); 392 (2); 337 (6); 325 (3); 308 (13); 297 (4); 272 (6); 252 (95); 213 (2); 212 (9); 186 (7); 179 (5); 128 (48); 124 (100).

MW: Found 476.9624.

c) The syn, anti bis-CpCo complex³ (50 mg), $\text{Fe}(\text{CO})_5$ (108 mg), in benzene (50 ml) were heated under reflux for 24h. After workup as in b) five products were isolated: recovered bis-CpCo starting material (35 mg; 80%), 6 (6 mg; 12%) and 9^{3a} (6.5 mg; 18%).

Reactions with CpCo(CO)₂. - a) 10 (175 mg) was dissolved in degassed *o*-xylene (30 ml) and a solution of $\text{CpCo}(\text{CO})_2$ (0.2 ml) in the same solvent (10 ml) was added while being irradiated (Philips 375W bulb) and heated under reflux for 4h. After filtration, washing with EtOAc and evaporation and purification on prep SiO_2 plates with EtOAc (15): hexane (85), the products shown in Scheme 2 were obtained, including 5.

b) A mixture of 9 and the bis-syn $\text{Fe}(\text{CO})_3$ complex (90 mg) was treated similarly with $\text{CpCo}(\text{CO})_2$. After workup the products were isolated, *inter alia* 4 and 6, as detailed in Scheme 2.

Competitive oxidations with Ce^{IV}. - We give one example of the general procedure: 2 (21 mg) and 9 (20 mg) were dissolved in EtOAc (1): MeOH (1). To this was added ceric ammonium nitrate (16 mg; 0.5 eq) and the whole was allowed to stand overnight at r.t. After evaporation of solvent the constitution of each mixture was obtained by $^1\text{H-NMR}$ (see Scheme 3).

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