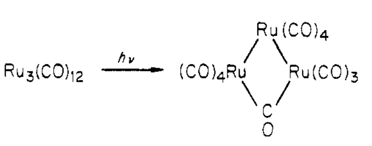
the ν_{CO} bands of the starting material (2062 (vs), 2032 (s), and 2012 (m) cm^{-1}) is accompanied by the appearance of very prominent new absorbances at 2040 (s) and 1999 (vs) cm^{-1} characteristic of $Ru(CO)_5$![11] Only minor other absorbances at 2074, 2082, 2108 (w), 2130, and 2140 cm^{-1}, suggesting the presence of some chlorocarbonyl ruthenium species,[12] were found in this initial spectrum. Continued photolysis leads to complete conversion to the latter products.[13] However, the identical products are formed if $Ru_3(CO)_{12}$ in octane solution is photolyzed under CO to completion giving only $Ru(CO)_5$, then CCl_4 is subsequently added, and the system is allowed to react in the dark. This thermal chlorination of $Ru(CO)_5$ in octane/1 M CCl_4 occurred with a first-order rate constant of about 1×10^{-4} s^{-1} at room temperature (~20 °C). The products of $Ru_3(CO)_{12}$ photolysis in octane/1 M CCl_4/Ar (1 atm) led to the slow formation of a product solution exhibiting a number of ν_{CO} bands in the IR, the more prominent of which were noted above as products under CO (1 atm).

The above results in CCl_4 solution demonstrate clearly that the principal photofragmentation pathway in octane does not occur via the intermediacy of a reactive diradical species. The role of CO in determining the quantum yields, the observation of $Ru(CO)_5$ as the primary photoreaction product under CO and in the presence of CCl_4, and the failure of CCl_4 to affect ϕ_d under CO (1 atm) indicate that the excited states and intermediates along the primary photoreaction potential surface are not intercepted by CCl_4 and that the eventual chlorocarbonyl products are the result of secondary thermal reactions of the $Ru(CO)_5$ product. A minor fragmentation pathway via radical intermediates may be reflected by the small ϕ_d values seen under argon. However, reaction of CCl_4 with the unsaturated intermediate proposed below might also account for this minor pathway.

Table I also summarizes ϕ_d values in tetrahydrofuran and diglyme solutions under CO (1 atm).[14] In each case, ϕ_d is markedly smaller than in octane under otherwise comparable conditions. That such changes are not simply due to solvent effects is demonstrated by decreased ϕ_d values in octane when small concentrations of THF or diglyme are added (Table I). Under such conditions low concentrations of these donor cosolvents added to octane act as quenchers of the photofragmentation, the quantitative behavior following Stern–Volmer type kinetics (ϕ_0/ϕ vs. [Q] plots linear).[15] However, the identical product ($Ru(CO)_5$) is formed by photolysis in octane, THF, or diglyme solutions.

That the reaction quantum yields are little affected by CCl_4, a radical trap, but are significantly affected by the presence of weak Lewis bases indicates that the key intermediate(s) in the photofragmentation is not radical in nature but is coordinatively unsaturated. We propose the species B shown in eq 3. Once formed by photolysis, B could be trapped by a weak donor such as THF or (competitively) by CO or other π-acid ligand (e.g., C_2H_4, Table I). Fragmentation of the resulting $Ru_3(CO)_{12}L$ adduct may prove facile; however, fragmentation of the analogous adduct of a hard base, for example, THF, may be much less so owing to the probable need to stabilize intermediates of low coordination number. Thus, the latter species would be expected to collapse back to the more stable $Ru_3(CO)_{12}$ starting material with loss of THF.



(3)

B

Studies are in progress to identify key intermediates of the proposed photofragmentation mechanism and to characterize better the thermal reactions of $Ru(CO)_5$ with CCl_4. It is notable that $Fe(CO)_5$ is essentially unreactive with CCl_4 under comparable conditions.[16,17]

Acknowledgment. This work is supported by the National Science Foundation. We thank Johnson-Matthey, Inc., for a loan of the ruthenium used in this study.

Registry No. $Ru_3(CO)_{12}$, 15243-33-1; $Ru(CO)_5$, 16406-48-7; CO, 630-08-0; CCl_4, 56-23-5.

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(11) Calderazzo, F.; L'Eplattenier, F. *Inorg. Chem.* **1967**, *6*, 1220–1224.

(12) These absorbances are consistent with the spectrum of $Ru_2(CO)_6Cl_4$: Johnson, B. F. G.; Johnston, R. D.; Lewis, J. *J. Chem. Soc. A* **1969**, 792–797.

(13) Note that $Ru(CO)_5$ does not absorb 405-nm light significantly so that further reactions of this species under these conditions represents thermal not photochemical processes.

(14) CO solubilities at 25 °C are relatively insensitive to the nature of these solvents ranging only from 0.006 mol/(L atm) in diglyme [M.S. Dissertation, J. Hildebrand, University of California, Santa Barbara, 1979] to ~0.012 M/(L atm) in octane [value estimated from that found in heptane, "Encyclopedia of Chemical Technology", 3rd ed.; Wiley: New York, 1978; Vol. 4, p 775].

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Synthesis, Structure, and Reactivity of Ru(η^6-C_6Me_6)[η^4-$C_6Me_4(CH_2)_2$]. An Unusual Transition-Metal *o*-Xylylene Complex[†]

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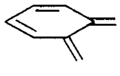
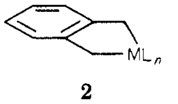
Received July 8, 1982

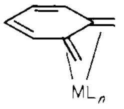
Summary: Deprotonation of $[Ru(C_6Me_6)_2]^{2+}$ generates the new *o*-xylylene complex $Ru(C_6Me_6)[C_6Me_4(CH_2)_2]$. The X-ray crystallographic study confirms that the metal is coordinated to the endocyclic diene system. The exocyclic methylenes are nucleophilic and can be reacted with electrophiles in a stepwise manner. This has allowed the isolation of a new *exo*-(methylene)cyclohexadienyl complex.

Transition metals are often valuable in stabilizing organic molecules which cannot survive in common laboratory conditions. For instance, many examples of cyclobutadiene complexes have been reported, and their use in organic synthetic applications has been explored.[1] *o*-Xylylene, 1, is another example of this type of reactive species. Here again, coordination of the molecule to a transition metal yields a stable complex. With this ligand,


1



2



3

[†] Dedicated to the memory of Professor Roland Pettit.

(1) Pettit, R. *J. Organomet. Chem.* **1975**, *100*, 205.

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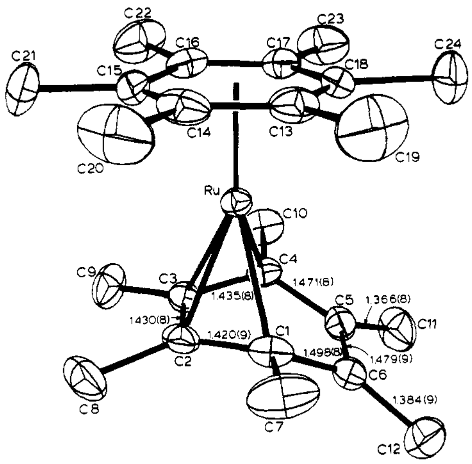
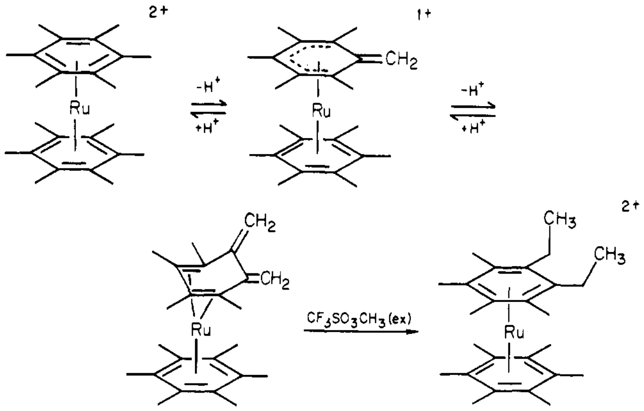


Figure 1. View of the structure of $Ru(C_6Me_6)[C_6Me_4(CH_2)_2]$ showing the atom labels and some distances of the coordinated *o*-xylylene ligand. The Ru–C1/2/3/4 distances are 2.204 (6), 2.119 (6), 2.137 (5), and 2.208 (5) Å, respectively. The Ru–arene carbon distances average 2.23 (1) Å. The arene ring C–C distances average 1.42 (3) Å, and the C-Me distances are 1.53 (2) Å.

Scheme I



two distinct bonding modes have been observed.[2-10] In **2** it coordinates as a chelating σ_2 ligand (a metallobenzocyclopentene),[6-9] while in **3** the metal is bound to the π system. In one case, $W[C_6H_4(CH_2)_2]_3$, the structure indicates an intermediate bonding mode of the *o*-xylylene ligand.[10] In each of the known monometal π complexes, the metal is believed to coordinate to the exocyclic diene.[2-5] We report here the high yield synthesis of a new *o*-xylylene complex, its crystal and molecular structure which proves that the metal binds to the *endocyclic diene*, and some preliminary studies on its reactivity toward electrophiles.

The use of potassium *tert*-butoxide to deprotonate alkyl groups of coordinated arenes has been observed.[5,11] Most recently Bennett and co-workers reported[5] the double deprotonation of $[Ru(ONO_2)(PR_3)_2(\eta^6\text{-}C_6Me_6)]NO_3$ in the presence of excess PR_3 to generate the related *o*-xylylene complex $Ru[C_6Me_4(CH_2)_2](PR_3)_3$. Once again, however, the metal is coordinated to the exocyclic diene. Bis(hexamethylbenzene)ruthenium dication $[Ru(C_6Me_6)_2]^{2+}$ is a stable 18-electron complex containing two planar η^6 aromatic rings. When 1.00 g (1.4 mmol) of $[Ru(C_6Me_6)_2](PF_6)_2$ is stirred with potassium *tert*-butoxide (0.63 g, 5.6 mmol) in 25 mL of tetrahydrofuran for 1.0 h, the solution turns bright yellow. After evaporation of the solvent, extraction of the residue with toluene, filtration, and evaporation of the toluene, $Ru(C_6Me_6)[C_6Me_4(CH_2)_2]$ is obtained as a yellow solid in 87% yield. The product can be recrystallized from toluene and has been analyzed by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, elemental analysis,[12] and single-crystal X-ray crystallography. The methylene hydrogens appear as doublets ($J = 1.07$ Hz) at 5.04 and 4.46 ppm, which is very close to the normal region for vinylogous protons. However, in all of the known *o*-xylylene π complexes the corresponding hydrogens appear near Me_4Si.[2-5] The ^{13}C resonance of the methylene carbons appear at 89.04 ppm, which is far downfield from the shift of 26.1 ppm of the analogous carbon in $Co[C_6H_4(CH_2)_2](\eta^5\text{-}C_5H_5)$.[4] These spectral features are consistent with binding the ruthenium to the endocyclic diene moiety in $Ru(C_6Me_6)[C_6Me_4(CH_2)_2]$.

For confirmation of the proposed structure, a single-crystal X-ray crystallographic study was conducted.[13] Figure 1 shows the structure of the complex with the atom labels and selected bond distances. The Ru is indeed bound to the endocyclic diene (C1–C2–C3–C4) while the exocyclic diene (C11–C5–C6–C12) is directed away from the Ru, making a 33.8° dihedral angle with the coordinated portion of the molecule. The distances between C11/5/6–C5/6/12 show that it is a relatively unperturbed conjugated diene. Conversely, the bonds between C1/2/3–C2/3/4 are almost identical which is typical of coordinated dienes. The C4/1–C5/6 distances of 1.471 (8) and 1.498 (8) Å indicate that there is still some electronic interaction between the two diene systems despite the bending of the ring. The two coordinated ring systems are oriented in such a way that the methyls are staggered, and the overall symmetry is C_s. The planes of the coordinated carbons of the two ligands are close to parallel making an angle of 5.8° with each other. The ruthenium to benzene ring center distance is 1.724 Å, and the analogous distance to the diene is 1.730 Å.

The reactivity of $Ru(C_6Me_6)[C_6Me_4(CH_2)_2]$ centers around the methylene carbons. In view of the fact that its synthesis is the result of deprotonation from these positions, it is not surprising that there exists a partial negative charge on these carbons. Addition of excess acid to $Ru(C_6Me_6)[C_6Me_4(CH_2)_2]$ results in instantaneous formation of $Ru(C_6Me_6)_2{}^{2+}$. This dication is in fact formed if any water or alcohol is present in the solvents.

Both the deprotonation of $Ru(C_6Me_6)_2{}^{2+}$ and the protonation of $Ru(C_6Me_6)[C_6Me_4(CH_2)_2]$ must proceed

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(2) Roth, R. W.; Meier, J. D. *Tetrahedron Lett.* **1967**, 2053.

(3) Chappell, S. D.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1981**, 319.

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(7) Lappert, M. F.; Martin, T. R.; Milne, C. R. C.; Atwood, J. L.; Hunter, W. E.; Pentilla, R. E. *J. Organomet. Chem.* **1980**, *192*, C35.

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(10) Lappert, M. F.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1981**, 485.

(11) Astruc, D.; Hamon, J. R.; Roman, E.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 7502.

(12) Data for $Ru(C_6Me_6)[C_6Me_4(CH_2)_2]$: MS, *m/e* 424 ($M^+$); ^1H NMR (C_6D_6) δ 5.04 (d, $J = 1$ Hz, 2 H), 4.46 (d, $J = 1$ Hz, 2 H), 1.66 (s, 18 H), 1.65 (s, 6 H), 1.43 (s, 6 H); ^{13}C NMR (C_6D_6, undecoupled) δ 150.50 (s), 92.04 (s), 89.04 (t), 84.93 (s), 60.31 (s), 20.01 (q), 14.87 (q). Anal. Calcd for $C_{24}H_{34}Ru$: C, 68.05; H, 8.09. Found: C, 68.12; H, 8.29.

(13) X-ray diffraction data for $Ru(C_6Me_6)[C_6Me_4(CH_2)_2]$: crystal system, monoclinic; space group $P2_1/n$; $a = 13.007$ (3) Å, $b = 9.966$ (2) Å, $c = 17.002$ (5) Å; $\beta = 111.95$ (2)°; volume = 2044 (2) Å^3; $Z = 4$; absorbance coefficient = 7.6 cm^{-1}; diffractometer, Enraf-Nonius CAD4; radiation, graphite-monochromatized Mo Kα; scan range, $0° \leq 2\theta \leq 50°$; reflections collected, 3590 unique, with 2138 with $F_o > 2.0(F_o)$; $R = 0.038$; $R_w = 0.057$.

through the cyclohexadienyl complex shown in Scheme I. We were able to isolate and characterize this species by the reaction of exactly 1.0 equiv of CF_3SO_3H with a suspension of $Ru(C_6Me_6)[C_6Me_4(CH_2)_2]$ in acetonitrile. The solvent was removed from the resulting clear yellow solution, leaving a yellow residue which was triturated with diethyl ether. The triflate salt was redissolved in acetonitrile and mixed with $NaBPh_4$. Addition of ether resulted in the formation of orange microcrystals of $[Ru(C_6Me_6)(C_6Me_5CH_2)]BPh_4$.[14] The NMR spectral features, particularly of the exocyclic methylene group, allow positive identification of this species. The ^1H NMR resonance at 3.57 ppm is nearly identical with that in $Fe(\eta^5\text{-}C_5H_5)(C_6Me_5CH_2)$ which appears at 3.60 ppm,[11] and the ^{13}C NMR spectrum exhibits a methylene carbon resonance at 86.3 ppm. $[Ru(C_6Me_6)(C_6Me_5CH_2)]^+$ can also be prepared and isolated by the deprotonation of $[Ru(C_6Me_6)_2]^{2+}$ with exactly 1.0 equiv of *tert*-butoxide.

Both of the methylene groups in $Ru(C_6Me_6)[C_6Me_4(CH_2)_2]$ can also be methylated by using $CF_3SO_3CH_3$, giving $[Ru(C_6Me_6)(C_6Me_4Et_2)](CF_3SO_3)_2$.[15] The ^1H NMR spectrum readily confirms that the two ethyl groups are adjacent to each other. That this is not required by the structure of the initial *o*-xylylene complex is a consequence of the intermediate in this reaction which is analogous to that in the protonation reaction. The complex $[Ru(C_6Me_6)(C_6Me_5CH_2)]^{1+}$ is amphoteric. Therefore, it may be capable of undergoing degenerate intramolecular proton shifts. The search for this exchange as well as the further characterization of the reactions of this new *o*-xylylene complex are currently underway.

Acknowledgment. We gratefully acknowledge the Research Corp. and the National Science Foundation (Grant CHE 8106096) for support of this work and Mr. Robert Stevens for assistance with the x-ray crystallographic study.

Registry No. $Ru(C_6Me_6)[C_6Me_4(CH_2)_2]$, 83005-40-7; $Ru(C_6Me_6)[C_6Me_5CH_2)]BPh_4$, 83005-42-9; $Ru(C_6Me_6)(C_6Me_4Et_2)](CF_3SO_3)_2$, 83005-44-1; $[Ru(C_6Me_6)_2](PF_6)_2$, 83005-45-2.

Supplementary Material Available: A listing of the structure factor amplitudes and a table of positional and thermal parameters (11 pages). Ordering information is given on any current masthead page.

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[14] Data for $[Ru(C_6Me_6)(C_6Me_5CH_2)]BPh_4$: ^1H NMR (CD_3CN) δ 7.28 (m, 8 H), 6.97 (t, 8 H), 6.84 (t, 4 H), 3.57 (s, 2 H), 2.08 (s, 3 H), 2.00 (s, 18 H), 1.83 (s, 6 H), 1.47 (s, 6 H); ^{13}C NMR (CD_3CN, undecoupled) δ 164.7 (q, BPh_4^-), 136.7 (d, BPh_4^-), 126.5 (d, BPh_4^-), 122.7 (d, BPh_4^-), 144.8 (s), 102.2 (s), 99.1 (s), 93.1 (s), 86.3 (t), 71.5 (s), 16.0 (s), 15.4 (s), 15.2 (s), 14.8 (s). Anal. Calcd for $C_{48}H_{55}BRu$: C, 77.51; H, 7.45. Found: C, 76.50; H, 7.74 (a small amount of the triflate salt from the metathesis contaminated this sample).

[15] Data for $[Ru(C_6Me_6)(C_6Me_4Et_2)](CF_3SO_3)_2$: ^1H NMR (CD_3CN) δ 2.49 (q, J = 8 Hz, 4 H), 2.16 (s, 6 H), 2.13 (s, 18 H), 2.12 (s, 6 H), 1.14 (t, J = 8 Hz, 6 H). Anal. Calcd for $C_{28}H_{40}F_6O_6RuS_2$: C, 44.73; H, 5.36. Found: C, 43.88; H, 5.37.

Metallametallocenes: Ferracobaltocene and Ferrarhodocene. New Aromatic Species[†,1]

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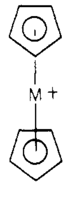
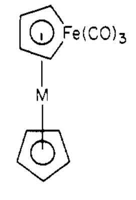
Received September 20, 1982

Summary: The novel mixed binuclear compounds (tricarbonylferracyclopentadiene)cyclopentadienylcobalt and (tricarbonylferracyclopentadiene)cyclopentadienylrhodium have been synthesized by two different pathways. X-ray crystallographic data obtained for the rhodium complex and a benzo derivative of the cobalt complex establish a sandwichlike or metallocene structure for these compounds.

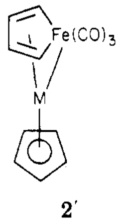
The concept of isolobal species introduced by Hoffman[2] suggests that electronicly similar species could be obtained by the exchange of a $Fe(CO)_3$ moiety for ^+CH, by virtue of the similarity of the symmetry and nodal characteristics of their frontier orbitals. Application of this isolobal interchange to the "aromatic" metallocenium species **1** leads to the formulation of the metallametallocene species **2** which might be similarly stabilized or exhibit "aromaticity".[3] We now report the syntheses of **2a,b** by two different routes and evidence pointing to the aromatic-like character of these species.



1a, M = Co
b, M = Rh

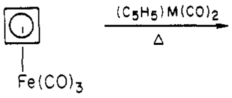


2a, M = Co
b, M = Rh



2′

Reaction of (cyclobutadiene)tricarbonyliron with excess $C_5H_5M(CO)_2$, M = Co, Rh, in hydrocarbon solvents at 110–130 °C led to metal insertion affording the air-stable complexes $(C_5H_5M)C_4H_4Fe(CO)_3$ (**2a**, M = Co; **2b**, M = Rh) in 15–30% yield (eq 1).[13] Solutions of the brick-red cobalt or yellow-orange rhodium complex in nondegassed solvents were quite stable, showing little evidence of oxidative decomposition even over extended time periods.[4] These complexes were characterized by IR, NMR, and high-resolution mass spectroscopy.[5]



$$\xrightarrow[\Delta]{(C_5H_5)M(CO)_2} \textbf{2a,b} \qquad (1)$$

M = Co, Rh

[†] Dedicated to the memory of Professor Rowland Pettit (Rolly), a treasured mentor and friend.

[*] To whom correspondence should be addressed at the Department of Chemistry, University of Texas at Austin, Austin, TX 78712.

(1) Portions of this work have been presented at the 25th Pentasectional American Chemical Society Meeting, Tulsa, Okla., April 1978, and at the 181st National American Chemical Society Meeting, Atlanta, Georgia, March, 1981.

(2) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. Elian, M. Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Ibid.* **1976**, *15*, 1148.

(3) (a) In analogy to ferrocene the cobaltocenium and rhodocenium cations 1 with "electron imbalances" of zero or with closed-shell electron configurations can be regarded as "aromatic", see e.g.: Haaland, A. *Acc. Chem. Res.* **1979**, *12*, 415. Gard, E.; Haaland, A.; Novak, D. P.; Seip, R. *J. Organomet. Chem.* **1975**, *88*, 181 and references therein. (b) For a discussion of delocalization or "aromaticity" in metallocycles, see: Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.

(4) The observed stability stands in strong contrast to that for solutions of the isolobal cobalta derivative, $(C_5H_5Co)C_4H_4CoC_5H_5$: Rosenblum, M.; North, B.; Wells, D.; Giering, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 1239.

(5) **2a**: mp 50–52 °C; IR (Skelly B) 1965 (vs), 2035 (vs) cm^{-1}; ^1H NMR (CS_2) δ 4.88 (s, C_5H_5), 5.88 ("dd", $H_2 = H_3$), 7.39 ("dd", $H_1 = H_4$); high resolution MS, *m/e* 315.9218 (P^+) (calcd 315.9232). **2b**: mp 69.5–71.5 °C; IR (Skelly B) 1965 (vs), 2035 (vs) cm^{-1}; ^1H NMR (CS_2) δ 5.30 (s, C_5H_5), 6.2 (m, $H_2 = H_3$), 7.1 ("dd", $H_1 = H_4$); high-resolution MS, *m/e* 359.8953 (P^+) (calcd 359.8944).

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