

(CO), 104.4 (C₅Me₅), 91.2 (C₅H₅), 72.1 (μ-CCH₂), 31.8, 22.2, 13.5 ((CH₂)₃CH₃); 8.8 (C₅(CH₃)₅). IR (CH₂Cl₂): 2030 (s), 2001 (w), 1842 (m) cm⁻¹.

cis-[(C₅Me₅)(CO)Fe][(C₅H₅)(CO)Fe](μ-CO)(μ-C=CH-(CH₂)₃CH₃) (34). NMe₃ (2.1 mmol) was added to a solution of 33 (86 mg, 0.14 mmol) in 3 mL of CH₂Cl₂ at -78 °C. Solvent was evaporated at ambient temperature, and the oily residue was crystallized from 2 mL of hexane at -78 °C to give 34 (40 mg, 51%). ¹H NMR (C₆D₆): δ 7.00 (t, *J* = 6.9 Hz, μ-C=CH), 4.51 (s, C₅H₅), 2.95 (m, =CHCH₂), 1.2-1.9 (m, 4 H), 1.46 (s, C₅Me₅), 1.08 (t, *J* = 7.0 Hz, CH₃). ¹³C{¹H} NMR (C₆D₆, 0 °C): δ 274.5, 272.1 (μ-CO, μ-C), 213.1, 212.1 (CO), 134.9 (C=CH-), 96.5 (C₅Me₅), 85.5 (C₅H₅), 37.1, 34.5, 23.1, 14.7 (CH₂CH₂CH₂CH₃), 9.3 (C₅(CH₃)₅). IR (CH₂Cl₂): 1983 (s), 1940 (w), 1769 (m) cm⁻¹. HRMS for C₂₄H₃₀Fe₂O₃: calcd, 478.0885; found, 478.0891.

cis-[(C₅Me₅)(CO)Fe][(C₅H₅)(CO)Fe](μ-CO)(μ-η²-*trans*-CH=CHCH(CH₃)₂)⁺PF₆⁻ (35). A solution of 32 (190 mg, 0.32 mmol) and isobutylene (0.72 mmol) in 10 mL of CH₂Cl₂ was warmed from -78 °C to ambient temperature. Solvent was evaporated, and the residue was recrystallized from CH₂Cl₂-ether to give 35 (172 mg, 82%). ¹H NMR (CDCl₃): δ 10.85 (d, *J* = 11.5 Hz, μ-CH=C), 5.03 (s, C₅H₅), 3.52 (dd, *J* = 9.3, 11.5 Hz, μ-CH=CH), 2.40 (m, CHMe₂), 1.90 (s, C₅Me₅), 1.46 (d, *J* = 6.5 Hz, CH₃). ¹³C{¹H} NMR (CD₃CN, 0 °C): δ 215.0 (CO), 180.6 (μ-CH=CH-), 106.6 (μ-CH=CH-), 103.7 (C₅Me₅), 87.7 (C₅H₅), 39.9 (CHMe₂), 26.1 (CH₃), 21.8 (CH₃), 9.6 (C₅(CH₃)₅). IR (CH₂Cl₂): 2015 (s), 1995 (m), 1859 (m) cm⁻¹.

Anal. Calcd for C₂₅H₂₉F₆Fe₂O₃P: C, 45.28; H, 4.79. Found: C, 44.91; H, 4.87.

[(C₅Me₅)(CO)Fe][(C₅H₅)(CO)Fe](μ-CO)(μ-CHCH=C(CH₃)₂) (36). NMe₃ (2.1 mmol) was added to a solution of 35 (86 mg, 0.14 mmol) in 3 mL of CH₂Cl₂ at -78 °C. Solvent was evaporated at ambient temperature, and the residue was dissolved in toluene. The toluene solution was filtered and evaporated to dryness. The resulting violet crystalline solid was washed with

hexane to give 36 (50 mg, 76%). ¹H NMR (CD₂Cl₂): δ 10.77 (d, *J* = 12.8 Hz, μ-CH), 6.73 (d, *J* = 12.8 Hz, μ-CH-CH=), 4.70 (s, C₅H₅), 2.10 (s, CH₃), 1.83 (s, CH₃), 1.66 (s, C₅Me₅). ¹³C NMR (C₆D₆, 0 °C): δ 275.4 (s, μ-CO), 214.4, 213.4 (s, CO), 165.8 (d, *J* = 132 Hz, μ-CH), 154.0 (d, *J* = 150 Hz, μ-CHCH=), 120.3 (s, CH=CMe₂), 96.6 (s, C₅Me₅), 85.6 (d, *J* = 180 Hz, C₅H₅), 26.3 (q, *J* = 128 Hz, =C(CH₃)CH₃), 19.0 (q, *J* = 128 Hz, =C(CH₃)CH₃), 9.1 (q, *J* = 128 Hz, C₅(CH₃)₅). IR (CH₂Cl₂): 1980 (s), 1916 (m), 1779 (m) cm⁻¹. HRMS: for C₂₃H₂₈Fe₂O₃: calcd, 464.0729; found, 464.0737.

[(C₅Me₅)(CO)Fe]₂(μ-CO)(μ-CH)⁺PF₆⁻ (37) and Isobutylene. The initial ¹H NMR spectrum obtained from a solution of [(C₅Me₅)(CO)Fe]₂(μ-CO)(μ-CH₂)¹² (38) (7.0 mg, 15 μmol) and (C₆H₅)₃C⁺PF₆⁻ (7.0 mg, 18 μmol) in 0.3 mL of CD₂Cl₂ had a broad (ω_{1/2} = 223 Hz) band centered at δ 13 in addition to other resonances. After 20 min, the broad resonance disappeared and peaks at δ 21.63 (μ-CH) and δ 1.84 (C₅Me₅) assigned to 37 appeared.

An impure sample of 37 was obtained from the reaction of 38 (128 mg, 0.26 mmol) and (C₆H₅)₃C⁺PF₆⁻ (95 mg, 0.25 mmol) in 4 mL of CH₂Cl₂ at ambient temperature. The solution was cooled to -78 °C, and hexane was added to precipitate a purple-black solid (120 mg) which was washed with hexane. ¹H NMR indicated a 1:0.5 ratio of 37:(C₆H₅)₃CX. When a solution of 37 (5 mg, 7 μmol) and isobutylene (30 μmol) in 0.3 mL of CD₂Cl₂ at ambient temperature was monitored by ¹H NMR, no new resonances were seen initially. After 24 h, the resonance at δ 21.6 due to 37 was still visible, but many resonances due to decomposition products were observed.

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Chemistry Derived from Ruthenium Atoms. 2.¹ Synthesis and Reactivity of the Monocarbonyl Complexes Formed from Ruthenium-Cyclohexadiene Cocondensates

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Ruthenium atoms generated from an electron beam furnace have been cocondensed with either 1,3- or 1,4-cyclohexadiene, and CO subsequently has been added at -196 °C. The initial product of the syntheses has been characterized as Ru(CO)(η⁵-C₆H₇)(η³-C₆H₉) (1). In solution at room temperature 1 underwent a thermal rearrangement to Ru(CO)(η⁴-C₆H₈)₂ (2) (*t*_{1/2} = 96 min at 31 °C). Prolonged reflux of 2 in the presence of free 1,3-cyclohexadiene and under CO (1 atm) yielded the bis(allyl) complex Ru(CO)₂(η³-C₁₂H₁₈) (5) via C-C coupling of the diene ligands. Hydride abstraction from 1 and 2 using [Ph₃C]BF₄ gave [Ru(CO)(η⁶-C₆H₆)(η³-C₆H₉)]BF₄ (3) and [Ru(CO)(η⁵-C₆H₇)(η⁴-C₆H₈)]BF₄ (4), respectively. The reverse reactions 3 → 1 and 4 → 2 occurred on treatment with NaBH₄, and the hydride additions were assigned exo to the ruthenium atom (deuterium labeling). The transformation 4 → 2 is not consistent with a charge-controlled nucleophilic addition.

Introduction

A large and diverse range of mononuclear ruthenium complexes bearing two C₆-C₈ cyclic hydrocarbon ligands are now known.²⁻¹² Convenient syntheses from chloro-

ruthenium complexes have been developed, chiefly by Bennett⁶ and by Vitulli,⁷ and in general the resulting or-

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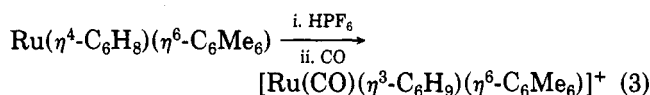
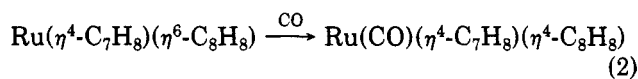
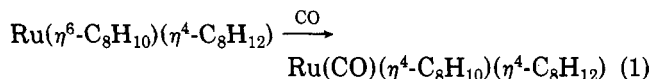
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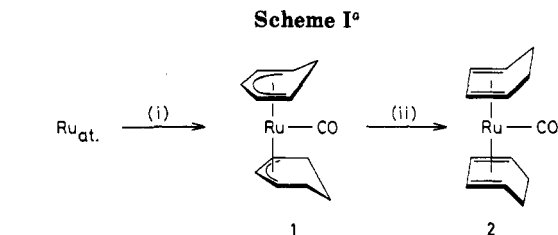
ganometallics do not carry additional ligands.¹³ In several cases it has proved possible to prepare monocarbonyl derivatives from these species by ligand addition without loss of a carbocycle. These reactions are shown in eq 1–3 and, metal atom techniques apart, represent the only preparations of monocarbonyl ruthenium species of this type.^{14–16} Hence, a ruthenium analogue of $\text{Fe}(\text{CO})(\eta^4\text{-C}_6\text{H}_8)_2$ ¹⁷ is not yet available by classical routes.



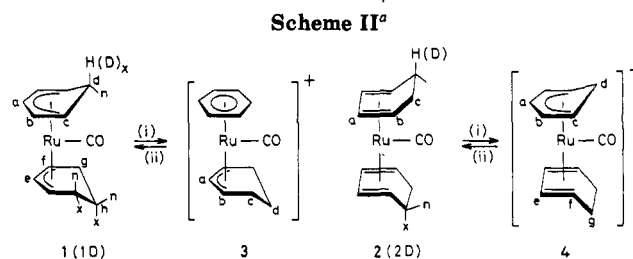
The use of ruthenium atoms in synthesis was first achieved, on a small scale (ca. 100 mg), by Timms and King, who reported spectroscopic data for the unstable $\text{Ru}(\text{C}_6\text{H}_6)_2$.¹⁸ More recently, gram quantities of ruthenium atoms have been made synthetically available by the positive hearth electron beam technique developed by Cloke and Green.^{19,20} We have used this method to prepare ruthenium–cyclohexadiene cocondensates as described in a preliminary communication.²¹ We now report on their low-temperature carbonylation as a route to monocarbonyl ruthenium complexes bearing two cyclic C_6 ligands.

Results and Discussion

The analogous iron–cyclohexadiene cocondensates have been studied both by Skell et al.²² and by Ittel et al.²³ The former group has reported the catalytic disproportionation of the cyclohexadiene to benzene and cyclohexene and isolated $\text{Fe}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-C}_6\text{H}_8)$ in very low yields. The latter workers have investigated the reaction of the cocondensate with $\text{P}(\text{OMe})_3$ at low temperature and isolated $\text{Fe}[\text{P}(\text{OMe})_3]_2(\eta^3\text{-C}_6\text{H}_7)(\eta^2\text{-C}_6\text{H}_8)$ as the major product. Osmium–cyclohexadiene cocondensates have not yet been studied, and our earlier communication²¹ is the only report of a ruthenium–cyclohexadiene cocondensate.



^a (i) Cocondensed with excess 1,3- or 1,4-cyclohexadiene at -196°C , followed by low-temperature CO addition. (ii) In solution at room temperature; $t_{1/2} = 96$ min (31°C , octane).



^a (i) $[\text{Ph}_3\text{C}]\text{BF}_4$ (1 equiv) in CH_2Cl_2 ; $1 \rightarrow 3$ at -20°C , $2 \rightarrow 4$ at room temperature. (ii) NaBH_4 or NaBD_4 (excess) in CH_2Cl_2 at -20°C . The lettering refers to the proton assignments (Experimental Section).

$(\text{OMe})_3]_2(\eta^4\text{-C}_6\text{H}_8)(\eta^2\text{-C}_6\text{H}_8)$ as the major product. Osmium–cyclohexadiene cocondensates have not yet been studied, and our earlier communication²¹ is the only report of a ruthenium–cyclohexadiene cocondensate.

Formation of Neutral Monocarbonyl Complexes.

The addition of CO at -196°C to either ruthenium–1,3-cyclohexadiene or ruthenium–1,4-cyclohexadiene cocondensates yielded, after workup, a temperature-sensitive orange oil. On the basis of IR, ^1H NMR, and ^{13}C NMR data the oil was identified as a mixture of two monocarbonyl ruthenium complexes in a 10:1 ratio. The major constituent was characterized as the thermally unstable $\text{Ru}(\text{CO})(\eta^5\text{-C}_6\text{H}_7)(\eta^3\text{-C}_6\text{H}_9)$ (1) (ca. 40% with respect to Ru_{at}) and with contaminant as $\text{Ru}(\text{CO})(\eta^4\text{-C}_6\text{H}_8)_2$ (2). Although the oil proved stable for several weeks at -20°C , attempts to isolate 1 from this mixture were unsuccessful. Low-temperature crystallization from pentane, for example, gave small quantities of yellow microcrystals but of an unchanged composition. Nevertheless, the crude oil proved a satisfactory source of 1 in a subsequent synthesis, and samples of 1 free from 2 were eventually isolated via the reduction of 3 (vide infra).

When solutions of crude 1 were warmed to room temperature and stirred for 24 h, good yields of crystalline 2 (ca. 30% with respect to Ru_{at}) could be isolated. The disappearance of 1, as followed by IR spectroscopy, was found to obey first-order kinetics ($t_{1/2}$ in octane = 96, 29, and 9.1 min at 31, 41, and 53°C , respectively), although the conversion to 2 was nonquantitative (65% isolated). Even in the solid state crude 1 is unstable, and after 10 days at room temperature the decay to 2 had neared completion.

The proposed structures for 1 and 2 are illustrated in Scheme I, symmetrical conformations (C_6 for 1, C_{2v} for 2) are indicated by the ^1H NMR spectra which remained temperature invariant to -70°C .

The direct formation of the kinetic product 1 on CO addition suggests that a hydride (or related agostic²⁴) species, $\text{RuH}(\eta^5\text{-C}_6\text{H}_7)(\eta^4\text{-C}_6\text{H}_8)$, could be the initial

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product laid down on cocondensation. An analogous hydride species has been postulated in the initial iron-cyclohexadiene cocondensate on the basis of the isolation of $\text{FeH}(\eta^5\text{-C}_6\text{H}_7)[\text{P}(\text{OMe})_3]_2$ when iron atoms are cocondensed with a mixture of $\text{P}(\text{OMe})_3$ and 1,3-cyclohexadiene.²³ An iron analogue of 1, however, has not been reported. Attempts to observe the proposed ruthenium hydride were made by extraction under argon of the Ru-1,3-cyclohexadiene cocondensate with pentane below -40°C . This yielded very air-sensitive orange oils from which no stable organometallics could be isolated. Furthermore, the ^1H NMR (toluene- d_8 , -40°C) indicated no characteristic hydride resonances upfield of Me_4Si .

The thermal isomerization (Scheme I) of the $\eta^5:\eta^3$ -coordination in 1 to the $\eta^4:\eta^4$ -coordination in 2 provides a rare example of a hydrogen shift between two coordinated C_6 rings. Although the conversion is formally a Ru(II) to Ru(0) reduction, it is evident that the more stable species 2 has less electron density available for $d\pi \rightarrow p\pi$ retrodonation to the carbonyl π^* orbitals ($\nu(\text{CO}) = 1956\text{ cm}^{-1}$ (1) and 1981 cm^{-1} (2)). It is interesting to note that for related molybdenum complexes a reverse order of stability apparently prevails. Thus, while $\text{Mo}(\text{CO})_2(\eta^4\text{-C}_6\text{H}_8)_2$ and $\text{Mo}(\text{CO})_2(\eta^5\text{-C}_6\text{H}_7)(\eta^3\text{-C}_6\text{H}_9)$ have both been isolated from the thermal reaction of $\text{Mo}(\text{CO})_6$ and 1,3-cyclohexadiene, the $\eta^5:\eta^3$ -coordination is of greater stability.²⁵

Reversible Hydride Abstractions. Hydride abstraction from 1 and 2 is readily effected (process i, Scheme II). Hence, when a sample of crude 1 (>90% purity) was treated with a near molar equivalent of $[\text{Ph}_3\text{C}]\text{BF}_4$ at -20°C , the cationic arene species $[\text{Ru}(\text{CO})(\eta^5\text{-C}_6\text{H}_7)(\eta^3\text{-C}_6\text{H}_9)]^+$ (3) was isolated in 45% yield (BF_4^- salt). Similar treatment of 2 (room temperature) yielded the cation $[\text{Ru}(\text{CO})(\eta^5\text{-C}_6\text{H}_7)(\eta^4\text{-C}_6\text{H}_8)]^+$ (4; 53% as BF_4^- salt). Despite the presence of 2 as an impurity in the samples of 1, contamination of 3 by 4 was not observed when 1 was the reagent in excess. Furthermore, the pentane extract after the reaction of crude 1 showed relative enrichment in 2, so that preferential hydride removal from 1 may be implicated.

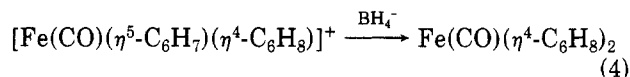
The cations 3 and 4 were characterized by ^1H and ^{13}C NMR, and symmetrical C_s structures are proposed. The hexamethylbenzene derivative of 3 had previously been prepared (eq 3¹⁶), and these cations are presumably structurally related to the series of $\text{RuCl}(\eta^6\text{-C}_6\text{H}_6)(\eta^3\text{-allyl})$ complexes reported by Rubezhov and co-workers.²⁶ The iron analogue of 4 is known,²⁷ and the closely related cation $[\text{Ru}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_6\text{H}_8)]^+$ has recently been reported.²⁸

The conformation of the cyclohexenyl ring in complexes 1 and 3, following the recent work of Crocker et al., may be assigned as boatlike.²⁸ The ^1H - ^1H coupling constants between the terminal allyl protons and the adjacent methylene protons of the cyclohexenyl ring are 6.9 and <0.2 Hz for 1 and 6.5 and <0.2 Hz for 3. These values are consistent with those observed for the boatlike conformation in the closely related $\text{Ru}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_6\text{H}_9)$ (6) (6.6, 0 Hz) and at variance with the values observed for the chair-like conformation in $\text{Mo}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_6\text{H}_9)$ (1.9, 1.8 Hz). The adoption of the boatlike conformation

by the cyclohexenyl ring in 1 and 3 may, like 6, be ascribed to the minimalization of interligand steric effects.²⁸

The hydride abstractions from 1 and 2 are directly reversible (Scheme II). Hence, on treatment with NaBH_4 at -20°C , 3 gave 1 and 4 gave 2. The transformations occurred in high yields (>70%) and cleanly, providing samples of 1 and 2 free from cross-contamination. The stereospecificities of the hydride additions were investigated by reduction of 3 and 4 with NaBD_4 . The mono-deuterated derivatives 1D and 2D respectively were isolated, and in both cases the deuterium atom was located exo to ruthenium on the basis of the ^1H NMR.²⁹

The transformation 4 \rightarrow 2 has an exact parallel in iron chemistry, as shown in eq 4.²⁷ These reactions are note-



worthy as exceptions to the charge density based rules proposed to govern the regioselectivity of nucleophilic addition.³⁰ A consecutive pathway, 4 \rightarrow 1 \rightarrow 2 for these reactions ($\text{M} = \text{Ru}$ or Fe), in accord with the aforementioned rules, can be rejected on the following grounds: (i) for $\text{M} = \text{Ru}$, the thermal isomerization 1 \rightarrow 2 cannot occur over the relevant time scale at -20°C , and an isomerization promoted by the reaction conditions can be excluded by the isolation of 1 from 3; (ii) for $\text{M} = \text{Ru}$ and Fe , the observed stereochemistry of the deuterium label on addition of BD_4^- to 4 is exo on a methylene group of 2 (for $\text{M} = \text{Fe}$, see ref 27), which is not consistent with a consecutive pathway.³¹ The observed exo stereochemistry of the deuterated derivatives also renders unlikely an initial attack at the carbonyl or metal center.

Following the recent work of Astruc et al.,³² these violations of the regioselectivity rules may be ascribed to an orbital control of the hydride additions to 4 ($\text{M} = \text{Ru}, \text{Fe}$). It is not yet possible, however, to predict if a particular nucleophilic addition will be subject to orbital rather than charge control. For example, unlike the similar behavior toward H^- of the ruthenium cation 4 and its iron analogue, addition of H^- to the cation $[\text{M}(\eta^6\text{-C}_6\text{H}_6)(\eta^5\text{-C}_6\text{H}_7)]^+$ is apparently subject to orbital control for $\text{M} = \text{Fe}$ ³² and yet consistent with charge control for $\text{M} = \text{Os}$.³³

Ligand-Induced Diene Coupling. Prolonged reflux (36 h) of $\text{Ru}(\text{CO})(\eta^4\text{-C}_6\text{H}_8)_2$ (2) under CO and in the presence of free 1,3-cyclohexadiene gave the bis(allyl) complex $\text{Ru}(\text{CO})_2(\eta^3:\eta^3\text{-C}_{12}\text{H}_{16})$ (5), isolated in 34% yield. The presence of free cyclohexadiene, which presumably enhances the thermal stability of 2, is essential to the progress of the reaction. In its absence the solution appeared black and colloidal after reflux and only traces of 5 were detected. The overall reaction parallels the more rapid and facile carbonylation of $\text{Ru}(\text{CO})(\eta^4\text{-2,3-dimethylbutadiene})_2$ which we recently reported to produce $\text{Ru}(\text{CO})_2(\eta^3:\eta^3\text{-C}_{12}\text{H}_{20})$ (7).¹ Hence, while the scope of

(29) In 1, the exo d proton was distinguished as a clean doublet (δ 2.65) as is often observed in η^5 -cyclohexadienyl systems (i.e., $J_{\text{dx}} \approx 0$ Hz; see ref 2). In 2, the exo (δ 1.54) and endo (δ 1.85) c protons were distinguished by $J_{\text{ben}} > J_{\text{bcx}}$ and $\delta_{\text{en}} > \delta_{\text{ex}}$ (see: Brown, D. A.; Fitzpatrick, N. J.; Glass, W. K.; Sayal, P. K. *Organometallics* 1984, 3, 1137). ^1H NMR of 1D and 2D are reported in the Experimental Section.

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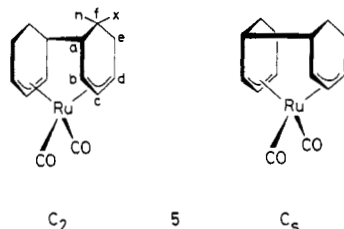
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ligand-induced diene coupling reactions in $ML(\text{diene})_2$ complexes ($M = \text{Fe}, \text{Ru}$) is not yet defined, it is now clear that the reaction type is not solely restricted to 2,3-dimethylbutadiene complexes.

The spectral data (IR, ^1H NMR, and ^{13}C NMR) indicate that only one isomer of **5** is formed in the reaction. They do not, however, distinguish between the two symmetrical isomers of **5** shown below. We propose, by analogy with the C_2 molecular symmetry determined crystallographically for **7**, that the C_2 isomer of **5** has been produced.

Complex **5**, or a related isomer, had previously been synthesized by Whitesides and Budnik on reflux of $\text{Ru}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_8)$ in 1,3-cyclohexadiene. No characterization



of the product was, however, reported.³⁴ We have eliminated the possibility that the carbonylation of **2** proceeds via formation of $\text{Ru}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_8)$ (the tricarbonyl is inert under similar conditions). A common intermediate for both reactions is, nevertheless, plausible.

Experimental Section

General Comments. Unless otherwise stated all manipulations were carried out under argon by using standard Schlenk techniques. Solvents were dried, distilled, and deaerated prior to use. 1,3- and 1,4-cyclohexadienes (Fluka) were distilled over CaH_2 at reduced pressure. $[\text{Ph}_3\text{C}]\text{BF}_4$, NaBH_4 , NaBD_4 (Fluka), and CO (Carbagas) were used as received. A commercial vapor synthesis plant (G.V. Planar; VSP 500) was used for the preparation of the condensates.²¹ Infrared spectra were recorded on a Perkin-Elmer 577 spectrometer and calibrated with polystyrene film. Mass spectra were recorded on a Finnigan 1020 GC-MS spectrometer in the electron ionization mode. NMR spectra were recorded on a Bruker WH-360 FT spectrometer (^1H , 360 MHz; ^{13}C , 90.55 MHz; D signal of solvent as lock; Me_4Si as internal reference). The proton assignments are based on selective proton-decoupling experiments. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, West Germany, and by the Mikrolabor of the ETH, Zürich, Switzerland.

Syntheses. **Carbonyl(1-5- η -cyclohexadienyl)(1-3- η -cyclohexenyl)ruthenium (1).** In a typical experiment, Ru atoms (1.0 g, 10 mmol) were cocondensed at -196°C with a large excess (30 mL) of either 1,3- or 1,4-cyclohexadiene over a period of 2 h. Carbon monoxide was immediately admitted to the reaction chamber and the temperature allowed to rise to ca. -20°C under a constant pressure of CO (1 atm). The condensate was then extracted from the reactor as an orange-brown solution in cold THF (300 mL) and immediately filtered through dry Florisil. The solvent was evaporated under reduced pressure without heating, and the oil obtained was taken up in cold pentane (200 mL). Activated carbon (2 g) was added to bring down polymeric products, and after the mixture was stirred for 5 min, filtration and solvent removal below 0°C yielded a temperature-sensitive oil which was stored overnight at -20°C . Further treatment with pentane and activated carbon and vacuum drying below 0°C gave 1300 mg of orange oil. It was characterized (IR, ^1H NMR, and ^{13}C NMR) as $\text{Ru}(\text{CO})(\eta^5\text{-C}_6\text{H}_7)(\eta^3\text{-C}_6\text{H}_9)$ (**1**; $\geq 90\%$ purity; ca. 40% yield from evaporated Ru) contaminated by $\text{Ru}(\text{CO})(\eta^4\text{-C}_6\text{H}_8)_2$ (**2**). Attempts to obtain **1** in a pure state from this oil were unsuccessful. In solution at room temperature the gradual formation of **2** is evident (see following section). The reduction $3 \rightarrow 1$ provided the only samples of **1** free from such contamination.

Data for **1**: IR (pentane) 1956 cm^{-1} (CO); ^1H NMR (CDCl_3 , 250 K) δ 5.03 (tt, $J_{ab} = 4.4$, $J_{ac} = 1.2$ Hz, 1 H, H_a), 4.74 (dd, $J_{bc} = 6.3$ Hz, 2 H, H_b), 4.52 (t, $J_{ef} = 6.5$ Hz, 1 H, H_e), 3.68 (dd, $J_{cdn} = 6.6$ Hz, 2 H, H_d), 3.56 (dd, $J_{fgx} = 6.9$ Hz, 2 H, H_f), 2.85 (dt, $J_{gem} = 12.8$ Hz, 1 H, H_{dn}), 2.65 (d, 1 H, H_{dx}), 2.03 (m, 2 H, H_{gx}), 1.78, 1.02 (2m, 4 H, H_{gn} , H_{hn} , H_{hx}); ^{13}C NMR (CDCl_3 , 250 K) δ 214.8 (s, CO), 94.2 (d, $J_{CH} = 165$ Hz), 82.7 (d, $J_{CH} = 170$, $^3J_{CH} = 3$ Hz), 72.3 (d, $J_{CH} = 162$ Hz), 48.8 (d, $J_{CH} = 156$ Hz), 46.5 (d, $J_{CH} = 163$ Hz), 28.6 (t, $J_{CH} = 132$, $^3J_{CH} = 4$ Hz), 28.4 (t, $J_{CH} = 128$ Hz), 20.2 (t, $J_{CH} = 128$ Hz).

Carbonylbis(1-4- η -cyclohexadiene)ruthenium (2). Crude **1** (1300 mg) was stirred at room temperature in pentane (200 mL) for 24 h. Activated carbon was added to the resulting cloudy solution which was then filtered. Concentration and cooling to -78°C gave pale orange microcrystals which were characterized as $\text{Ru}(\text{CO})(\eta^4\text{-C}_6\text{H}_8)_2$ (**2**; 850 mg; 65% yield from **1**, 30% from evaporated Ru). Alternatively, crude **1** may be heated in vacuo (60°C) and the resulting brown oil extracted with pentane in the presence of activated carbon. The decay of **1**, as followed in octane by IR, was found to follow first-order kinetics ($t_{1/2} = 96$ min at 31°C , 29 min at 41°C , and 9.1 min at 53°C). Data for **2**: mp 99°C dec; IR (pentane) 1981 cm^{-1} (CO); MS (70 eV, ^{102}Ru) m/e (relative intensity) 290 (M^+ , 24), 262 (48), 260 (100), 180 (82), 102 (15); ^1H NMR (CDCl_3) δ 4.65 (m, $^3J_{ab} \approx 5$, $^4J_{ab} \approx 2$ Hz, 4 H, H_a), 3.41 (m, 4 H, H_b), 1.85 (dm, $J_{gem} = 10$ Hz, 4 H, H_{cn}), 1.54 (dm, 4 H, H_{cx}); ^{13}C NMR (CDCl_3) δ 216.7 (s, CO), 78.6 (d, $J_{CH} = 167$ Hz, C_a), 58.9 (d, $J_{CH} = 157$ Hz, C_b), 25.0 (t, $J_{CH} = 128$ Hz, C_c). Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{ORu}$: C, 53.96; H, 5.57. Found: C, 54.08; H, 5.54.

Carbonyl(η -benzene)(1-3- η -cyclohexenyl)ruthenium Tetrafluoroborate (3). A freshly prepared sample of crude **1** (400 mg, purity $\geq 90\%$, ca. 1.3 mmol of **1**) was dissolved in CH_2Cl_2 (30 mL) at -20°C . Addition of a near molar equivalent of $[\text{Ph}_3\text{C}]\text{BF}_4$ (410 mg, 1.25 mmol) resulted in an orange-red solution which was stirred at -20°C for 1 h. The solvent was then evaporated under reduced pressure and the oily residue washed with cold pentane. Recrystallization of the residue from acetone-THF deposited a microcrystalline material at low temperature. It was separated from the mother liquor by filtration and washed with small quantities of cold THF. Vacuum drying gave a fawn powder (210 mg) characterized as $[\text{Ru}(\text{CO})(\eta^6\text{-C}_6\text{H}_6)(\eta^3\text{-C}_6\text{H}_9)]\text{BF}_4$ (**3**; 45% based on added trityl). Data for **3**: mp 160°C dec; IR (CHCl_3) 2020 cm^{-1} (CO); ^1H NMR (CD_3CN) δ 6.50 (s, 6 H, C_6H_6), 5.30 (dd, $J_{ab} = 6.5$, $J_{bcx} = 6.5$ Hz, 2 H, H_b), 5.07 (t, 1 H, H_a), 2.43 (dddd, $J_{gem} = 18$, $J_{cdn} = 7.9$, $J_{cdx} = 1.4$ Hz, 2 H, H_{cx}), 1.80 (m, $J_{cdx} = 7.0$ Hz, 2 H, H_{cn}), 1.37, 1.22 (2m, $J_{gem} = 14$ Hz, 2 H, H_{dx} , H_{dn}); ^{13}C NMR (CD_3CN) δ 198.7 (s, CO), 99.0 (d, $J_{CH} = 179$ Hz, C_6H_6), 80.6 (d, $J_{CH} = 171$ Hz, C_a), 64.0 (d, $J_{CH} = 163$ Hz, C_b), 28.5 (t, $J_{CH} = 129$ Hz, C_c), 18.2 (t, $J_{CH} = 129$ Hz, C_d). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{BF}_4\text{ORu}$: C, 41.62; H, 4.03. Found: C, 41.85; H, 4.25.

Carbonyl(1-4- η -cyclohexadiene)(1-5- η -cyclohexadienyl)ruthenium Tetrafluoroborate (4). Complex **2** (350 mg, 1.21 mmol) was dissolved in CH_2Cl_2 (30 mL). A near molar equivalent of $[\text{Ph}_3\text{C}]\text{BF}_4$ (380 mg, 1.15 mmol) was then added and the yellow-orange solution stirred at room temperature for 1 h. The solvent was evaporated under reduced pressure and the residue washed with pentane. Two recrystallizations from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ at -78°C gave a pale yellow microcrystalline powder which was dried in vacuo (230 mg). It was characterized as $[\text{Ru}(\text{CO})(\eta^5\text{-C}_6\text{H}_7)(\eta^4\text{-C}_6\text{H}_8)]\text{BF}_4$ (**4**; 53% yield). Data for **4**: mp 122°C dec; IR (CHCl_3) 2048 cm^{-1} (CO); ^1H NMR (CDCl_3) δ 6.88 (tt, $J_{ab} = 5.2$, $J_{ac} = 1.3$ Hz, 1 H, H_a), 5.89 (m, $^3J_{ef} \approx 5$, $^4J_{ef} \approx 2$ Hz, 2 H, H_e), 5.55 (dd, $J_{bc} = 7.0$ Hz, 2 H, H_b), 4.60 (dddd, $J_{cdn} = 6.0$, $J_{cdx} = 0.9$ Hz, 2 H, H_d), 4.28 (m, $J_{fgn} = 1.8$ Hz, 2 H, H_f), 3.00 (dt, $J_{gem} = 14.5$ Hz, 1 H, H_{dn}), 2.64 (dt, 1 H, H_{dx}), 2.01 (dm, $J_{gem} = 12$ Hz, 2 H, H_{gn}), 1.63 (dm, 2 H, H_{gx}); ^{13}C NMR (CDCl_3) δ 208.4 (s, CO), 96.5 (d, $J_{CH} = 178$ Hz), 92.8 (d, $J_{CH} = 175$ Hz), 83.9 (d, $J_{CH} = 176$ Hz), 72.6 (d, $J_{CH} = 165$ Hz), 61.5 (d, $J_{CH} = 171$ Hz), 28.8 (t, $J_{CH} = 137$ Hz), 22.8 (t, $J_{CH} = 133$ Hz). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{BF}_4\text{ORu}$: C, 41.62; H, 4.03. Found: C, 42.00; H, 4.28.

Dicarbonyl(2-4:2'-4'- η -1,1'-bicyclohex-3-ene-2,2'-diyl)ruthenium (5). Complex **2** (350 mg, 1.21 mmol) was dissolved in THF (60 mL), and 20 molar equiv (2.4 mL) of 1,3-cyclohexadiene was added. The solution was saturated with CO by freeze-thaw cycles and then refluxed under CO (1 atm). The reaction as

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monitored by IR was complete after 36 h. The yellow solution was then evaporated to dryness under reduced pressure. The orange oil obtained was extracted with pentane (80 mL) in the presence of activated carbon (200 mg). Concentration of the filtrate and cooling to -78°C gave yellow microcrystals which were dried in vacuo and subsequently characterized as $\text{Ru}(\text{CO})_2(\eta^3\text{-C}_5\text{H}_5)_2$ (5; 130 mg, 34%). Traces of $\text{Ru}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_6)$ were detected in the mother liquor. Data for 5: mp 86°C ; IR (pentane) $2020, 1951\text{ cm}^{-1}$ (CO); MS (70 eV, ^{102}Ru), m/e (relative intensity) 318 (M^+ , 14), 290 (10), 262 (40), 260 (87), 208 (21), 180 (100), 102 (44); $^1\text{H NMR}$ (CDCl_3) δ 5.70 (dd, $J_{bc} = 6.0, J_{cd} = 6.5$ Hz, 2 H, H_c), 4.70 (ddd, $J_{dex} = 6.5, J_{bd} = 1.5$ Hz, 2 H, H_d), 3.49 (ddd, $J_{ab} = 7.0$ Hz, 2 H, H_b), 2.87 (ddd, $J_{gem} = 15.5, J_{enf} = 11, 7$ Hz, 2 H, H_{en}), 2.73 (dddd, $J_{exf} = 7.5, 1.3$ Hz, 2 H, H_{ex}), 2.58 (dd, $J_{af} = 5.5, <0.5$ Hz, 2 H, H_a), 1.38 (m, $J_{gem} \approx 13$ Hz, 4 H, $\text{H}_{fm}, \text{H}_{fx}$); $^{13}\text{C NMR}$ (CDCl_3) δ 203.6 (s, CO), 101.1 (d, $J_{CH} = 164$ Hz), 82.8 (d, $J_{CH} = 157$ Hz), 55.1 (d, $J_{CH} = 163$ Hz), 53.4 (d, $J_{CH} = 132$ Hz, C_a), 31.8 (t, $J_{CH} = 129$ Hz), 27.2 (t, $J_{CH} = 127$ Hz). Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{Ru}$: C, 52.99; H, 5.08. Found: C, 53.22; H, 5.38.

Reaction of 3 with Borohydride. Complex 3 (110 mg, 0.29 mmol) was dissolved in CH_2Cl_2 (40 mL) and the solution cooled to -20°C . An excess of NaBH_4 (120 mg, 3.2 mmol) was added and the mixture stirred at -20°C for 1 h. The solvent was then evaporated under reduced pressure at -20°C , and the resulting solids were extracted with cold pentane (2×30 mL). The pentane solution was evaporated under reduced pressure at -20°C , yielding

1 (70 mg, 82%) as a yellow oil. No trace of 2 was detected. Under similar conditions with NaBD_4 , the formation of $\text{Ru}(\text{CO})(\eta^5\text{-C}_6\text{H}_6\text{D})(\eta^3\text{-C}_6\text{H}_9)$ (1D) was observed. The deuterium was assigned exo on the methylene of the cyclohexadienyl ring from the $^1\text{H NMR}$ (CDCl_3 , 250 K): 1D as for 1 except for δ 2.83 (t, $J_{cdn} = 6$ Hz, $J_{HD} < 1$ Hz, 1 H, H_{dn}) and no signal at δ 2.65.

Reaction of 4 with Borohydride. Complex 4 (135 mg, 0.36 mmol) was dissolved in CH_2Cl_2 (40 mL) and the solution cooled to -20°C . An excess of NaBH_4 (120 mg, 3.2 mmol) was added and the mixture stirred at -20°C for 1 h. The solvent was evaporated under reduced pressure at -20°C , and the resulting solids were extracted with cold pentane (2×30 mL). The pentane solution was evaporated under reduced pressure at -20°C , yielding 2 (75 mg, 72%) as a yellow oil. No trace of 1 was detected. The reaction was repeated at -50°C with similar results. With NaBD_4 the formation of $\text{Ru}(\text{CO})(\eta^4\text{-C}_6\text{H}_7\text{D})(\eta^4\text{-C}_6\text{H}_8)$ (2D) was observed. The deuterium was assigned exo on a methylene group from the $^1\text{H NMR}$: 2D as for 2 except for δ 1.85 (m, $J_{HD} \approx 1.7$ Hz, 4 H, H_{cn}) and 1.54 (dm, 3 H, H_{cx}).

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Registry No. 1, 103349-61-7; 1D, 103349-67-3; 2, 92468-32-1; 2D, 103349-68-4; 3, 103349-63-9; 4, 103349-65-1; 5, 103349-66-2; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1.

Dicarbonyl(η^5 -cyclopentadienyl)ruthenium Complexes of Cycloheptatrienyliene and Two Isomeric Benzocycloheptatrienylienes

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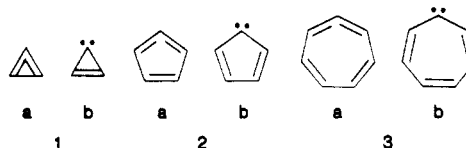
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Dicarbonyl(1,3,5-cycloheptatrienyl)(η^5 -cyclopentadienyl)ruthenium [$(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2(\text{C}_7\text{H}_7)$] (13; as a mixture of isomers) and two benzannelated analogues, dicarbonyl(1,2-benzocycloheptatrien-5-yl)(η^5 -cyclopentadienyl)ruthenium (22) and dicarbonyl(1,2-benzocycloheptatrien-4-yl)(η^5 -cyclopentadienyl)ruthenium (19), have been prepared by reaction of the corresponding cycloheptatrienyllithiums with RpBr ($\text{Rp} = \text{dicarbonyl}(\eta^5\text{-cyclopentadienyl})\text{ruthenium}$). Hydride abstraction from these σ complexes with triphenylcarbenium hexafluorophosphate gave the corresponding carbene complexes 15, 20, and 19, respectively. In all cases the salts behaved like their iron analogues in that they exhibited properties of carbene σ complexes (e.g., 15b) rather than allene π complexes (e.g., 15a). Substitution of tributylphosphine for carbonyl on the parent 15 did not change this structural preference. The barrier to rotation about the carbon-metal bond in the phosphine-substituted carbene complex 29 was found to be 8.5 kcal/mol which is 1.1 kcal/mol less than that of the corresponding iron complex. Attempts to prepare $\text{C}_7\text{H}_7\text{COCO}(\text{CO})_4$ (as a potential precursor to a cobalt analogue of the cycloheptatrienyliene complex 15) by reaction of $\text{Co}(\text{CO})_4^-$ with $\text{C}_7\text{H}_7\text{COCl}$ failed; the only isolated product was the cycloheptatrienyl cluster compound 11.

Introduction

Strained organic molecules¹ have received extensive attention over the past several decades. Of these, one of the more unusual subgroups includes the strained cyclic, conjugated allenes 1a, 2a, and 3a which have as their re-

spective valence isomers, carbenes 1b, 2b, and 3b. To date



the attention that has been devoted to the question of structural preference in these isomeric pairs has varied from none to rather extensive. For instance, although there can be little question but that the lowest energy form of

(1) Cf. Greenberg, A.; Liebman, J. F. *Strained Organic Compounds*; Academic Press: New York, 1978. March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; pp 130-140. Carey, F. A.; Sundberg *Advanced Organic Chemistry*; 2nd ed.; Plenum: New York, 1985; pp 141-144 and references therein.