wissenschaftlichen Forschung; F.M. thanks Mr. A. Ravazzolo for technical assistance.

Registry No. 1, 79681-91-7; 1′a, 79681-92-8; 1′b, 79732-92-6; 2, 103751-91-3; 2′a, 103834-15-7; 2′b, 103751-93-5; 3, 103751-95-7; 3′a, 103751-97-9; 3′b, 103833-28-9; 4, 103751-98-0; 4′a, 103751-99-1; 4′b, 103833-29-0; 5, 103752-00-7; 5′a, 103752-01-8; 5′b, 103881-20-5; 6′a, 103752-03-0; 6′b, 103833-31-4; 7, 96151-63-2; 7′a, 88898-37-7; 7′b, 88929-95-7; C_6H_5C<<tbdCH, 536-74-3; CH_3C<<tbdCH, 74-99-7; C_6H_5C<<tbdCLi, 4440-01-1; $C_6H_5CH_2CH_2MgBr$, 3277-89-2.

Supplementary Material Available: Tables of positional parameters and their estimated standard deviations and the general temperature factor expressions (10 pages); listings of the values of F_o and F_c (23 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of Pentamethylcyclopentadienyl Ruthenium Formyl and α-Hydroxy Complexes

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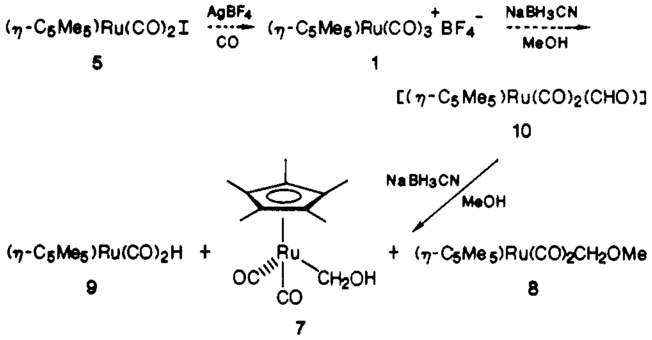
The transition-metal complexes—$(\eta\text{-}C_5Me_5)Ru(CO)_2CH_2OH$ (**7**), $(\eta\text{-}C_5Me_5)Ru(CO)_2CHO$ (**10**), and $(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)CHO$ (**11**)—were synthesized and studied as models for intermediates thought to be involved in the reduction of CO to organic oxygenates by transition-metal catalysts. Complex **7** was prepared by $NaBH_3CN$ reduction of $(\eta\text{-}C_5Me_5)Ru(CO)_3{}^+BF_4{}^-$ (**1**). Compound **10** was synthesized by reduction of **1** with $[Ph_3PCuH]_6$, but it could not be isolated in pure form. Pure crystalline **11** was isolated from the reduction of $(\eta\text{-}C_5Me_5)Ru(CO)_2(PMe_2Ph)^+I^-$ (**2**) with $NaBH_4$ in tetrahydrofuran/water. Formyl complexes **10** and **11** were shown to decompose by radical chain mechanism as evidenced by the fact that the addition of 9,10-dihydroanthracene, a hydrogen atom donor, to solutions of **10** or **11** drastically slowed their decomposition. The intermediate formed from the decomposition of **11** was shown to undergo electron transfer with $(\eta\text{-}C_5R_5)Ru(CO)_2I$ (R = H, Me). An X-ray structure of **11** was completed.

Introduction

It has been proposed that the catalytic reduction of carbon monoxide by transition-metal complexes to form organic oxygenates proceeds through a mechanism involving formyl and α-hydroxymethyl complexes.[1] In recent years, intensive effort has gone into modeling these intermediates.

A number of neutral mononuclear formyl[2-5] and α-hydroxy complexes have been isolated,[2,7] and several X-ray structures of formyl complexes have been completed.[6] We report here the full details of the synthesis and characterization of $(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)CHO$,[8] $(\eta\text{-}C_5Me_5)Ru(CO)(PEt_3)CHO$, and $(\eta\text{-}C_5Me_5)Ru(CO)_2CH_2OH$.[9] In addition, the radical-catalyzed decompositon of the formyl complexes is discussed along with the detailed X-ray structure analysis of $(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)CHO$.

Scheme I



Results

Syntheses of $(\eta\text{-}C_5Me_5)Ru(CO)_3{}^+BF_4{}^-$ (1), $(\eta\text{-}C_5Me_5)Ru(CO)_2(PMe_2Ph)^+I^-$ (2), and $(\eta\text{-}C_5Me_5)Ru(CO)_2(PEt_3)^+BF_4{}^-$ (4). Prior to the present work, some cationic complexes of the type $(\eta\text{-}C_5H_5)Ru(CO)_2L^+$ had been synthesized by the reaction of $(\eta\text{-}C_5H_5)Ru(CO)_2Cl$ with $AlCl_3$ and L in benzene.[10] These preparations required a counterion-exchange step that can be avoided by using $AgBF_4$ instead of $AlCl_3$. Thus, high yields of $(\eta\text{-}C_5Me_5)Ru(CO)_3{}^+BF_4{}^-$ (**1**) and $(\eta\text{-}C_5Me_5)Ru(CO)_2(PEt_3)^+BF_4{}^-$ (**4**) are obtained by reaction of the corresponding

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(11) Indirect proof comes from decomposition of $(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)CHO$ (**11**) in the presence of $(\eta\text{-}C_5Me_5)Ru(CO)_2I$ (**4**). Details will be published elsewhere: Nelson, G. O., in preparation.

halides (η-C_5Me_5)Ru(CO)$_2$I (**5**) and (η-C_5Me_5)Ru(CO)(PEt$_3$)I (**6**), respectively, with $AgBF_4$ under 50 psi of CO.

Compound **2**, (η-C_5Me_5)Ru(CO)$_2$PMe$_2$Ph$^+$I$^-$, is prepared in an unusual fashion. When (η-C_5Me_5)Ru(CO)$_2$I (**5**) and PMe$_2$Ph (slight excess) in a toluene solution are heated to 80 °C, no reaction takes place. However, upon addition of a small amount of 2,2-azobis(2-methylpropionitrile) (AIBN), an immediate reaction occurs which results in the precipitation of a 77% yield of white crystalline **2**. The remaining orange toluene solution contains (η-C_5Me_5)Ru(CO)(PMe$_2$Ph)I (**3**) (23%) (ratio of **2**/**3** = 3.3). Interestingly, when this reaction is run under 80 psi of CO, the ratio of **2**/**3** is eight (88% yield **2**).

Compounds **1**, **2**, and **4** have been characterized by their ^{1}H NMR, ^{13}C NMR, and IR spectra and by elemental analysis.

Preparation and Reactivity of (η-C_5Me_5)Ru(CO)$_2$CH$_2$OH (7). Several years ago Cutler and coworkers reported that the reduction of (η-C_5H_5)Fe(CO)$_3^+$ with NaBH$_3$CN in methanol led to the isolation of (η-C_5H_5)Fe(CO)$_2$CH$_2$OCH$_3$.[12] Trapping experiments indicated that (η-C_5H_5)Fe(CO)$_2$CH$_2$OH was formed as an intermediate, but it was unstable in the presence of methanol and formed the alkoxy methyl complex as the final product. We have found that reduction of (η-C_5Me_5)Ru(CO)$_3^+$BF$_4^-$ (**1**) with excess NaBH$_3$CN in methanol produces a reasonable yield (~60%) of (η-C_5Me_5)Ru(CO)$_2$CH$_2$OH (**7**) which is stable in methanol solution (Scheme I). When 1 equiv of reductant is used, (η-C_5Me_5)Ru(CO)$_2$CH$_2$OCH$_3$ (**8**) becomes the major product (<10% **7**). The hydride (η-C_5Me_5)Ru(CO)$_2$H (**9**) is a consistent contaminant no matter what the reaction conditions are.

Lin and co-workers have similarly reported that (η-C_5H_5)Ru(CO)$_3^+$(PF$_6$)$^-$ reacts with excess NaBH$_3$CN to produce (η-C_5H_5)Ru(CO)$_2$CH$_2$OH.[7f] This η-C_5H_5 analogue, like the iron derivative, reacts slowly with methanol to produce the alkoxy methyl species.

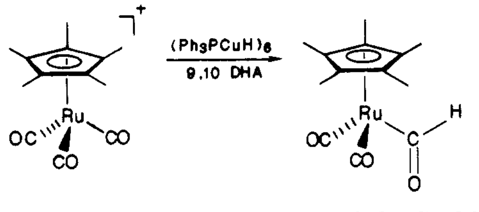
In one experiment, the cation **1** was added to a room-temperature methanol solution containing excess NaBH$_3$CN, and an IR spectrum of the carbonyl region was immediately recorded. This spectrum showed a 50/50 mixture of the starting cation, and a formyl complex with stretches at 2010, 1970, and 1610 cm^{-1}. The peaks observed here compare favorably with the IR spectrum for (η-C_5Me_5)Ru(CO)$_2$CHO (**10**) generated by a separate method (vide infra) except for the formyl carbonyl which is 35 cm^{-1} lower in the NaBH$_3$CN reduced complex. As has been suggested by others,[12] the shift in the IR spectrum is probably caused by the formation of a Lewis acid adduct with BH$_2$CN. After several additional minutes, peaks that represent (η-C_5Me_5)Ru(CO)$_2$R (R = –H, –CH$_2$OH, –CH$_2$OCH$_3$) appear. (CO stretches for these compounds are coincident.) Within 20 min the reaction is complete. The formation of hydride could be related to the radical-catalyzed decomposition of neutral metal formyls (vide infra) and to the special sensitivity we have observed with Lewis acid adducts; however, addition of hydrogen atom donors, such as 9,10-dihydroanthracene, causes no difference in the final ratio of isolated complexes. The amount of hydride observed varies from 5 to 30%.

As was indicated earlier, α-hydroxymethyl complex **7**, unlike the η-C_5H_5 derivative, is stable in methanol. A CD$_3$OD solution of **7**, even after being left standing for hours, showed no loss of the original complex when analyzed by using NMR. However, when a trace of CF$_3$COOH is added to the solution, **7** is rapidly converted to (η-C_5Me_5)Ru(CO)$_2$CH$_2$OCD$_3$. This conversion is confirmed by isolation of the product, redissolution in benzene-d_6, and comparison of ^{1}H NMR chemical shifts with those of (η-C_5Me_5)Ru(CO)$_2$CH$_2$OCH$_3$ (**8**).

Finally, it should be noted that even under 4000 psi of CO (80 °C), no CO is inserted into the metal–α-hydroxymethyl carbon bond. Additional details concerning complex **7** are contained in an earlier communication.[9]

Reduction of (η-C_5Me_5)Ru(CO)$_3^+$BF$_4^-$ (1) with [Cu(Ph$_3$)H]$_6$: Observation of (η-C_5Me_5)Ru(CO)$_2$CHO (10). When we began our work, very few stable transition-metal neutral formyls were known, and none of these contained ruthenium as the transition-metal center. Casey and coworkers had reported observation of (η-C_5H_5)Ru(CO)$_2$CHO obtained by reduction of (η-C_5H_5)Ru(CO)$_3^+$PF$_6^-$ with K$^+$HB(i-Pr)$_3^-$.[5] However, this formyl complex was extremely unstable, decomposing at –90 °C. We also had trouble obtaining pure, stable formyl complexes with this type of reagent. For instance reduction of (η-C_5Me_5)Ru(CO)$_3^+$BF$_4^-$ (**1**) with LiBH(Et)$_3$ always produced solutions of the hydride (η-C_5Me_5)Ru(CO)$_2$H (**9**).

While searching for mild methods to generate formyl complexes from cationic carbonyls, we discovered that the neutral copper hydride cluster [Ph$_3$PCuH]$_6$[13] efficiently transfers one hydride to a carbonyl on (η-C_5Me_5)Ru(CO)$_3^+$BF$_4^-$ (**1**) to produce the formyl complex (η-C_5Me_5)Ru(CO)$_2$CHO (**10**). There are only a few other cases in which a carbonyl in one complex has been reduced by the hydride of another transition metal.[14] Typically, 1 equiv of red [Ph$_3$PCuH]$_6$ dissolved in THF is added to a THF slurry of cation **1**. The resultant solution turns pale yellow with concomitant precipitation of a yellow, copper-containing solid, presumably (Ph$_3$PCu)$_6$H$_5^+$BF$_4$. IR and ^{1}H NMR spectra show that such solutions contain a ~1:1 mixture of **9** and **10**. We have discovered that the key to obtaining solutions of pure **10** lies in doing the reduction in the presence of a good hydrogen atom donor. Thus, when the above reduction is conducted in the presence of 5 equiv of 9,10-dihydroanthracene (9,10-DHA), **10** is formed quantitatively as shown by using IR and NMR. Even in the presence of 9,10-DHA, **10** decomposes over several hours (in the absence of 9,10-DHA, total decomposition rates for **10** vary from rapid to several hours), and attempts to isolate the formyl always give mixtures of **9** and **10**. The radical nature of the decomposition will be discussed further.



Synthesis and Characterization of the Stable Formyls (η-C_5Me_5)Ru(CO)(PPhMe$_2$)CHO (11) and (η-C_5Me_5)Ru(CO)(PEt$_3$)CHO (12). Although [Ph$_3$PCuH]$_6$ will reduce (η-C_5Me_5)Ru(CO)$_2$(PMe$_2$Ph)$^+$I$^-$ (**2**), a more convenient route to **11** utilizes Graham's technique of reaction of the organometallic cation with 1 equiv of NaBH$_4$ in THF/H$_2$O. Following this route, a 95% yield of pale

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yellow crystalline (η-C_5Me_5)Ru(CO)(PMe_2Ph)CHO (**11**) can be isolated. Complex **11** shows the characteristic downfield formyl proton in the ^1H NMR at δ 14.75 (J_{PH} = 2 Hz) and the formyl carbon in the ^{13}C NMR at δ 271.8 (J_{C-P} = 14.6 Hz). The formyl carbonyl stretch appears at 1601 cm^{-1} (THF) in the IR spectrum.

Complex **11** is stable in degassed C_6D_6 solutions at room temperature, but when heated to 40 °C or above, it decomposes at varying rates to a 1:1 mixture of (η-C_5Me_5)Ru$(CO)_2$H (**9**) and (η-C_5Me_5)Ru(CO)(PMe_2Ph)H (**13**) (free phosphine can be observed in the NMR). This decomposition can be easily followed by observing the NMR signal of the η-C_5Me_5 group for the various complexes. For **11**, **9**, and **13** this signal appears at δ 1.47, 1.74, and 1.77, respectively. During the decomposition, the signals at δ 1.74 and 1.77 increase at approximately the same rate, whereas the signal at δ 1.47 decreases. One also notices that the formyl proton signal at δ 14.75 decreases, whereas hydride signals at δ −10.20 (**9**) and −11.37 (**13**; d, J_{H-P} = 37 Hz) increase. A C_6D_6 solution of **11** containing 2 equiv of 9,10-DHA requires as long as 14 days to fully decompose, whereas a solution from the same pot, but containing no hydrogen donor, decomposes within 1 h (40 °C). Although the absolute rates vary with each solution of complex **11** prepared, the effect of 9,10-dihydroanthracene is always to slow drastically the rate of decomposition. Note that even though a 1:1 mixture of **9** and **13** is formed during the decompositon, **9** reacts with free phosphine to produce **13** at a somewhat slower rate than formyl decomposition. In other words, the presence of 9,10-DHA affects the rate of substitution in the same manner it affects the rate of formyl decomposition. Photolysis of a solution of **11** produces similar results. In one experiment, when a solution of **11** in C_6D_6 was photolyzed by using a rayonet containing 3500-Å UV lamps, the formyl complex had decomposed within 1 min to a 1:1 mixture of **9** and **13**. When a sample of **11** from the same solution but containing 2 equiv of 9,10-DHA was photolyzed, 5 min were required for decomposition to reach the same point.

Initially, we thought that 9,10-DHA might be directly involved in the pathway of **11** to **9**; however, deuterium labeling studies seem to indicate otherwise. When (η-C_5Me_5)Ru(CO)(PMe_2Ph)CDO (**11**-d_1) is decomposed in C_6D_6 at 70 °C, **13**-d_1 is formed quantitatively (**9**-d_1 is initially observed but substitutes rapidly). Decomposition of **11**-d_1 in the presence of 9,10-DHA (much slower rate) gives mostly **13**-d_1, but a small amount (<5%) of **13** is sometimes also observed. Independent experiments indicate that in some solutions **13**-d_1 slowly gives **13** when heated with 9,10-DHA.

Owing to radical-initiated exchange reactions of the products, crossover experiments with these compounds have been difficult to perform. For instance, one crossover was attempted by heating a solution containing a 1:1 ratio of (η-C_5Me_5)Ru(CO)(PMe_2Ph)CHO (**11**) and (η-C_5Me_5)Ru(CO)(PEt_3)CDO (**12**-d_1). Complex **12**-d_1 is synthesized by reducing (η-C_5Me_5)Ru$(CO)_2$(PEt_3)$^+BF_4^-$ with $NaBD_4$ in THF/H_2O. Compound **12**-d_1 is isolated as a pale yellow, air-sensitive oil which has been identified by ^1H NMR, ^{13}C NMR, and IR spectroscopy. Separate experiments with **12** indicate that its decomposition is also slowed in the presence of 9,10-DHA. However, with **12**, PEt_3 is lost faster than CO producing mixtures that are initially rich in (η-C_5Me_5)Ru$(CO)_2$H (**9**) (initial ratio of **9** to (η-C_5Me_5)Ru(CO)(PEt_3)H (**14**) $\approx$ 2:1) but eventually have **14** as the only hydride present. Spectral recordings on the formyl derivative **12** and the analogous hydride (η-C_5Me_5)Ru(CO)(PEt_3)H (**14**) show that formyl and hydride proton chemical shifts are different from those observed for **11** and **13**. When a 1:1 mixture of **11** and **12**-d_1 is heated at 70 °C for a total of 30 min, **11** is 90% decomposed and **12**-d_1 is only 30% decomposed. Also, at this point, some of the crossover product (η-C_5Me_5)Ru(CO)(PEt_3)H (**14**) appeared as well as the expected **9** and **13**. However, as indicated earlier, control experiments show that the hydride complexes can readily exchange with free ligands in solution. Since free PEt_3 and PMe_2Ph are formed in the formyl decompositions, hydride **14** might arise by an exchange reaction rather than by attack of (η-C_5Me_5)Ru(CO)(PEt_3)· on (η-C_5Me_5)Ru(CO)(PMe_2Ph)CHO (**11**). Therefore, further control experiments are necessary to check the validity of this result.

Another attempt at a crossover was made by synthesis of (η-C_5Me_4Et)Ru(CO)(PMe_2Ph)CHO (**15**). Unfortunately, 400-MHz NMR spectra showed that **11** and **15** and **13** and (η-C_5Me_4Et)Ru(CO)(PMe_2Ph)H (**16**) have exactly the same chemical shift for hydrogens of the formyl and hydride ligands. Mass spectra of mixtures of these complexes also proved to be ambiguous.

Decomposition of 11 in the Presence of (η-C_5R_5)Ru$(CO)_2$I (R = Me, 5; R = H, 17). When formyl complex **11** is allowed to decompose in the presence of 1 equiv of (η-C_5Me_5)Ru$(CO)_2$I (**5**), the observed phosphine-containing products are (η-C_5Me_5)Ru(CO)(PMe_2Ph)I (**3**) and (η-C_5Me_5)Ru$(CO)_2$(PMe_2Ph)$^+I^-$ (**2**) (ratio of **3**/**2** = 4). Approximately 1 equiv of (η-C_5Me_5)Ru$(CO)_2$H (**9**) is also formed. When the reactions are allowed to take place in benzene, increasing the ratio of **5**/**11** results quantitatively in a decrease in the product ratio of **3**/**2**. The same reaction proceeds in acetone producing much more of salt **2** than in the reaction just discussed (ratio of **2**/**3** = 7). Also, in acetone the final product ratio is less sensitive to added iodide complex **5**. When formyl complex **11** is decomposed (benzene) in the presence of 1 equiv of (η-C_5H_5)Ru$(CO)_2$I (**17**), the salt **2** is the dominant product (ratio **2**/**3** = 7). One equivalent of (η-C_5H_5)Ru$(CO)_2$H (**18**) is also observed. It should be noted that observation of **18** as the only hydride complex in this latter reaction does not necessarily preclude the formation of the other possible hydride complexes. Thus, when a acetone-d_6 solution containing (η-C_5Me_5)Ru$(CO)_2$H (**9**), (η-C_5Me_5)Ru(CO)(PMe_2Ph)H (**13**), and an excess of (η-C_5H_5)Ru$(CO)_2$I (**17**) is gently heated, the ^1H NMR peaks for the two starting hydrides at δ −10.5 and −11.9 diminish while the hydride peak for (η-C_5H_5)Ru$(CO)_2$H (**18**) appears (δ −10.9) and increases until it is the only observable metal hydride. Concurrent formation of iodide complexes **3** and **5** is noted.

Crystal and Molecular Structures of (η-C_5Me_5)Ru(CO)(PMe_2Ph)CHO[16] (11). Complete details of the X-ray analysis for **11** are given in the crystal structure analysis report obtainable as supplementary material as described in a later section of this paper. The final atomic coordinates for non-hydrogen and non-group atoms are contained in Table I, and the refined anisotropic thermal parameters for non-hydrogen atoms are presented in Table II. Final atomic positions for the hydrogen atoms of **11** are given in Table III. Tables I–III are contained in the supplementary material. A perspective view of the structure which illustrates the numbering scheme is shown for **11** in Figure 1. Bond lengths and bond angles for the structure are given in Tables IV and V.

The presence of the formyl ligand is evident from the Ru–C_2–O_2 angle, and the location of the formyl hydrogen which points somewhat toward the pentamethylcyclo-

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[16] Structure solved by Cynthia S. Day, Crystalytics Co., P.O. Box 82286, Lincoln, NE 68501.

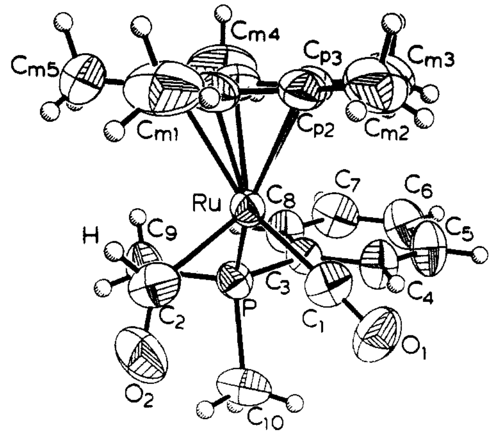

Figure 1. A perspective view of the structure of 11.

Table IV. Bond Lengths (Å) in Crystalline $(C_5(CH_3)_5)Ru(CO)(CHO)(P(C_6H_5)(CH_3)_2)$[a]

type[b]	length	type[b]	length
Ru–P	2.282 (1)	C_3–C_4	1.388 (4)
		C_3–C_8	1.391 (4)
Ru–C_1	1.857 (3)	C_4–C_5	1.382 (5)
		C_5–C_6	1.377 (5)
Ru–C_2	2.036 (4)	C_6–C_7	1.370 (5)
		C_7–C_8	1.385 (5)
Ru–C_{p1}	2.257 (3)		
Ru–C_{p2}	2.264 (3)	C_{p1}–C_{p2}	1.425 (5)
Ru–C_{p3}	2.298 (3)	C_{p1}–C_{p5}	1.422 (5)
Ru–C_{p4}	2.315 (3)	C_{p2}–C_{p3}	1.409 (5)
Ru–C_{p5}	2.293 (4)	C_{p3}–C_{p4}	1.409 (5)
Ru–C_{pg}[c]	1.944 (...)	C_{p4}–C_{p5}	1.401 (5)
P–C_3	1.824 (3)	C_{p1}–C_{m1}	1.507 (5)
P–C_9	1.812 (4)	C_{p2}–C_{m2}	1.509 (5)
P–C_{10}	1.823 (4)	C_{p3}–C_{m3}	1.509 (5)
		C_{p4}–C_{m4}	1.525 (5)
O_1–C_1	1.134 (4)	C_{p5}–C_{m5}	1.515 (6)
O_2–C_2	1.106 (5)		
C_2–H	0.84 (4)		
P···C_1	2.900 (3)	P···C_{pg}[c]	3.801 (...)
P···C_2	2.926 (4)	C_1...C_{pg}[c]	3.418 (...)
C_1···C_2	2.786 (5)	C_2···C_{pg}[c]	3.501 (...)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] The symbol C_{pg} is used to denote the center of gravity for the pentamethylcyclopentadienyl ring and is therefore listed without an estimated standard deviation.

pentadienyl ring. This geometry is in contrast to that reported for the formyl ligand in $(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CHO)$ where the oxygen (CHO) is angled toward the η-C_5H_5 ring.

In light of recent discussions by Casey and co-workers on the structure of formyl complexes,[6] several other points are worth noting. The formyl C=O bond length (1.106 (5) Å) in 11 is extremely short, in fact, shorter than the terminal C≡O bond (1.134 (4) Å). Although Casey points to relatively short C=O formyl bond lengths in several complexes,[6] in none of the structures reported has a formyl C=O bond length been observed to be shorter than a terminal C≡O bond length in the same structure. In addition, the Ru–C_2–O_2 angle (140.0°) is opened more than in any other reported structure. The Ru–C_2 bond length (2.036 Å) is shorter than the Ru–C bond length in the recently reported structure of $[(\eta\text{-}C_5H_5)Ru(CO)_2]_2(\mu\text{-}CH_2)$ (2.18 Å),[17] but it is comparable to that reported for the cationic formyl complex *trans*-$[Ru(CDO)(CO)(dppe)_2][SbF_6]\cdot CH_2Cl_2$ (2.09 Å).[18] Unfortunately, we do not yet have a structure of the acetyl system analogous to 11 for comparison purposes. The exact reasons for the seemingly unusual structural features of the formyl ligand are still unclear.

Table V. Bond Angles (deg) in Crystalline $(C_5(CH_3)_5)Ru(CO)(CHO)(P(C_6H_5)(CH_3)_2)$[a]

type[b]	angle	type[b]	angle
$PRuC_1$	88.3 (1)	$RuPC_3$	114.1 (1)
$PRuC_2$	85.1 (1)	$RuPC_9$	115.2 (1)
C_1RuC_2	91.3 (1)	$RuPC_{10}$	116.8 (1)
		C_3PC_9	105.7 (2)
$PRuC_{p1}$	150.5 (1)	C_3PC_{10}	101.5 (1)
$PRuC_{p2}$	148.0 (1)	C_9PC_{10}	101.8 (2)
$PRuC_{p3}$	112.3 (1)		
$PRuC_{p4}$	97.1 (1)	RuC_1O_1	177.2 (3)
$PRuC_{p5}$	114.2 (1)		
$PRuC_{pg}$[c]	128.0 (...)	RuC_2O_2	140.0 (3)
		RuC_2H	104 (3)
C_1RuC_{p1}	121.1 (1)	O_2C_2H	116 (3)
C_1RuC_{p2}	97.1 (1)		
C_1RuC_{p3}	106.7 (1)	$C_{p2}C_{p1}C_{p5}$	107.4 (3)
C_1RuC_{p4}	140.6 (1)	$C_{p1}C_{p2}C_{p3}$	108.2 (3)
C_1RuC_{p5}	156.5 (1)	$C_{p2}C_{p3}C_{p4}$	107.6 (3)
C_1RuC_{pg}[c]	128.1 (...)	$C_{p3}C_{p4}C_{p5}$	109.1 (3)
		$C_{p4}C_{p5}C_{p1}$	107.7 (3)
C_2RuC_{p1}	95.2 (1)		
C_2RuC_{p2}	126.1 (1)	PC_3C_4	118.2 (2)
C_2RuC_{p3}	154.7 (1)	PC_3C_8	123.3 (2)
C_2RuC_{p4}	128.0 (1)	$C_4C_3C_8$	118.5 (3)
C_2RuC_{p5}	96.9 (1)	$C_3C_4C_5$	120.9 (3)
C_2RuC_{pg}[c]	123.2 (...)	$C_4C_5C_6$	120.0 (3)
		$C_5C_6C_7$	119.8 (3)
$C_{p1}RuC_{p2}$	36.7 (1)	$C_6H_7C_8$	120.6 (3)
$C_{p1}RuC_{p5}$	36.4 (1)	$C_7C_8C_3$	120.2 (3)
$C_{p2}RuC_{p3}$	36.0 (1)		
$C_{p3}RuC_{p4}$	35.6 (1)	$C_{p2}C_{p1}C_{m1}$	127.2 (3)
$C_{p4}RuC_{p5}$	35.4 (1)	$C_{p5}C_{p1}C_{m1}$	125.0 (3)
		$C_{p1}C_{p2}C_{m2}$	125.6 (3)
$C_{p1}RuC_{p3}$	60.5 (1)	$C_{p3}C_{p2}C_{m2}$	125.9 (3)
$C_{p1}RuC_{p4}$	59.8 (1)	$C_{p2}C_{p3}C_{m3}$	126.7 (3)
$C_{p2}RuC_{p4}$	59.5 (1)	$C_{p4}C_{p3}C_{m3}$	125.5 (3)
$C_{p2}RuC_{p5}$	60.4 (1)	$C_{p3}C_{p4}C_{m4}$	124.8 (3)
$C_{p3}RuC_{p5}$	59.8 (1)	$C_{p5}C_{p4}C_{m4}$	125.6 (3)
		$C_{p1}C_{p5}C_{m5}$	124.9 (3)
		$C_{p4}C_{p5}C_{m5}$	127.1 (3)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] The symbol C_{pg} is used to denote the center of gravity for the pentamethylcyclopentadienyl ring and is therefore listed without an estimated standard deviation.

Discussion

Synthesis and Reactivity of α-Hydroxymethyl Complex 7. The reduction of cationic carbonyl complexes with $NaBH_3CN$[7f,9,12] is one of several routes to transition-metal α-hydroxymetal compounds.[7] Because the necessity of using an excess of the $NaBH_3CN$ reagent in this case and in others is not readily understood, an explanation awaits further work. A comprehensive discussion of methodology for the synthesis of α-hydroxy complexes as well as factors that affect their stability and reactivity has recently been published by Gladysz.[7j]

Carbon monoxide insertion into a metal–α-hydroxymethyl bond has only been observed in two cases and assumed in a third.[7j] Gladysz has pointed out that this reaction has been attempted in the moderately polar solvent THF with the cyclopentadienyl-substituted compounds[7j] and that a more polar solvent such as CH_3NO_2 may help the reaction proceed.[7f] However, the lack of CO

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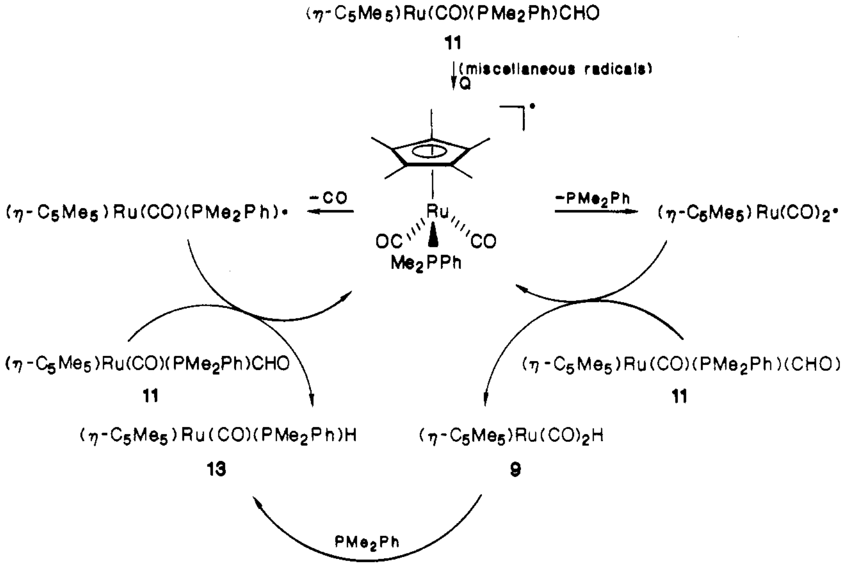
(17) Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679–1680.

(18) Smith, G.; Cole-Hamilton, D. J.; Thorton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 2501–2507.19.

Scheme II



insertion in the cyclopentadienyl systems is probably more strongly linked to the ligand environment since even the alkyl complexes, which should insert CO more readily, are sluggish in these systems.[7f]

Synthesis and Decomposition of Formyl Complexes 10, 11, and 12. This study reports a convenient hydride donor, $[Ph_3PCuH]_6$,[13] that may be useful for the reduction of other cationic metal species. The reaction of the copper cluster with $(\eta\text{-}C_5Me_5)Ru(CO)_3{}^+BF_4{}^-$ in the presence of a hydrogen atom donor to give a quantitative yield of $(\eta\text{-}C_5Me_5)Ru(CO)_2CHO$ (**10**) is one of only a few examples in which a transition-metal hydride has been used to reduce the carbonyl of another transition-metal complex.[14] The advantage of this reductant is that a noninteractive cation that precipitates out of solution becomes the coproduct. A disadvantage is that hydride transfer does not take place as efficiently to cationic substrates containing more basic ligands such as PMe_2Ph. Graham's technique ($NaBH_4/H_2O/THF$)[2e] represents the best alternative for synthesis of formyl complexes from cationic carbonyl complexes containing basic ligands.

Our inability to isolate pure samples of $(\eta\text{-}C_5Me_5)Ru(CO)_2(CHO)$ (**10**) led us to attempt the synthesis of phosphine-substituted systems. Gladysz had shown that substituting Ph_3P for CO in $(\eta\text{-}C_5H_5)Re(CO)(NO)CHO$ greatly stabilized that system so that $(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CHO)$ is a stable, crystalline solid at room temperature.[7b] Similarly, we have found that phosphines greatly stabilize the pentamethylcyclopentadienyl ruthenium formyl complexes. Specifically, it has been shown that PMe_2Ph is a very convenient substituent in the ruthenium system because of the crystallinity and stability it lends to the corresponding formyl complex. The stabilization has been presumed to arise from an increase in the carbene-like character of the formyl ligand through increased electron donation from the metal center. However, considering the proposed mode of decomposition of these compounds (vide infra), one can more clearly see the stabilization as the effect of the electron-donating phosphine on the energy of the pathway for formation of the proposed 19-electron intermediate $(\eta\text{-}C_5Me_5)Ru(CO)_2(L)$.

The unique aspect of the study of these formyl complexes has been the discovery that hydrogen atom donors greatly aid in the stabilization of these compounds in solution. We were led to this discovery by the observation that different solutions of the neutral formyl complexes showed varying rates of decomposition, behavior that is reminiscent of what has been observed in radical-initiated decomposition of transition-metal complexes.[15] A decomposition mechanism consistent with the stabilization of these compounds by hydrogen atom donors is illustrated in Scheme II. We are proposing that **11** decomposes by a pathway initiated by cleavage of the carbon-to-hydrogen bond of the formyl group by miscellaneous radicals (Q·). The 19-electron intermediate formed by this reaction can lose carbon monoxide or phosphine to form 17-electron radical complexes that are chain carriers which produce the final observed hydride complexes upon reaction with a molecule of the starting formyl complex. The data presented here indicate that the rate of phosphine and/or carbon monoxide loss to form the 19-electron intermediate varies depending upon the phosphine used. The deuterium-labeling study appears to indicate that hydrogen atom donors (at least 9,10-DHA) stabilize the formyl systems by trapping miscellaneous radicals formed thermally or photochemically in the presence of the formyl complex and not by direct intervention in a radical chain involving the ruthenium compounds. However, the exact nature of the initiation of the radical chain is still unknown. Kochi has proposed separately the same efficient radical chain pathway for the decomposition of neutral and anionic transition-metal formyl complexes, and his work has shown that $(n\text{-}Bu)_3SnH$ is an efficient scavenger for stabilization of formyl complexes.[19] Recently, Kochi has also shown that electrochemical reduction of various 18-electron carbonyl-containing complexes in the presence of $(n\text{-}Bu)_3SnH$ produces the corresponding anionic or neutral formyl complexes.[19c] This unique synthetic route to formyl complexes provides strong proof for the presence of a 19-electron intermediate in the reverse decomposition reaction.

Electron-Transfer Chemistry. The decomposition of formyl complex **11** in the presence of $(\eta\text{-}C_5R_5)Ru(CO)_2I$ to produce $(\eta\text{-}C_5Me_5)Ru(CO)_2(PMe_2Ph)^+I^-$ (**2**) as one product indicates that the intermediate formed in this reaction is a reductant and will transfer an electron to appropriate metal substrates. We believe this intermediate is the 19-electron species $(\eta\text{-}C_5Me_5)Ru(CO)_2(PMePh)$ and, in fact, is the same kind of compound produced by the

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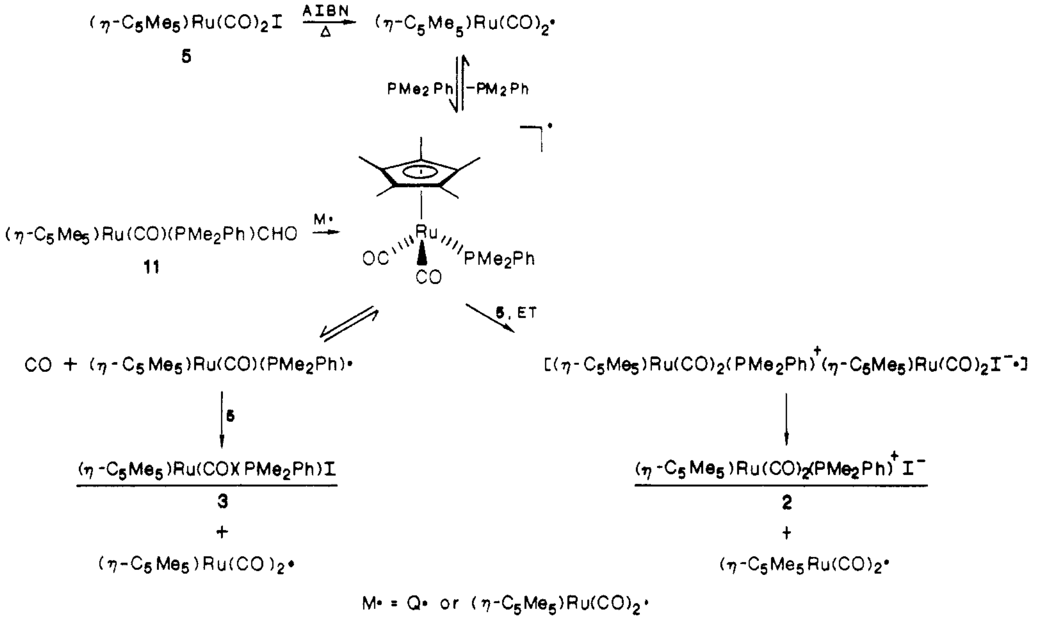
(19) (a) Narayanan, B. A.; Amatore, C.; Casey, C. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6351–6352. (b) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1984**, *3*, 802–804. (c) Narayanan, B. A.; Kochi, J. K. *J. Organomet. Chem.* **1984**, *272*, C49–C53.

Scheme III



photochemical reaction of metal dimers with PMe_2Ph as reported by Tyler.[20] We propose that this 19-electron species is also involved in the very rapid formation of **2** and **3** in the reaction of (η-C_5Me_5)$Ru(CO)_2I$ (**5**) with PMe_2Ph in the presence of AIBN at 80 °C. A speculative mechanism that accounts for all the data obtained thus far is shown in Scheme III. Thus reaction of 17-electron (η-C_5Me_5)$Ru(CO)_2$· with PMe_2Ph produces the 19-electron intermediate which can then lose a ligand or undergo electron transfer to **5**. The former results ultimately in the substitution product **3** (via an associative mechanism) where as the latter produces salt **2** along with the 17-electron reactant. The reaction of PMe_2Ph with (η-C_5Me_5)$Ru(CO)_2$· must be very fast since the AIBN catalyzed reaction is over in a few seconds. The fact that more of the salt **2** is formed in the presence of CO or in polar solvents is not surprising since loss of CO at some point is required for formation of **3**, and polar solvents favor charged intermediates. The fact that a high ratio of **2** to **3** is formed in the decomposition of **11** in the presence of (η-C_5H_5)$Ru(CO)_2I$ (**17**) is probably due to this iodide having a lower reduction potential than the permethylated species **5**.[22]

Summary

Transition-metal α-hydroxymethyl and formyl complexes of the type (η-C_5Me_5)Ru(CO)(L)R have been synthesized and characterized. Formyl complexes of this type have been shown to decompose by a novel radical chain route, and the 19-electron intermediate formed in this reaction can undergo electron transfer if appropriate substrates are present. The radical-catalyzed decomposition of formyl complexes, reported here and by others,[19] may be an innate property of transition metal ligated formyl and, therefore, related to known catalytic systems that reduce CO. In this context, Kochi's report of the reverse of this reaction, formation of ligated formyl via hydrogen atom abstraction, is important since it shows that there is a route to these complexes other than carbon monoxide insertion into a metal hydride bond.[19c]

Experimental Section

General Data. All manipulations of complexes and solvents were conducted by using standard Schlenk techniques. Solvents were degassed under nitrogen and purified by distillation from standard drying agents. Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian EM360, JEOL, 400 MHz; ^{13}C, JEOL, 400 MHz; IR, Perkin-Elmer 421. NMR chemical shifts are reported in δ vs. Me_4Si. [(η-C_5Me_5)$Ru(CO)_2]_2$ was prepared by a modification of the synthesis by King.[21] $[PPh_3CuH]_6$ was obtained by modification of a literature method.[13] (η-C_5H_5)$Ru(CO)_2I$ was prepared by a method previously recorded in the literature.[22] The ligands PMe_2Ph and PEt_3 were purchased from Strem and used as received. $AgBF_4$ was purchased from Aldrich and dried under high vacuum (10^{-4} mmHg) before use. AIBN was purchased from Alfa. Elemental analyses were done by analytical, in-house methods.

[(η-C_5Me_5)$Ru(CO)_2]_2$. $Ru_3(CO)_{12}$ (3.83 g, 6 mmol) was slurried in a solution of C_5Me_5H (2.45 g, 18 mmol) in 80 mL of decane, and the mixture was heated to 165 °C (we found that boiling the solution resulted in much lowered yields of the desired complex) and held at that temperature for 3 h. After ~10 min, all the $Ru_3(CO)_{12}$ was in solution and CO evolution was observed. After 30 min, dark red crystals of [(η-C_5Me_5)$Ru(CO)_2]_2$ began to precipitate. After heating was stopped, the decane solution was allowed to cool, and the pure dimer was isolated by filtration. Washing with pentane and drying in vacuo afforded an almost quantitative yield of [(η-C_5Me_5)$Ru(CO)_2]_2$ which was identified by comparison of spectroscopic values with those in the literature.[21]

(η-C_5Me_5)$Ru(CO)_2I$ (5). [(η-C_5Me_5)$Ru(CO)_2]_2$ (5.0 g, 8.6 mmol) was dissolved in 100 mL of $CHCl_3$ containing a 2% molar excess of iodine. After 3 h, the dark red chloroform solution was treated with 2 × 50 mL of 10% sodium thiosulfate in water and then was dried over sodium sulfate. The solution was evaporated to give a red-orange solid that was subjected to column chromatography on silica gel (50 × 15 cm). Elution with toluene developed a bright orange band which was collected and solvent stripped to afford orange, crystalline **5** (6.1 g, 1.46 mmol, 85% yield).

Anal. Calcd for $C_{12}H_{15}IO_2Ru$: C, 34.34; H, 3.57. Found: C, 34.24; H, 3.56. IR (CH_2Cl_2): 2030, 1981 cm^{-1}. ^1H NMR (C_6D_6): δ 1.62 (C_5Me_5). ^{13}C NMR ($CDCl_3$): δ 10.7 (C_5*Me*$_5$), 100.0 (C_5Me_5), 198.4 (CO).

(η-C_5Me_5)Ru(CO)(PEt_3)I (6). (η-C_5Me_5)$Ru(CO)_2I$ (1.0 g, 2.4 mmol) and 2 equiv of PEt_3 were dissolved in 50 mL of degassed toluene in a Schlenk tube. The Schlenk tube was fitted with a bubbler, and the solution was then photolyzed with a 550-W medium-pressure mercury lamp for 4 h (the IR spectrum no longer showed dicarbonyl complex). The solution was rotovaped to

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[20] Stiegman, A. E.; Goldman, A. S.; Leslie, D. B.; Tyler, D. R. *J. Chem. Soc. Chem. Commun.* **1984**, 632–633.

[21] King, R. G.; Iqbal, M. A.; King, A. D., Jr. *J. Organomet. Chem.* **1979**, *171*, 53.

[22] Haines, R. J.; duPreez, A. L. *J. Chem. Soc. Dalton Trans.* **1972**, 944–948.

dryness, and the residue was chromatographed on silica gel where it eluted with toluene. The red-orange band was collected, and the solution was stripped to give 0.84 g (69% yield) of analytically pure **6**.

Anal. Calcd for $\mathrm{C_{17}H_{30}IOPRu}$: C, 40.07; H, 5.89. Found: C, 40.00; H, 5.93. IR ($\mathrm{CH_2Cl_2}$); 1978 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.08 ($-\mathrm{CH_2}\mathit{CH}_3$, dt, $J_{\mathrm{H-H}} = 6.3$ Hz, $J_{\mathrm{P-H}} = 15.8$ Hz), 1.88 ($-\mathit{CH}_2\mathrm{CH_3}$, q, $J_{\mathrm{C-H}} = 6.3$ Hz), 1.92 ($\mathrm{C_5}\mathit{Me}_5$, $J_{\mathrm{P-H}} = 2$ Hz). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 8.7 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 10.9 ($\mathrm{C_5}\mathit{Me}_5$), 20.9 ($\mathit{C}\mathrm{H_2CH_3}$, $J_{\mathrm{C-P}} = 28$ Hz), 95.2 ($\mathit{C}_5\mathrm{Me_5}$, $J_{\mathrm{C-P}} = 13$ Hz), 206.5 (CO, $J_{\mathrm{C-P}} = 20$ Hz).

(η-$\mathrm{C_5Me_5}$)Ru(CO)$_3$$^+BF_4$$^-$ (1). An orange solution of **5** (2.0 g, 4.8 mmol) in 30 mL of $\mathrm{CH_2Cl_2}$ was treated with $\mathrm{AgBF_4}$ (0.93 g, 4.8 mmol) under 60 psi of CO. Stirring for 2 h resulted in formation of a gray precipitate and a colorless solution. Filtration followed by addition of diethyl ether precipitated analytically pure **1** as a fluffy, white solid in 82% (1.6 g) yield.

Anal. Calcd for $\mathrm{C_{13}H_{15}O_3RuBF_4}$: C, 38.28; H, 3.68. Found: C, 38.40; H, 3.68. IR ($\mathrm{CH_2Cl_2}$): 2110, 2050 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 2.27 ($\mathrm{C_5Me_5}$). ^{13}C NMR ($\mathrm{CDCl_3}$) δ 10.5 ($\mathrm{C_5}\mathit{Me}_5$), 106.8 ($\mathit{C}_5\mathrm{Me_5}$), 191.0 (CO).

(η-$\mathrm{C_5Me_5}$)Ru(CO)$_2$(PMe$_2$Ph)$^+$I$^-$ (2). Approximately 100 mg of AIBN was added to an orange toluene (50 mL) solution of **5** (2.0 g, 4.8 mmol) and 2 equiv of $\mathrm{PMe_2Ph}$. When the solution was heated to 80 °C on a steam bath, white crystals precipitated almost instantly. The crystals were collected by filtration and washed with hexane to yield of 2.0 g (75%) of pure **2**.

Anal. Calcd for $\mathrm{C_{20}H_{26}IO_2PRu}$: C, 43.13; H, 4.67. Found: C, 43.17; H, 4.71. IR ($\mathrm{CH_2Cl_2}$): 2065, 2018 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 1.91 ($\mathrm{C_5Me_5}$, d, $J_{\mathrm{H-P}} = 1.5$ Hz), 2.06 ($\mathrm{PMe_2}$, d, $J_{\mathrm{H-P}} = 11$ Hz), 7.48–7.71 ($\mathrm{C_6H_5}$, m). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 10.5 ($\mathrm{C_5}\mathit{Me}_5$), 20.0 ($\mathrm{PMe_2}$, d, $J_{\mathrm{C-P}} = 37.8$ Hz), 103.4 ppm ($\mathit{C}_5\mathrm{Me_5}$), 129.7, 130.2, 131.9 ($\mathrm{C_6H_5}$, $\mathrm{C_{ipso}}$ not observed), 198.0 (CO).

Evaporation of the filtrate to dryness and chromatography of the residue (toluene, 2 × 20 cm silica gel) led to isolation of ~20% yield of orange crystalline (η-$\mathrm{C_5Me_5}$)Ru(CO)(PMe$_2$Ph)I (**3**).

Anal. Calcd for $\mathrm{C_{19}H_{26}IOP\ Ru}$: C, 43.11; H, 4.9. Found: C, 42.87; H, 4.88. IR ($\mathrm{CH_2Cl_2}$): 1935 cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.53 ($\mathrm{C_5Me_5}$, d, $J_{\mathrm{P-H}} = 2$ Hz) 1.63 ($\mathrm{PMe_2}$, d, $J_{\mathrm{P-H}} = 2$ Hz), 1.83 ($\mathrm{PMe_2}$, $J_{\mathrm{P-H}} = 2$ Hz). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 18.0 ($\mathrm{PMe_2}$, d, $J_{\mathrm{C-P}} = 30$ Hz), 21.5 ($\mathrm{PMe_2}$, d, $J_{\mathrm{C-P}}$ 35 Hz), 10.3 ($\mathrm{C_5}\mathit{Me}_5$), 95.5 ($\mathit{C}_5\mathrm{Me_5}$), 128.4 ($\mathrm{C_6H_5}$, d, $J_{\mathrm{C-P}} = 10$ Hz), 129.6 ($\mathrm{C_6H_5}$, d, $J_{\mathrm{C-P}} = 3$ Hz), 130.4 ($\mathrm{C_6H_5}$, d, $J_{\mathrm{C-P}} = 10$ Hz), 137.4 ($\mathrm{C_6H_5}$, d, $J_{\mathrm{C-P}} = 42$ Hz).

(η-$\mathrm{C_5Me_5}$)Ru(CO)$_2$PEt$_3$$^+BF_4$$^-$ (4). This complex was prepared in a fashion analogous to **1**. The isolated yield of the complex by using 0.5 g (0.98 mmol) of (η-$\mathrm{C_5Me_5}$)Ru(CO)(PEt$_3$)I was 0.42 g (86%).

Anal. Calcd for $\mathrm{C_{18}H_{30}BF_4O_2PRu}$: C, 43.43; H, 6.0. Found: C, 43.55; H, 6.03. IR ($\mathrm{CH_2Cl_2}$): 2045, 1998 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 1.10 ($\mathrm{pCH_2}\mathit{CH}_3$, dt, $J_{\mathrm{P-H}} = 16$, $J_{\mathrm{H-H}} = 8$ Hz), 1.96 ($\mathrm{P}\mathit{CH}_2\mathrm{CH_3}$, dq, $J_{\mathrm{P-H}} = 8$, $J_{\mathrm{H-H}} = 8$ Hz), 2.08 ($\mathrm{C_5Me_5}$, $J_{\mathrm{P-H}} = 2$ Hz). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 10.2 ($\mathrm{C_5}\mathit{Me}_5$), 7.8 ($\mathrm{CH_2}\mathit{CH}_3$), 19.2 ($\mathit{CH}_2\mathrm{CH_3}$, d, $J_{\mathrm{C-P}} = 32$ Hz) 103.1 ($\mathit{C}_5\mathrm{Me_5}$), 198.9 (CO, d, $J_{\mathrm{C-P}} = 15$ Hz).

(η-$\mathrm{C_5Me_5}$)Ru(CO)$_2$CH$_2$OH (7). (η-$\mathrm{C_5Me_5}$)Ru(CO)$_3$$^+BF_4$$^-$ (1) (0.50 g, 1.2 mmol) was added to a −50 °C solution of $\mathrm{NaBH_3CN}$ (0.225 g, 3.6 mmol) in 20 mL of degassed methanol. The resulting mixture was allowed to warm to room temperature, and then it was stirred for 2 h. The methanol was stripped, and the residue was extracted with pentane (2 × 15 mL). Cooling the pentane to −78 °C resulted in formation of white crystals of (η-$\mathrm{C_5Me_5}$)Ru(CO)$_2$CH$_2$OH (0.24 g, 60%).

Anal. Calcd for $\mathrm{C_{13}H_{18}O_3Ru}$: C, 48.23; H, 5.56. Found: C, 48.34; H, 5.60. IR ($\mathrm{C_6D_6}$): 1997, 1932 cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$) δ 4.96 ($\mathrm{CH_2}$, d, $J = 6$ Hz), 1.68 ($\mathrm{C_5Me_5}$), 0.88 (−OH, t, $J = 6$ Hz). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 10.3 ($\mathrm{C_5}\mathit{Me}_5$), 55.8 ($\mathit{CH}_2\mathrm{OH}$), 100.8 ($\mathrm{C_5Me_5}$), 205.0 (CO).

The mother liquor from the above crystallization contained (η-$\mathrm{C_5Me_5}$)Ru(CO)$_2$H (**9**) and (η-$\mathrm{C_5Me_5}$)Ru(CO)$_2$CH$_2$OCH$_3$ (**8**). Complex **9** was identified from its IR and ^{1}H NMR spectra. IR ($\mathrm{C_6H_6}$); 2000, 1941 cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.74 ($\mathrm{C_5Me_5}$), −10.2 (RuH, s). Complex **8** was identified from the similarity of its IR and ^{1}H NMR spectra to (η-$\mathrm{C_5H_5}$)Ru(CO)$_2$CH$_2$OCH$_3$. IR ($\mathrm{CH_2Cl_2}$): 2000, 1935 cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 4.60 ($\mathrm{CH_2}$, s), 3.28 ($\mathrm{CH_3}$, s), 1.65 ($\mathrm{C_5Me_5}$, s).

Attempted Reaction of 7 with Carbon Monoxide. Complex **7** (300 mg) was dissolved in 50 mL of degassed THF, and the solution was placed in an autoclave in a glass liner under an argon atomsphere. The solution was heated to 80 °C and then submitted to 4000 psi of CO for 3 h. The resulting solution was evaporated to dryness on an oil pump, and the residue was dissolved in benzene-d_6. ^{1}H NMR and IR analyses showed that most of the starting material was recovered. A small amount of hydride **9** and pentamethylcyclopentadienyl ruthenium carbonyl dimer was also observed.

Preparation of [Ph$_3$PCuH]$_6$. (Nitrato)bis(triphenylphosphine)copper (I) (17.3 g, 26 mmol) and THF (80 mL) were added to an 8-oz Fischer-Porter bottle equipped with a magnetic spin bar. The mixture was degassed, and potassium *tert*-butoxide (2.98 g, 26 mmol) was added as a solid under a stream of argon while the mixture was stirred. The bottle was sealed, flushed with hydrogen, and pressurized with hydrogen (80 psi). The mixture was stirred under this pressure for 16 h. After 1 h, the color of the mixture was dark red. The mixture was transferred by canula to a 500-mL flask, and the solvent was evaporated. The residue was extracted with 250 mL of toluene and filtered through Celite. The filtrate was concentrated to about 100 mL (or until solids began to form), and then it was layered with acetonitrile (300 mL). After the layers had mixed, the product was collected by filtration (under argon), washed with acetonitrile (50 mL), and dried under vacuum (yield 5.4 g (64%)).

Synthesis of Formyl Complexes. Preparation of ($\mathrm{C_5Me_5}$)Ru(CO)$_2$CHO (10). [Ph$_3$PCuH]$_6$ (238 mg, 0.1 mmol), (η-$\mathrm{C_5Me_5}$)Ru(CO)$_3$$^+BF_4$$^-$ (50 mg, 0.1 mmol), and 9,10-dihydroanthracene (169 mg, 0.9 mmol) were added to a 25-mL Schlenk flask equipped with a magnetic spin bar. The flask was connected to a THF still, chilled to −78 °C, and flushed with argon. THF (7 mL) was distilled onto the mixture. The flask was disconnected from the still, again flushed with argon by evacuation and refilling, and allowed to warm to room temperature while the mixture was stirred. When the temperature approached 20 °C, the red color of the [Ph$_3$PCuH]$_6$ gradually dissipated and a yellow solid precipitated, which indicated the formation of (Ph$_3$PCu)$_6$H$_5$$^+BF_4$$^-$. The IR spectrum of the solution displayed absorptions at 2020 (s), 1965 (s), and 1642 (m) cm^{-1}. The solution was transferred to a small, three-neck flask equipped with a vacuum adapter which was then filled with argon. The solvent was evaporated, and the residue was taken up in degassed $\mathrm{C_6D_6}$. The $\mathrm{C_6D_6}$ solution was filtered through cotton into a syringe and was transferred to an NMR tube filled with argon. The ^{1}H NMR spectrum was recorded and displayed absorptions of (δ) 1.5 (s, 15 H) and 14.0 (s, 1 H).

The ^{1}H NMR spectrum of the yellow solid (400 MHz, $\mathrm{CD_2Cl_2}$, δ) displayed absorptions at 7.2 (m), 6.8 (t), 4.1 (heptet). The integration of the aromatic signals to the heptet was roughly 20:1. Anal. Calcd for $\mathrm{C_{108}H_{90}BCu_6F_4P_6}$: C, 63.53; H, 4.41; Cu, 18.68; P, 9.12; B, 0.54. Found: C, 57.59; H, 4.24; Cu, 17.50; B, 0.64; P, 8.20. ESCA analysis: Cu/P ratio of 1:1, Cu/F ratio of 3:2. Reaction of the cationic complex with $\mathrm{LiHBEt_3}$ at 0 °C regenerates the neutral copper hydride [Ph$_3$PCuH]$_6$.

The procedure just discussed was repeated, except that hydroquinone (110 mg) was used in place of 9,10-dihydroanthracene. The IR spectrum consisted of the ruthenium hydride (~60%) and the formyl complex (~40%).

Reaction of [Ph$_3$PCuH]$_6$ with (η-$\mathrm{C_5Me_5}$)Ru(CO)$_2$PMe$_2$Ph$^+$I$^-$ (2). [Ph$_3$PCuH]$_6$ (300 mg, 0.15 mmol), (η-$\mathrm{C_5Me_5}$)Ru(CO)$_2$PMe$_2$Ph$^+$I$^-$ (**2**) (86 mg, 0.15 mmol), and 9,10-dihydroanthracene (138 mg, 0.77 mmol) were added to a 25-mL, three-neck flask equipped with a magnetic spin bar, rubber septum, and vaccum adapter. The mixture was chilled to 0 °C, and THF (5 mL) was distilled into the flask. The mixture was degassed by repeatedly filling the flask with argon and then evacuating it. After the mixture was degassed, it was stirred as it warmed to room temperature and then was stirred for 1 h at room temperature. The IR spectrum of the solution contained absorptions at 1932 (vs), 1915 (m), and 1601 (m) cm^{-1}.

The solvent was evaporated to dryness, and the residue was triturated with degassed $\mathrm{C_6D_6}$. The $\mathrm{C_6D_6}$ solution was transferred by canula to a pipet containing a plug of glass wool and was filled with argon. The solution was filtered into an NMR tube. The ^{1}H NMR spectrum displayed absorption at δ 1.4 (d, 15 H), 1.7 (d, 7 H), and 14.8 (d, 1 H). The phosphinomethyl groups were spread between δ 1 and 2 (detailed below).

LiBH(Et)$_3$. Several attempts to synthesize (η-$\mathrm{C_5Me_5}$)Ru(CO)$_2$CHO (**10**) from (η-$\mathrm{C_5Me_5}$)Ru(CO)$_3$$^+BF_4$$^-$ (**1**) and LiBH(Et)$_3$

were made. In each case a room temperature workup led to isolation of mixtures of (η-C_5Me_5)Ru$(CO)_2$H (**9**) and [(η-C_5Me_5)Ru$(CO)_2]_2$. When 1 equiv of LiHB$(Et)_3$ in THF was added to a −78 °C slurry of **1** in THF, a clear pale yellow solution was formed. When an aliquot was withdrawn and an IR spectrum immediately recorded (degassed, room temperature), peaks were observed (THF) at 2002, 1940, 1925, and 1565 cm^{-1}. Over a 30-min period, the peaks at 1925 and 1565 cm^{-1} diminished while those at 2002 and 1940 cm^{-1} grew. Presumably, the BEt_3 adduct of the formyl was formed and was unstable at room temperature.

$NaBH_4$. $NaBH_4$ (15 mg, 0.39 mmol) in 1 mL of 1:1 THF/H_2O was added to a room temperature slurry of (η-C_5Me_5)Ru$(CO)_2$-$(PMe_2Ph)^+I^-$ (**2**) in THF under an argon atomsphere. Immediate bubbling took place, and a clear, pale yellow solution was formed. The THF/H_2O was removed by vacuum, and the crude material remaining was treated with 3 mL of toluene. Filtration of the solution followed by slow addition of hexane (15 mL) by vacuum transfer resulted in formation of pale yellow crystals of (η-C_5Me_5)Ru(CO)$(PhPMe_2)$CHO (**11**) (150 mg, 95%).

Anal. Calcd for $C_{20}H_{27}O_2PRu$: C, 55.67; H, 6.26. Found: C, 55.23; H, 6.27. IR (THF): 1934, 1601 cm^{-1}. ^1H NMR (C_6D_6): δ 1.47 (C_5Me_5, d, J_{P-H} = 1.5 Hz), 1.4–2.0 (PMe_2, m), 7.5 (C_6H_5, m), 14.75 (CHO, d, J_{P-H} = 2 Hz). ^{13}C NMR (C_6D_6) δ 9.91 ($C_5\mathit{Me}_5$), 15.27 (PMe, d, J_{C-P} = 31.7 Hz), 18.72 (PMe, d, J_{C-P} = 35.4 Hz), 98.88 (C_5Me_5), 223.66 (CO, d, J_{C-P} = 18.3 Hz), 271.83 (CHO, d, J_{C-P} = 14.6 Hz).

(η-C_5Me_5)Ru(CO)(PEt_3)CHO (**12**) was synthesized in a similar manner but was never obtained in crystalline form. Air sensitivity did not allow purification of the complex by other methods; therefore, a good elemental analysis was not obtained.

IR (C_6D_6): 1933, 1601 cm^{-1}. ^1H NMR (C_6D_6): δ 0.86 ($PCH_2\mathit{CH}_3$, dt, J_{H-H} = 7.9 Hz, J_{P-H} = 15.8 Hz), 1.51 ($P\mathit{CH}_2CH_3$, q, J_{H-H} = 7.9 Hz), 1.72 ($C_5\mathit{Me}_5$, d, J_{P-H} = 2 Hz), 14.73 (RuCHO, d, J_{P-H} = 2 Hz). ^{13}C NMR (C_6D_6): δ 8.29 ($PCH_2\mathit{C}H_3$), 10.04 ($C_5\mathit{Me}_5$), 18.20 ($P\mathit{C}H_2CH_3$, d, J_{C-P} = 30 Hz), 98.35 (C_5Me_5), 207.40 (CO, J_{C-P} = 18 Hz), 253.30 (CHO, J_{C-P} = 15 Hz).

Decomposition of (η-C_5Me_5)Ru(CO)(PMe_2Ph)CHO (11). (η-C_5Me_5)Ru$(CO)_2PMe_2Ph^+I^-$ (80 mg, 0.14 mmol) and THF (3 mL) were added to a 25-mL, three-neck flask equipped with a magnetic spin bar, vacuum adapter, and rubber septum. The mixture was degassed, $NaBH_4$ (12 mg, 0.4 mmol) was dissolved in degassed THF (0.75 mL), and water (0.1 mL) was added. The mixture was stirred for 8 min. The solvent was evaporated to dryness, and the residue was triturated with degassed C_6D_6 (1 mL) and was filtered through cotton into a 2-mL syringe. One-half of the solution was transferred to an NMR tube containing 9,10-dihydroanthracene (63 mg, 0.35 mmol), and the other half was transferred to an empty NMR tube. The two solutions were frozen, and the tubes were sealed under vacuum. The initial ^1H NMR spectra showed the formyl complex as the only compound present (other than 9,10-dihydroanthracene) in both solutions. The two tubes were placed in a constant temperature bath monitored at 40 °C. Periodically the tubes were removed and quenched by immersion in an ice/salt mixture so that their ^1H NMR spectra could be recorded. Spectra were recorded after 3, 8, 18, 33, and 60 min. After 60 min, the sample which did not contain 9,10-dihydroanthracene had almost completely decomposed into a mixture of (η-C5Me5)Ru$(CO)_2$H (**9**) and (η-C_5Me_5)Ru(CO)(PMe_2Ph)H (**13**), whereas the sample containing 9,10-dihydroanthracene showed no appreciable decomposition. Heating was continued until the formyl complex in the sample containing 9,10-dihydroanthracene was almost completely decomposed. This operation required 14 days. The decomposition products were still a 1:1 mixture of **9** and **13**. Repeating these experiments with pure crystalline **11** gave analogous results.

Decomposition of 11 in the Presence of (η-C_5R_5)Ru$(CO)_2$I (R = Me, 5; R = H, 17). In a dry box, 16 (0.04 mmol), 20 (0.05 mmol), and 20 mg of formyl complex **11** were weighed into three separate Schlenk tubes containing 15 (0.04 mmol), 58 (0.14 mmol), and 116 mg (0.28 mmol) of **5** respectively. The Schlenk tubes were connected to an argon line outside the box, and 3 mL of degassed bezene was added to each mixture. The solutions were stirred overnight and then were heated to 65 °C for 15 min to ensure full decomposition of the formyl complex. The benzene was removed by vacuum pump, and the residue of each reaction was dissolved in CD_2Cl_2. ^1H NMR showed a ratio of **2** to **3** of 0.2, 0.6, and 2.5, respectively, as products in the three reactions. The only hydride observed in all three reactions was (η-C_5Me_5)Ru-$(CO)_2$H (**9**).

The above reaction was repeated wtih formyl complex **11** (20 mg, 0.05 mmol) and (η-C_5H_5)Ru$(CO)_2$I (**17**) (18 mg, 0.05 mmol) as reactants. The observed ratio of **2** to **3** was 7. The only hydride observed in this reaction was (η-C_5H_5)Ru$(CO)_2$H (δ −10.9 in ^1H NMR) which was identified by comparison of the ^1H NMR spectrum with that of an authentic sample synthesized by reduction of $\eta C_5Ru(CO)_3{}^+BF_4{}^-$.[23]

Crystallographic Summary for (η-C_5Me_5)Ru(CO)-(PMe_2Ph)CHO (11). Single crystals of **11** were obtained by slow diffusion of hexane into a toluene solution of **11** cooled to −78 °C. Pertinent crystal data and all the details of data collection were listed in the crystal structure analysis report. Least-squares refinement of the cell dimensions was based on 15 computer-centered reflections. Intensity data were collected with the use of the ω scans on a computer-controlled four-circle Nicolet autodiffractometer with Mo Kα radiation (λ = 0.71073 Å). The intensity data were reduced to relative squared amplitudes, $[F_o]^2$, by means of standard Lorentz and polarization corrections. Of the 4730 reflections collected, 3498 are considered observed by applying the rejection criterion $I < 3\ \delta(I)$ where $\delta(I)$ where $\delta\ (I)$ is the standard deviation in intensity computed from $\delta^2(I) = C_t + B/k^2$, C_t is the total count for scanning, k is the ratio of scanning time to total background time (in this case $k = {}^1/_2$), and B is the total background count. The six standard reflections, monitored every 300 reflections collected, did not vary significantly in intensity during data collection.

The atomic positons of all non-hydrogen atoms were found by using heavy-atom Patterson techniques. The hydrogen atomic positions were found by using standard difference Fourier techniques or were generated by using idealized sp^2 or sp^3 hybridization and a C–H bond length of 0.95 A. The hydrogen atom of the formyl ligand was refined as a normal isotropic atom. The structure was initially refined by using cascade block diagonal least-squares procedures with minimization of the function $\sum\omega([F_0] - [F_c])^2$ (where $\omega = 1/\delta_F{}^2$). The final cycles of unit-weighted full-matrix least-squares refinement, which employs anisotropic thermal parameters for non-hydrogen atoms, isotropic thermal parameters for hydrogen atoms, and anomalous dispersion corrections, converge to give final values of 0.029 and 0.028 for R_1 and R_2, respectively.

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Registry No. **1**, 86853-54-5; **2**, 88296-33-7; **3**, 103817-62-5; **4**, 103817-64-7; **5**, 86862-65-9; **6**, 103817-65-8; **7**, 86853-55-6; **8**, 86853-57-8; **9**, 82728-97-0; **10**, 88296-34-8; **11**, 88296-35-9; **12**, 103817-66-9; **13**, 88296-36-0; **17**, 31781-83-6; [(η-C_5Me_5)Ru$(CO)_2]_2$, 70669-56-6; $Ru_3(CO)_{12}$, 15243-33-1; C_3Me_5H, 41539-64-4; $[Ph_3PCuH]_6$, 33636-93-0; $(Ph_3P)_2Cu(NO_3)$, 14494-93-0; (η-C_5H_5)Ru$(CO)_2$H, 57349-59-4.

Supplementary Material Available: Experimental parameters for data collection, summary of least-squares refinement cycles, positional and thermal parameters (isotropic) (Table I), anisotropic thermal parameters (Table II), calculated positions for hydrogen atoms (Table III), and nonbonded distances for the structure of **11** (17 pages); a listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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