Stereochemical Studies on the Interconversion of Alkylidenecarbene, Carbene, and Alkyl Ligands in Chiral Cyclopentadienyl Ruthenium Complexes†

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Pseudotetrahedral (S,S)-$(\eta$-$C_5H_5)$Ru{$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}Cl (**1**), (S_{Ru},R_C)-**1'a**, and (R_{Ru},R_C)-$(\eta$-$C_5H_5)$Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}Cl (**1'b**) have been used to investigate the stereochemistry of alkylidenecarbene and carbene formation. Depending on conditions **1'a** and **1'b** can react stereospecifically with terminal acetylenes, in the presence of halogen scavengers, to give the corresponding alkylidene complexes [{Ru}=C=CHR]PF_6 (R = C_6H_5, **2'a** and **2'b**; R = CH_3, **6'a** and **6'b**). Retention of configuration at ruthenium was confirmed by an X-ray crystal structure of **6'a**. **2'a** and **2'b** are converted with base to the corresponding phenylacetylide complexes {Ru}C≡CC_6H_5 (**5'a** and **5'b**), which, in turn, regenerated **2'a** and **2'b** on reaction with HPF_6. Neither reaction changes the stereochemistry at the metal. **2'a** and **2'b** react further with CH_3OH stereospecifically and with retention of the configuration at ruthenium to give the methoxycarbene complexes [{Ru}=$C(OCH_3)CH_2C_6H_5$]PF_6 (**3'a** and **3'b**). The crystal structure of **3'b** has also been determined. **3'a** and **3'b** react with $LiAlH_4$ in THF at low temperature to give the 2-phenylethyl complexes {Ru}C-$H_2CH_2C_6H_5$ (**4'a** and **4'b**) with retention of configuration. Labeling studies have demonstrated that the two hydrogen atoms of the new formed methylene group arise from $LiAlH_4$. The summary of crystal data is as follows. For **6'a**: a = 11.469 (4) Å, b = 14.976 (4) Å, and c = 20.696 (7) Å with Z = 4 in space group $P2_12_12_1$ (no. 19). For **3'b**: a = 12.555 (4) Å, b = 12.651 (4) Å, and c = 24.198 (8) Å with Z = 4 in space group $P2_12_12_1$ (no. 19).

The stereochemical fate of the metal atom in the course of simple reactions of transition-metal organometallic compounds has recently[1] aroused much interest[2] due to the increasing importance of asymmetric catalysis using homochiral transition-metal complexes[3] and to the discovery of stereospecific transformations of organic ligands within transition metal complexes which can be useful for organic synthesis.[4]

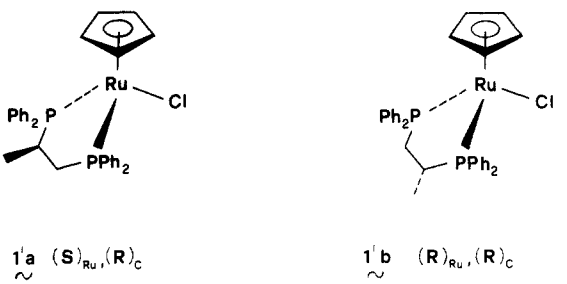
Alkylidenecarbene and carbene complexes of cyclopentadienylruthenium(II) derivatives are readily accessible.[5] If these ligands have different substituents, they are two-dimensional chiral simplexes[6] (i.e., they are prochiral), and their reactions can, therefore, be used to investigate asymmetric induction by chiral center(s) on the ligand and/or on the metal. Rhenium complexes containing such ligands have been recently studied[7] and have shown interesting phenomena in the transmission of the chiral information by the metal.

We have recently synthesized chiral complexes of the type $(\eta$-$C_5H_5)$Ru{$Ph_2PCHRCHR'PPh_2$}X, in which chiral centers are located on the metal atom and/or on the diphosphine ligand.[8] We report here on the stereochemical course of some reactions connected with the formation and the transformation of complexes containing alkylidenecarbene and carbene moieties starting from the above complexes. Some results have appeared in a preliminary form.[9]

Results

The reactions reported in Scheme I have been carried out starting with[8] (S,S)-$(\eta$-$C_5H_5)$Ru{$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}Cl (**1**) as well as with (S_{Ru},R_C)-**1'a**, and (R_{Ru},R_C)-$(\eta$-$C_5H_5)$Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}Cl (**1'b**)

Chart I



1'a $(S)_{Ru},(R)_C$ **1'b** $(R)_{Ru},(R)_C$

(Chart I). Typical NMR parameters of the reaction products are reported in Table I.

† Dedicated to Professor Piero Pino on the occasion of his 65th birthday.

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Scheme I

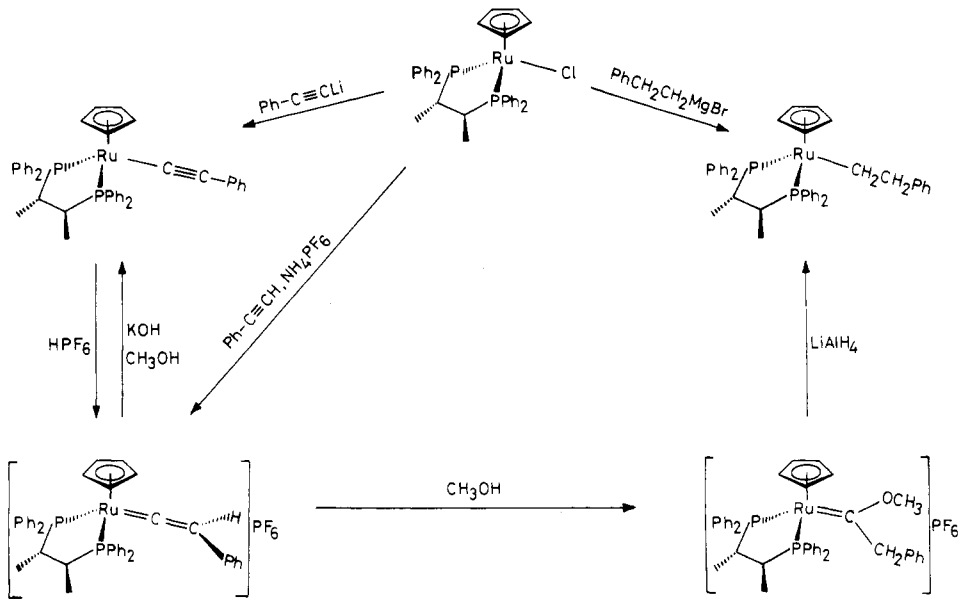

Table I. Some NMR Parameters of the Complexes Investigated[a]

	^{1}H		^{31}P			^{13}C	
complex	Cp	H or OCH_3	P_A	P_B	J_{P-P}	Cp	[Ru]=C
2	5.17	4.62	76.6	71.5	34.2	93.6	354
2'a	5.44	4.50	80.0	61.0	27.9	92.4	355
2'b	5.32	3.60	83.7	63.5	29.3	93.4	354
6'a	5.16	5.02	83.1	67.9	25.8	92.0	347
6'b	5.15	3.89	90.7	74.1	23.8	92.6	347
3	5.06	2.98	89.3	80.6	37.8	nd	nd
3'a	5.03	2.86	92.2	67.6	32.8	nd	nd
3'b	5.08	3.01	84.0	76.6	33.1	nd	nd
4	4.62		97.0	83.1	42.0	84.0	
4'a	4.77		100.4	74.3	35.7	82.9	
4'b	4.66		89.6	82.4	36.3	83.5	
5	4.49		89.1	77.1	34.2	84.1	
5'a	4.67		91.7	68.8	31.1	nd	
5'b	4.62		89.0	79.4	24.7	nd	

[a] Chemical shifts in δ; coupling constants in Hz.

(a) Formation of the Benzylidenecarbene (and of the Ethylidenecarbene) Complexes. The reaction of **1** with $C_6H_5C{\equiv}CH$ in boiling methanol, using NH_4PF_6 or KPF_6 as the halogen scavenger, following the procedure described in the literature[5c] for the analogous diphos complex (diphos is 1,2-ethanediylbis(diphenylphosphine)) is not chemoselective. In fact (S,S)-$[(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH(CH_3)PPh_2\}\{C{=}CHC_6H_5\}]PF_6$ (**2**) forms together with about 10–15% of the corresponding methoxycarbene complex (S,S)-$[(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH(CH_3)PPh_2\}\{C(OCH_3)CH_2C_6H_5\}]PF_6$ (**3**). The analogous reaction of either **1'a** or **1'b** under the same conditions shows comparable chemoselectivity and is neither stereospecific nor stereoselective. Almost equimolar amounts of the rose-pink benzylidenecarbene complexes (S_{Ru},R_C)-**2'a** and (R_{Ru},R_C)-$[(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH_2PPh_2\}\{C{=}CHC_6H_5\}]PF_6$ (**2'b**) are formed which are contaminated with about 15% of the methoxycarbene complexes (S_{Ru},R_C)-(**3'a**) and (R_{Ru},R_C)-$[(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH_2PPh_2\}\{C(OCH_3)CH_2C_6H_5\}]PF_6$ (**3'b**) as revealed by ^{1}H and ^{31}P NMR spectroscopy on the crude reaction mixture. In contrast the chemoselective transformation of **1'a** and **1'b** (which gives rise to **2'a** and **2'b**, respectively) are completely stereospecific when carried out at room temperature for a period of 2.5–3 h. Neither **2'a** nor **2'b** gave crystals suitable for X-rays analysis, so we carried out the same reaction with propyne as the acetylenic substrate. Analogous to the previous reactions, the corresponding ethylidenecarbene complexes **6'a** and **6'b** were stereospecifically formed. The similarity of the ^{31}P NMR parameters of **2'a** to **6'a** and of **2'b** to **6'b** strongly implies the same stereochemical pathway for the reactions with the two different acetylenes, as logically expected. The crystal structure determination (see infra) of **6'a** shows retention of configuration at the ruthenium atom (when compared with the precursor **1'a**[8] during the formation of the alkylidenecarbene complexes. Furthermore, the conformation of the alkylidenecarbene[10] ligand is the one in which the plane of the vinylidene ligand is nearly orthogonal to the plane containing the centroid of the cyclopentadienyl ligand, the ruthenium atom, and the un-

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substituted carbon atom of the ethylidene carbene ligand. Such a conformation (which is the one also present in solution)[11] implies the possible existence of two diastereomeric rotamers, which have in fact been identified through low-temperature ^{31}P NMR spectroscopy.[11]

(b) Formation of the Methoxybenzylcarbene Complexes. **2** reacts in boiling methanol over a period of more than 24 h to give yellow crystals of the corresponding methoxybenzylcarbene complex **3**.[5b] Use of CH_3O^2H gives $[^2H_2]$-**3**, which is completely and only deuterated at the methylenic benzylic carbon atom.[12] The analogous reactions of either **2'a** or **2'b** with unlabeled methanol give stereospecifically **3'a** and **3'b**, respectively, according to ^1H and ^{31}P NMR on the crude reaction product (Table I). The assignment of the absolute configuration at the ruthenium atom follows from the crystal structure determination on **3'b** (vide infra).

(c) Formation of the 2-Phenylethyl Complexes. The methoxycarbene complex **3** does not show the typical reactivity of Fischer-like carbene complexes toward hydride nucleophiles.[13] We expected attack at the carbene carbon atom to form an α-methoxyalkyl complex.[14] In fact, **3** reacts with $LiAlH_4$ in boiling THF to give two products in a 65:35 molar ratio as determined by NMR of the crude product mixture. The more abundant product forms in almost quantitative yield (>95%) when the reaction is carried out at −70 °C in the same solvent. Elemental and NMR analysis showed this product is (S,S)-$(\eta$-$C_5H_5)$Ru{$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}$CH_2CH_2C_6H_5$ (**4**); the other product formed at higher temperature has not yet been identified. The analogous reaction with $LiAl^2H_4$ gives $[^2H_2]$-**4** which is completely and exclusively deuterated at the carbon atom (of the 2-phenylethyl group) directly bound to ruthenium. Reaction of either **3'a** or **3'b** under the same reaction conditions gave the corresponding 2-phenylethyl complexes (S_{Ru},R_C)-**4'a** and (R_{Ru},R_C)-$(\eta$-$C_5H_5)$Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}$CH_2CH_2C_6H_5$ (**4'b**) with selectivity higher than 90%. These reactions are completely stereospecific according to NMR analysis of the crude products. **4'a** and **4'b** are also stereospecifically formed with about 70% chemoselectivity in the reaction of either **1'a** or **1'b** with $C_6H_5CH_2CH_2MgBr$. Byproducts in these alkylation reactions include the corresponding hydrido complexes[2i] (S_{Ru},R_C)-**7'a** and (R_{Ru},R_C)-$(\eta$-$C_5H_5)$Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}H (**7'b**) which also form stereospecifically. We have previously shown that such alkylation reactions take place with retention of configuration at ruthenium,[15] and we may therefore conclude that in the reaction of **3'a** and **3'b** with $LiAlH_4$ the configuration at ruthenium is also retained.

(d) Interconversion of Benzylidenecarbene and Phenylethynyl Complexes. The benzylidenecarbene complexes **2**, **2'a**, and **2'b** are easily deprotonated[5a,b,d] when treated with KOH in methanol quantitatively giving rise to the corresponding phenylethynyl complexes. When either **2'a** or **2'b** are used as starting materials, (S_{Ru},R_C)-**5'a** and (R_{Ru},R_C)-$(\eta$-$C_5H_5)$Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}C≡CC_6H_5 (**5'b**) are formed in completely stereospecific reactions. The reaction of either **1'a** or **1'b** with $C_6H_5C{\equiv}CLi$ to give **5'a** and **5'b**, respectively, is also stereospecific. The stereochemical course of this last reaction is expected to

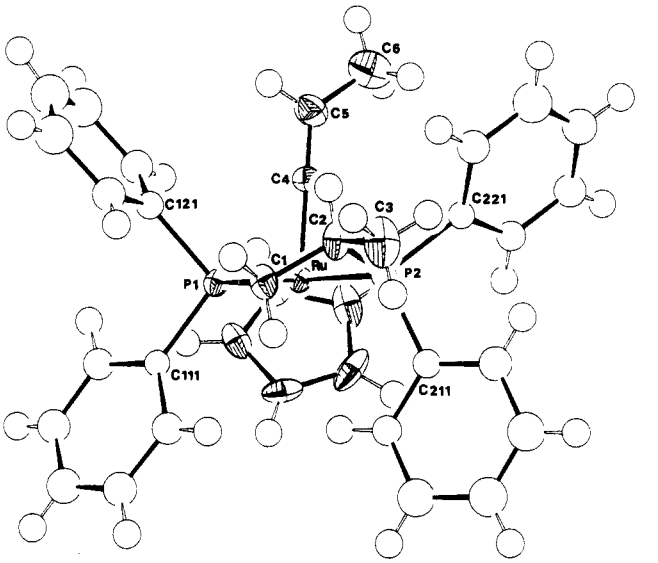

Figure 1. View of the cation (S_{Ru},R_C)-[$(\eta$-$C_5H_5)$Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}{C=$CHCH_3$}]$^+$ (**6'a**) in its absolute configuration.

Table II. Distances (Å) from the P_1-Ru-P_2 Plane and Torsion Angles (deg)[a] Defining the Conformation of the Phenyl Rings for Complexes 3'b and 6'a

	6'a		3'b	
atom(s)	dist	angle	dist	angle
C(1)	0.04		0.42	
C(2)	−0.63		−0.33	
C(3)	−0.54		−0.14	
C(111)	1.38		1.14	
C(121)	−1.43		−1.55	
C(211)	1.61		1.56	
C(221)	−1.01		−1.28	
Ru-P(1)-C(111)-C(11*Z*)		−79.6		−60.4
Ru-P(1)-C(121)-C(12*Z*)		22.8		−36.9
Ru-P(2)-C(211)-C(21*Z*)		−68.6		70.8
Ru-P(2)-C(211)-C(22*Z*)		−29.5		40.0

[a] *Z* takes the value of 6 or 2 depending on which ortho carbon atom (with respect to C_{ipso}) is closer to the ruthenium atom.

Table III. Bond Distances for Complexes 3'b and 6'a

	3'b	6'a
Ru-P(1)	2.286 (4)	2.297 (2)
Ru-P(2)	2.299 (4)	2.289 (2)
Ru-C/C(4)	1.93 (2)	1.839 (10)
Ru-Cp(mean)	2.27	2.24
Cp-Cp(mean)	1.40	1.39
P(1)-C(1)	1.86 (1)	1.83 (1)
P(1)-C(111)	1.79 (1)	1.80 (1)
P(1)-C(121)	1.81 (1)	1.84 (1)
P(2)-C(2)	1.85 (1)	1.83 (1)
P(2)-C(211)	1.84 (1)	1.79 (1)
P(2)-C(221)	1.84 (1)	1.83 (1)
C(1)-C(2)	1.54 (2)	1.49 (1)
C(2)-C(3)	1.53 (2)	1.54 (1)
C-O	1.38 (2)	
O-C(4)	1.45 (2)	
C-C(5)	1.46 (2)	
C(4)-C(5)		1.25 (1)
C(5)-C(6)		1.41 (2)

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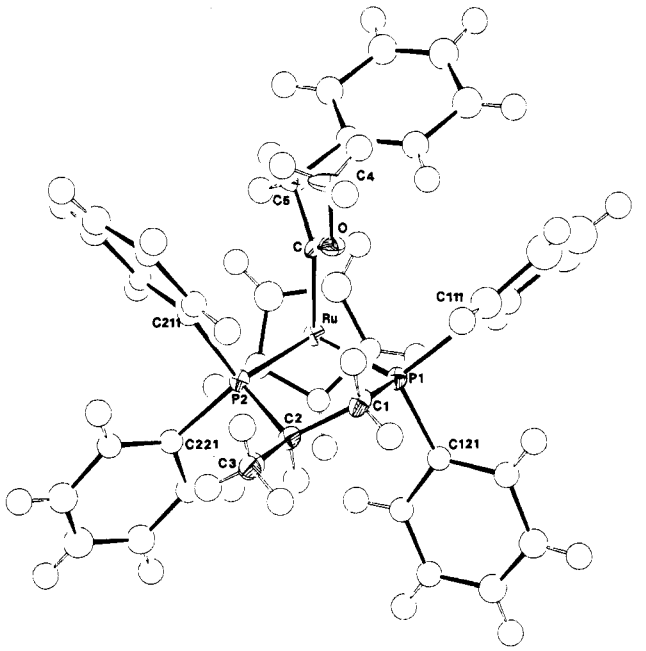

Figure 2. View of the cation (R_{Ru},R_C)-$[(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH_2PPh_2\}\{C(OCH_3)CH_2Ph\}]^+$ (**3′b**) in its absolute configuration.

occur with retention of configuration at the metal, as noted for the alkylation with Grignard reagents.[15] Therefore the configuration at the metal must also be retained in the deprotonation reaction. The phenylethynyl complexes can be reprotonated back to the benzylidenecarbene complexes by using HPF_6 or HBF_4. As expected, the reaction is stereospecific and takes place with retention of configuration at the metal.

Crystal Structure of 3′b and 6′a. Views of the (S_{Ru},R_C)-$[(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH_2PPh_2\}\{C{=}CHCH_3\}]PF_6$ (**6′a**) and (R_{Ru},R_C)-$[(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH_2PPh_2\}\{C(OCH_3)CH_2Ph\}]PF_6$ (**3′b**) cationic complexes, showing their absolute configurations, are given in Figures 1 and 2, respectively. The ruthenium atoms in the two compounds have different absolute configurations. This results in different arrangements of the λ conformation and the phenyl rings of the two metallodiphosphine moieties (Table II). The bonding parameters within the two cations are reported in Tables III and IV. With the exception of the Ru–C bond lengths and the orientation of the carbene units, which deserve some comments, all the other interactions are similar and comparable to those found in the related $(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH_2PPh_2\}L]^{n+}$ species (n = 0, L = Cl,[8] $SnCl_3$,[17] CH_3;[15] n = 1, L = CH_3CN[18]).

It has been recently pointed out[19] that for metal carbene complexes [LnM–CRR′) the metal–carbon bond order, as indicated by the M–C length, depends on the relative π-donor abilities of all the carbene atom substituents. In particular, the different behavior of the $[(CO)_5Cr]$ fragment, which interacts weakly with the carbene atom but allows it to interact strongly with R or R′, and that of the $[(\eta\text{-}C_5H_5)Mn(CO)_2]$ fragment, which being a good π-donor does the opposite, has been stressed. A pictorial representation of this observation can be obtained from a localized molecular orbital analysis as in ref 20.

Table IV. Bond Angles (deg) for Complexes 3′b and 6′a[a]

	3′b	6′a
P(1)–Ru–P(2)	83.4 (1)	83.5 (1)
P(1)–Ru–C/C(4)	90.8 (5)	93.8 (3)
P(1)–Ru–Cp*	128.4	125.5
P(2)–Ru–C/C(4)	89.6 (5)	85.4 (4)
P(2)–Ru–Cp*	129.2	130.2
Cp*–Ru–C/C(4)	122.7	125.2
Ru–P(1)–C(1)	110.8 (4)	109.5 (3)
Ru–P(1)–C(111)	117.6 (5)	115.7 (3)
Ru–P(1)–C(121)	118.3 (5)	118.3 (3)
C(1)–P(1)–C(111)	104.6 (7)	106.2 (5)
C(1)–P(1)–C(121)	101.9 (6)	104.3 (4)
C(111)–P(1)–C(121)	101.6 (6)	101.6 (4)
Ru–P(2)–C(2)	108.4 (4)	107.7 (3)
Ru–P(2)–C(211)	114.1 (5)	116.6 (3)
Ru–P(2)–C(221)	120.9 (5)	118.0 (4)
C(2)–P(2)–C(211)	110.4 (6)	106.8 (5)
C(2)–P(2)–C(221)	100.5 (6)	103.7 (4)
C(211)–P(2)–C(221)	101.5 (6)	102.8 (4)
Ru–C–C(5)	126 (1)	
Ru–C–O	119 (1)	
O–C–C(5)	115 (1)	
Ru–C(4)–C(5)		175 (1)
C(4)–C(5)–C(6)		128 (1)

[a] Cp* is the centroid of the $\eta\text{-}C_{55}H_5$ ligand.

The $(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH_2PPh_2\}$ fragment should have a π-donor ability more similar to that of $[(\eta\text{-}C_5H_5)Mn(CO)_2]$, and, therefore, for **3′b** we expect short Ru–C and "normal" C_{sp^2}–OCH_3 bond distances. For **6′a**, we would anticipate an even shorter Ru–C interaction due to the sp nature of the carbon atom.[21] Indeed the Ru–C bond distance in **6′a** is 1.839 (10) Å compared to 1.845 (7) Å for the similar complex[22] $[(\eta\text{-}C_5H_5)Ru\{P(CH_3)_3\}_2\{C{=}CHCH_3\}]^+$. However, the Ru–C bond length in **3′b** is longer at 1.92 (2) Å while a value of 2.169 (6) Å was found for the Ru–C single bond in $(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH_2PPh_2\}CH_3$.[15]

In **3′b** we have found the C(4),O,C(5) plane "coplanar" to that defined by Cp* (the centroid of the cyclopentadienyl ring), Ru, and C(4) atoms (dihedral angle 16°).[23] In contrast[10] the plane of the ethylidenecarbene ligand in **6′a** is "orthogonal" to the corresponding Cp*,-Ru,C(4) plane (dihedral angle 70°).

Discussion

The assignment of the absolute configuration at ruthenium for complexes **1′a**, **1′b**, **6′a**, **6′b**, **3′a**, and **3′b** follows from the crystal structure analyses carried out on **1′a**, **6′a**, and **3′b**. The assignment for complexes **2′a**, **2′b**, **4′a**, **4′b**, **5′a**, and **5′b** is based on the assumption that similar reactions have similar stereochemical outcome. In fact, we have previously found that the reaction of **1′a** and **1′b** with methylmagnesium bromide takes place stereospecifically with retention of the configuration at ruthenium.[15] The reasonable assumption that other metathesis reactions (such as those with $C_6H_5CH_2CH_2MgBr$ or $C_6H_5C{\equiv}CLi$) should also follow the same stereochemical course allows us to identify the absolute configuration at the metal for complexes **4′a**, **4′b**, **5′a**, and **5′b**. Similarly we assume the reaction of **1′a** and **1′b** with $CH_3C{\equiv}CH$ has the same stereochemical course as that with $C_6H_5C{\equiv}CH$, and

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therefore we can stereochemically identify **2'a** and **2'b**.

The formation of the alkylidenecarbene complexes from terminal acetylenes was expected, given the reports of the analogous behavior of the triphenylphosphine- and diphos-containing complexes.[5b] Previous work[24] suggests the most probable reaction pathway might involve (a) oxidative addition of the acetylene (possibly preceded by π-complex formation[25]) to form a hydrido alkynyl complex, (b) deprotonation to the neutral alkynyl complex, and (c) protonation at the substituted carbon atom of the alkynyl ligand. Recent theoretical calculations, however,[26] suggest a mechanism involving slippage of an η^2-coordinated alkyne to η^1-geometry, followed by hydrogen migration to the C_β carbon atom. The acidity of the hydrogen atom in the resulting alkylidenecarbene complex makes labeling experiments (e.g., with RC≡CD) meaningless, since alcoholic solvents must be used.

In the reaction, carried out in boiling methanol, between either **1'a** or **1'b** and phenylacetylene, complete epimerization at the ruthenium atom takes place. It should be noted, however, that both **2'a** and **2'b** must be optically stable under the reaction conditions used, since they react stereospecifically in boiling methanol (over a period of about 24 h) to give the corresponding methoxycarbene complexes **3'a** and **3'b**. Furthermore the stereochemical course of alkynyl complex protonation to the corresponding benzylidenecarbene complexes was found to take place stereospecifically with retention of configuration at the ruthenium atom. This is, in fact, to be expected if the proton attack takes place directly on the alkynyl ligand and does not involve the ruthenium atom. The aforementioned epimerization should therefore most probably take place at the level of η^2-acetylene complexes, if their further transformation is slow with respect to their formation. In fact, analogous olefin complexes[27] were found to be labile.

The stereochemical courses of the reactions of benzylidenecarbene complexes with basic methanol to form phenylacetylenic complexes are not surprising, since reagent attack would only be expected at the organic ligand. Less expected is the very chemoselective reaction of methoxybenzylcarbene complexes with $LiAlH_4$ at low temperature. Theoretical considerations[10b] and almost all literature[14] precedents suggest nucleophilic addition of the hydride to the carbon atom directly bound to ruthenium should take place. In fact, we carried out this reaction in an attempt to prepare secondary 1-methoxy-2-phenylethyl complexes and to study asymmetric induction as influenced by different configurations at the metal.[28] The reaction has precedent in the formation of the byproduct[29] $(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)C_2H_5$ (although in much lower yield) when the corresponding ethoxymethylcarbene complex is treated with $NaBH_4$ to give ~50% yield of the $(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)CH(OC_2H_5)CH_3$. Labeling studies in both our system and the iron case[29] have shown the two hydrogen atoms involved in transforming the carbene carbon atom into a methylene group arise from the metal hydride. This suggests that the observed transformation involves only the carbene ligand.

The simultaneous formation of the aforementioned ethyl- and (1-ethoxyethyl)iron complexes in the presence of excess $NaBH_4$ implies the ethoxyethyl complex is not a precursor to the ethyl complex. If this is also true for our complexes, then the formation of the methylene group should be a consequence of a nucleophilic substitution followed by a nucleophilic addition of the hydride. However, at least one other alternative appears possible, i.e., reduction[31] of a phenylacetyl complex formed by demethylation of the methoxycarbene ligand.[32,33] At the present, however, detailed mechanistic conclusions are not possible. Nevertheless this reaction allows us to obtain, in pure form, 2-phenylethyl complexes, which are not accessible by metathesis reactions of halide complexes with the Grignard reagent.

In the case of complex **4** the greater separation of ^1H NMR signals has allowed us, through a two-dimensional J-decoupled NMR experiment,[4] to identify H–H and P–H coupling constants for the methylenic protons of the carbon atoms bound to ruthenium. Vicinal H–H coupling constants (14 and 4 Hz) indicate, on the basis of the Karplus relationship, the expected antiperiplanar conformation around the CH_2–CH_2 bond. The similar P–H coupling constants (3.0, 8.8, 4.4, and 7.6 Hz, respectively) for those methylenic protons may again result from an almost antiperiplanar conformation around the P_2Ru–CH_2 bond, which might not have been expected.[34]

Experimental Section

General Procedure. All manipulations were performed under an atmosphere of nitrogen by using Schlenk techniques. Diethyl ether, tetrahydrofuran, pentane, benzene, and toluene were refluxed over $LiAlH_4$ and distilled under nitrogen. CH_2Cl_2 was purified by distillation from CaH_2. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker WH90 or AM300WB spectrometer. Infrared spectra were measured by using Perkin-Elmer 983 G and 177 instruments. Mass spectra were obtained on a Hitachi/Perkin-Elmer RMU-6L instrument. Chemicals were obtained from Fluka. Complexes **1**, **1'a**, and **1'b** were prepared according to previously[8] published procedures.

Preparation of $[(\eta\text{-}C_5H_5)Ru(diphosphine)(C{=}CHC_6H_5)]PF_6$ (2, 2'a, and 2'b). A 0.500-g (0.80-mmol) sample of finely ground **1** was stirred at room temperature with 0.450 g of NH_4PF_6 in 20 mL of CH_3OH containing 2 mL of phenylacetylene. After 2 h CH_3OH and most of the excess of phenylacetylene were removed under vacuum. The residue was washed three times with 20 mL of n-pentane, dried, and then dissolved in 20 mL of CH_2Cl_2. This solution was filtered through Celite and the CH_2Cl_2 subsequently evaporated under vacuum. The microcrystalline rose-pink complex **2** was washed again with *n*-pentane and dried; yield 604 mg (~90%). Analogously starting with 0.681 g (1.11 mmol) of **1'a** (diastereomeric purity 98 ± 2%), 0.64 g of KPF_6, 4 mL of phenylacetylene, and 20 mL of CH_3OH gave 0.869 g (95% yield) of **2'a** (diastereomeric purity 97 ± 2%) after 2.8-h reaction time and similar workup.

Similarly from 0.518 g (0.84 mmol) of **1'b** (diastereomeric purity 97 ± 2%) 0.638 g (92% yield) of **2'b** (diastereomeric purity 97 ± 2%) were obtained. **2**: ^1H NMR ($CDCl_3$, δ) CH_3 0.83–1.28 (m, 6 H), CH 2.5–3.2 (m, 2 H) =CH 4.60 (t, 1 H, J_{P-H} 1.7 Hz), C_5H_5 5.17 (s, 5 H), C_6H_5 6.44–6.54 and 6.93–7.70 (m, 25 H); ^{31}P NMR ($CDCl_3$) (δ from H_3PO_4) 71.5 and 76.6 (d, J_{P-P} = 34.2 Hz); ^{13}C NMR (CD_2Cl_2, δ) CH_3 15.0 (t, J_{P-C} = 5.2 Hz), CH_3 15.2 (t, J_{P-C} = 4.9 Hz), CH 38.4 (t, J_{P-C} = 15.4 Hz), CH 38.8 (t, J_{P-C} = 13.4 Hz), C_5H_5 93.6 (s), =CH and C_6H_5 118–134 (m), =C= 354 (dd,

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J_{P-C} = 12.7 and 16.4 Hz). Anal. Calcd for $C_{41}H_{39}F_6P_3Ru$: C, 58.64; H, 4.68. Found: C, 58.39; H, 4.66.

2'a: ^1H NMR ($CDCl_3$) CH_3 1.27 (ddd, 3 H, J_{H-H} 6.5 Hz, J_{P-H} = 12 and 1.5 Hz), CH and CH_2 2.25 and 3.2 (m, 3 H), =CH 4.50 (t, 1 H, J_{P-H} = 1.5 Hz), C_5H_5 5.42 (s, 5 H), C_6H_5 6.17–6.23 and 6.82–7.73 (m, 25 H); ^{31}P NMR ($CDCl_3$, δ from H_3PO_4) 80.0 and 60.1 (d, J_{P-P} = 27.9 Hz); ^{13}C NMR ($CDCl_3$) CH_3 15.2 (dd, J_{P-C} 4 and 18 Hz), CH_2 32.6 (dd, J_{P-C} = 15 and 35 Hz), CH 34.0 (dd, J_{P-C} = 11 and 25 Hz), C_5H_5 92.4 (s), C_6H_5 and =CH 117–126, =C= 354.7 (q, J_{P-C} = 13.3 and 17.8 Hz). Anal. Calcd for $C_{40}H_{37}F_6P_3Ru$: C, 58.18; H, 4.52. Found: C, 58.35; H, 4.67.

2'b: ^1H NMR (CD_2Cl_2, δ) CH_3 1.15 (dd, J_{H-H} = 6.9 Hz, J_{P-H} = 14.5 Hz), CH and CH_2 2.86–3.37 (m, 3 H), =CH 5.07 (t, 1 H, J_{P-H} = 1.5 Hz), C_5H_5 5.31 (s, 5 H), C_6H_5 6.54–6.57 and 6.95–7.71 (m, 25 H); ^{31}P NMR ($CDCl_3$, δ from H_3PO_4) 81.9 and 67.3 (d, J_{P-P} = 25.8 Hz); ^{13}C NMR ($CDCl_3$) CH_3 17.3 (dd, J_{P-C} = 2 and 13 Hz), CH 36.0 (dd, J_{P-C} = 12 and 33 Hz), CH_2 37.2 (dd, J_{P-C} = 15 and 36 Hz), C_5H_5 93.4 (s), C_6H_5 and =CH 95–136, =C= 354.3 (t, J_{P-C} = 15 Hz). Anal. Calcd for $C_{40}H_{37}F_6P_3Ru$: C, 58.18; H, 4.52. Found: C, 58.72; H, 4.47.

Preparation of [(η-C_5H_5)Ru(diphosphine)(C=CHCH$_3$)]PF_6 (6'a and 6'b). A 0.300-g (0.49-mmol) sample of **1'a** (diastereomeric purity 98 ± 2%) was combined with 0.240 g (1.48 mmol) of NH_4PF_6 under an atmosphere of propyne in 20 mL of CH_3OH until a yellow-orange solution was obtained (2 h). The solvent was removed under vacuum and the crude product recrystallized from CH_2Cl_2/*n*-hexane to give 0.318 g of **6'a** (diastereomeric purity 93 ± 2%) (85% yield). Analogously starting with 0.300 g of **1'b** (diastereomeric purity 97 ± 2%) 0.337 g of **6'b** (diastereomeric purity 95 ± 2%) was recovered (90% yield).

6'a: ^1H NMR (CD_2Cl_2, δ) CCH_3 0.92 (d, 3 H, J_{H-H} = 7.6 Hz), CH_3 1.35 (ddd, 3 H, J_{H-H} = 6.4 Hz, J_{P-H} = 12.8 and 1.5 Hz), CH 2.34 (m, 1 H), CH_2 3.10 (m, 2 H), =CH 3.60 (dq, 1 H, J_{H-H} = 7.6 Hz, J_{P-H} = 1.5 Hz), C_5H_5 5.32 (s, 5 H), C_6H_5 7.57 (m, 20 H); ^{31}P NMR (CD_2Cl_2, δ from H_3PO_4) 83.7 and 63.5 (d, J_{P-P} = 29.3 Hz); ^{13}C NMR (CD_2Cl_2/$CDCl_3$ 3:1; δ) CH_3 15.9 (dd, J_{P-C} = 5 and 21 Hz), CH_2 34.1 (d, J_{P-C} = 34 Hz), CH 34.2 (dd, J_{P-C} = 13 and 34 Hz), C_5H_5 92.0 (s), =CH 107 (s), C_6H_5 129–137, =C= 347 (dd, J_{P-C} = 14 and 18 Hz). Anal. Calcd for $C_{35}H_{35}F_6P_3Ru$: C, 55.05; H, 4.62. Found: C, 54.96; H, 4.61.

6'b: ^1H NMR (CD_2Cl_2, δ) CH_3 1.00 (dd, 3 H, J_{H-H} = 6.8 Hz, J_{P-H} = 12.8 Hz), CH_3 (d, 3 H, J_{H-H} = 8.2 Hz), CH and CH_2 2.96 (m, 3 H), =CH 3.89 (m, 1 H), C_5H_5 5.15 (s, 5 H), C_6H_5 7.46 (m, 20 H); ^{31}P NMR (CD_2Cl_2, δ from H_3PO_4) 90.7 and 74.1 (d, J_{P-P} = 23.8 Hz); ^{13}C NMR (CD_2Cl_2/$CDCl_3$, 3:1; δ) CH_3 17.6 (d, J_{P-C} = 8.8 Hz), CH_2 35 (dd, J_{P-C} = 12 and 33 Hz), CH 37.7 (dd, J_{P-C} = 15 and 25 Hz), C_5H_5 92.6 (s), =CH 109 (s), C_6H_5 128–138 (m), =C= 346.6 (t, J_{P-C} = 15 Hz). Anal. Calcd for $C_{35}H_{35}F_6P_3Ru$: C, 55.05; H, 4.62. Found: C, 54.84; H, 4.57.

Preparation of [(η-C_5H_5)Ru(diphosphine){C(OCH$_3$)-CH$_2$C$_6$H$_5$}]PF_6 (3, 3'a, and 3'b). A 1.32-g (2.1-mmol) sample of **1** was refluxed in CH_3OH with 1.31 g of KPF_6 and 5 mL of phenylacetylene for 48 h. Solvent and excess phenylacetylene were removed under vacuum, and the residue was dissolved in CH_2Cl_2 and filtered through Celite. **3** was crystallized through slow diffusion of diethyl ether and was then filtered and dried; yield 1.80 g (98%). A preparation starting with 0.100 g of **2**, which was refluxed for 48 h in CH_3OH, gave 0.095 g (92% yield) of **3**. Similarly 0.530 g (0.64 mmol) (diastereomeric purity 97 ± 2%) of **2'a** was refluxed for 48 h in methanol. Methanol was then removed under vacuum. ^1H NMR analysis of the crude reaction mixture showed a 97 ± 2% diastereomeric composition. The crude reaction product was dissolved in CH_2Cl_2 and filtered through Celite. Slow diffusion of diethyl ether resulted in precipitation of yellow crystals of **3'a** which were filtered and dried; yield 0.495 g (90%). Analogously 0.480 g (0.58 mmol) of **2'b** (diastereomeric purity 98 ± 2%) was refluxed in 20 mL of CH_3OH for 48 h. Cooling at room temperature resulted in formation of yellow crystals of **3'b**. The suspension was cooled to −20 °C. Filtration, washing with diethyl ether, and drying gave 0.420 mg (87% yield) of **3'b**. The diastereomeric composition of the crude reaction product (97 ± 2% by ^1H NMR) was determined by drying of a small part of the hot methanol solution of **3'b**.

3: ^1H NMR (CD_2Cl_2, δ) CH_3 0.94 (dd, 3 H, J_{H-H} = 6.8 Hz, J_{H-P} = 12.9 Hz), CH_3 1.33 (q, 3 H, J_{H-H} = 7.1 Hz, J_{H-P} = 12.3 Hz), CH 2.1 (m, 1 H), CH 3.15 (m, 1 H), OCH_3, 2.95 (s, 3 H), CH_2 3.23 and 4.11 (dd, 2 H, J_{H-H} = 16.1 Hz), C_5H_5 5.12 (s, 5 H), C_6H_5 6.16 (d, 2 H) and 7.0–7.7 (m, 23 H); ^{31}P NMR (CD_2Cl_2, δ from H_3PO_4) 89.0 and 80.9 (d, J_{P-P} = 38 Hz). Anal. Calcd for $C_{42}H_{43}F_6OP_3Ru$: C, 57.86; H, 4.97. Found: C, 58.01; H, 4.78.

3'a: ^1H NMR (CD_2Cl_2, δ) CH_3 1.07 (ddd, 3 H, J_{H-H} = 6 Hz, J_{H-P} = 13 and 1.4 Hz), CH and CH_2 2.20 and 3.20 (m, 3 H), OCH_3 2.87 (s, 3 H), CH_2 3.50 and 3.18 (dd, 2 H, J_{H-H} = 15.8 Hz), C_5H_5 5.09 (s, 5 H), C_6H_5 6.18–6.29 (m, 2 H), 6.92–7.97 (m, 23 H); ^{31}P NMR (CD_2Cl_2, δ from H_3PO_4) 67.6 and 92.2 (d, J_{P-P} = 37.8). Anal. Calcd for $C_{41}H_{41}F_6OP_3Ru$: C, 57.42; H, 4.82. Found: C, 57.15; H, 4.99.

3'b: ^1H NMR (CD_2Cl_2, δ) CH_3 1.41 (dd, 3 H, J_{H-H} = 6.8 Hz, J_{H-P} = 12.1 Hz), CH and CH_2 2.2–3.1 (m, 3 H), OCH_3 3.01 (s, 3 H), CH_2 3.63 and 4.15 (dd, J_{H-H} = 15.0 Hz), C_5H_5 5.08 (s, 5 H), C_6H_5 6.42–6.53 (m, 2 H), 7.11–7.72 (m, 23 H); ^{31}P NMR (CD_2Cl_2, δ from H_3PO_4) 76.6 and 84.0 (d, J_{P-P} = 34.1 Hz). Anal. Calcd for $C_{41}H_{41}F_6OP_3Ru$: C, 57.42; H, 4.82. Found: C, 56.67; H, 5.04.

Reaction of 3,3'a and 3'b with $LiAlH_4$: Synthesis of (η-C_5H_5)Ru(diphosphine)$CH_2CH_2C_6H_5$ (4, 4'a, and 4'b). A 5-mL sample of a saturated tetrahydrofuran solution of $LiAlH_4$ was slowly added to a suspension of 0.420 g (0.48 mmol) of **3** in 20 mL of THF cooled at −70 °C. The reaction mixture was left for 6.5 h at −70 °C and overnight at room temperature. THF was removed under vacuum. The residue was dissolved in 10 mL of benzene, and the excess $LiAlH_4$ was cautiously hydrolyzed with H_2O. The benzene solution was dried with Na_2SO_4 and concentrated to 3 mL. Slow diffusion of 50 mL of *n*-pentane gave yellow crystals of **4** (0.235 g, 70% yield). ^1H NMR analysis of a small amount of the benzene solution shows a chemoselectivity higher than 95%.

Analogously starting with 0.440 g (0.51 mmol) of **3'a** having a 97 ± 2% diastereomeric purity 0.260 g (0.38 mmol, 75% yield) of **4'a** (diastereomeric purity 97 ± 2%) was obtained. In the similar reaction of 0.400 g (0.47 mmol) of **3'b** (diastereomeric purity 96 ± 2%), the crystallization of **4'b** (diastereomeric composition of the crude reaction product 95 ± 2%) from the benzene/*n*-pentane solution was carried out at −80 °C; yield 63 mg (25%).

4: ^1H NMR (C_6D_6, δ) CH_3 0.71 (dd, 3 H, J_{H-H} = 6.7 Hz, J_{H-P} = 10.4 Hz), CH_3 0.78 (dd, 3 H, J_{H-H} = 7.1 Hz, J_{H-P} = 10.4 Hz), CH 1.52 (m, 1 H), CH 2.25 (m, 1 H), CH_2^{α} 0.60 and 0.84 (m, 2 H), CH_2^{β} 1.91 and 2.26 (dt, J_{H-H} = 14 and ~4 Hz), C_5H_5 4.62 (s, 5 H), C_6H_5 6.8–7.8 (m, 25 H); ^{31}P NMR (C_6D_6, δ from H_3PO_4) 83.1 and 97.0 (d, J_{P-P} = 42.0 Hz); ^{13}C NMR (C_6D_6) CH_3 13.8 (dd, J_{C-P} = 4.6 and 18.4 Hz), CH_3 15.8 (dd, J_{C-P} = 4.6 and 16.9 Hz), CH 36.0 (dd, J_{C-P} = 17.6 and 29.3 Hz), CH 42.8 (dd, J_{C-P} = 21.9 and 28.1 Hz), CH_2^{α} 5.1 (t, J_{P-C} = 11.0 Hz), CH_2^{β} 44.1 (s), C_6H_5 126–150. Anal. Calcd for $C_{41}H_{42}P_2Ru$: C, 70.57; H, 6.07. Found: C, 70.82; H, 6.06.

4'a: ^1H NMR (C_6D_6, δ) CH_3 0.81 (dd, 3 H, J_{H-H} = 6 Hz, J_{P-H} = 9.5 Hz), CH and CH_2 1.30 and 2.40 (m, 3 H), CH_2^{α} 0.75–0.85 (m, 2 H), CH_2^{β} 1.80 and 2.31 (dt, 2 H, J_{H-H} = 4 and 14 Hz), C_5H_5 4.77 (s, 5 H), C_6H_5 6.74–7.70 (m, 25 H); ^{31}P NMR (C_6D_6, δ from H_3PO_4) 100.4 and 74.3 (d, J_{P-P} = 35.7 Hz); ^{13}C NMR (C_6D_6, δ) CH_3 16.6 (dd, J_{C-P} = 4.7 and 16.8 Hz), CH 31.3 (dd, J_{P-C} = 15 and 28 Hz), CH_2 36.9 (dd, J_{C-P} = 21 and 29 Hz), CH_2^{α} 6.2 (t, J_{C-P} = 11.5 Hz), CH_2^{β} 44.3 (s), C_5H_5 82.9 (s), C_6H_5 123–150. Anal. Calcd for $C_{40}H_{40}P_2Ru$: C, 70.26; H, 5.90. Found: C, 69.88; H, 5.65.

4'b: ^1H NMR (C_6D_6, δ) CH_3 0.89 (dd, 3 H, J_{H-H} = 6.7 Hz, J_{P-H} = 0.7 Hz), CH, CH_2, and CH_2^{β} 2.0–2.4 (m, 5 H), CH_2^{α} 0.77–1.2 (m, 2 H), C_5H_5 4.66 (s, 5 H), C_6H_5 6.82–7.76 (m, 25 H); ^{31}P NMR (C_6D_6, δ from H_3PO_4) 89.6 and 82.4 (d, J_{P-P} = 36.3 Hz); ^{13}C NMR (C_6D_6, δ) CH_3 15.9 (dd, J_{C-P} = 4.2 and 16.9 Hz), CH_2 37.2 (dd, J_{C-P} = 18.3 and 31.4 Hz), CH 38.2 (dd, J_{C-P} = 18.7 and 27.3 Hz), CH_2^{α} 4.7 (t, J_{C-P} = 11.2 Hz), CH_2^{β} 45.6 (s), C_5H_5 83.5 (s), C_6H_5 124–150. Anal. Calcd for $C_{40}H_{40}P_2Ru$: C, 70.26; H, 5.90. Found: C, 69.83; H, 5.72.

Reaction of 1, 1'a, and 1'b with $C_6H_5CH_2CH_2MgBr$. **1** (60 mg, 0.096 mmol) dissolved in 5 mL of toluene was treated with 1 mL of a 1.7 M solution of $C_6H_5CH_2CH_2MgBr$ in ether. The solution was stirred for 48 h at room temperature and then hydrolyzed cautiously with water. The separated organic phase was dried over Na_2SO_4. The solvent was removed under vacuum, and

Table V. Details of Data Collection and Structure Determination for Compounds 3′b and 6′a

	3′b	6′a
formula	$C_{41}H_{41}F_6OP_3Ru$	$C_{35}H_{35}F_6P_3Ru$
M_r	857.8	763.6
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
a, Å	12.555 (4)	11.469 (4)
b, Å	12.651 (4)	14.976 (4)
c, Å	24.198 (8)	20.696 (7)
V, Å^3	3843.4	3554.7
Z	4	4
ρ, g cm^{-3}	1.48	1.43
μ(Mo Kα), cm^{-1}	5.82	6.18
cryst size, m	0.27 × 0.14 × 0.14	0.25 × 0.15 × 0.12
radiatn (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
scan type	ω scan	ω scan
scan width, deg	1.4 + 0.347 tan θ	1.6 + 0.347 tan θ
data collection range, deg	$3 < \theta < 24°$	$3 < \theta < 23°$
part of the sphere	$+h,+k,+l$	$+h,+k,+l$
no. of unique data	3401	2793
no. of data used in the refinement	1530	1783
cryst decay	no decay	no decay
max and min transmissn factors	1.00–0.81	1.00–0.91
weighting fudge factor	0.03	0.03
R	0.053	0.044
R_w	0.057	0.052
GOF	1.85	1.98

the residue was dissolved in C_6D_6. ^1H and ^{31}P NMR analysis showed quantitative formation of **4** (40%) and hydrido complex (*S,S*)-(η-C_5H_5)Ru{$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}H (**7**) (60%).

Analogously **1′a** (diastereomeric purity 98%) gives a 65:35 mixture of **4′a** and **7′a**, both having a diastereomeric purity higher than 98%. In the similar reaction of **1′b** (diastereomeric purity 86%) **4′b** and **7′b** are formed in a 70:30 ratio; also in this reaction the diastereomeric composition is maintained.

Preparation of (η-C_5H_5)Ru(diphosphine)(C≡CC_6H_5) (5, 5′a, and 5′b). To a CH_2Cl_2 solution containing 0.300 g (0.36 mmol) of **2** was added 0.2 g (33.4 mmol) of KOH in CH_3OH; the color instantaneously turned from red to yellow. The solvents were removed under reduced pressure, and yellow crystals of **5** were obtained through crystallization from CH_2Cl_2/*n*-hexane; yield 0.225 g (90%). Analogously starting with 0.300 g (0.36 mmol) of **2′a** (diastereomeric composition 98 ± 2%) 0.197 g (0.29 mmol) of **5′a** was obtained; the diastereomeric composition of the crude reaction product was 96 ± 2%. In a similar way 0.300 g (0.36 mmol) of **2′b** (diastereomeric purity 98 ± 2%) gave 0.200 g (0.29 mmol) of **5′b** (diastereomeric purity 97 ± 2%).

5: ^1H NMR ($CDCl_3$, δ) CH_3 0.80 and 0.95 (dd, 6 H, J_{H-H} = 6.6 Hz, J_{P-H} = 11.7 Hz), CH 1.89 and 2.89 (m, 2 H), C_5H_5 4.49 (s, 5 H), C_6H_5 6.96–8.26 (m, 25 H); ^{31}P NMR ($CDCl_3$) (δ from H_3PO_4) 89.1 and 77.1 (d, J_{P-P} = 34.2 Hz); ^{13}C NMR (C_6D_6, δ) CH_3 15.3 (dd, J_{C-P} = 4.7 and 15.2 Hz), CH_3 17.1 (d, J_{C-P} = 17.3 Hz), CH 36.4 (dd, J_{C-P} = 17.0 and 27.8 Hz), CH 39.5 (dd, J_{C-P} = 16.8 and 34.4 Hz), C_5H_5 84.1 (s), PhC≡ 112.9 (s), RuC≡ 116.5 (dd, J_{C-P} = 21.5 and 26 Hz), C_6H_5 123–144. Anal. Calcd for $C_{41}H_{38}P_2Ru$: C, 70.98; H, 5.52. Found: C, 69.67; H, 5.42.

5′a: ^1H NMR ($CDCl_3$, δ) CH_3 1.10 (dd, 3 H, J_{H-H} = 7.0 Hz, J_{P-H} = 10.6 Hz), CH_2 and CH 1.75–3.10 (m, 3 H), C_5H_5 4.67 (s, 5 H), C_6H_5 6.5–8.0 (m, 25 H); ^{31}P NMR ($CDCl_3$, δ from H_3PO_4) 91.7 and 68.8 (d, J_{P-P} = 31.1 Hz). Anal. Calcd for $C_{40}H_{36}P_2Ru$: C, 70.67; H, 5.34. Found: C, 69.62; H, 5.23.

5′b: ^1H NMR ($CDCl_3$, δ) CH_3 0.90 (dd, 3 H, J_{H-H} = 6.7 Hz, J_{P-H} = 12.5 Hz), CH and CH_2 2.40–2.80 (m, 3 H), C_5H_5 4.62 (s, 5 H), C_6H_5 6.5–8.1 (m, 25 H); ^{31}P NMR ($CDCl_3$, δ from H_3PO_4) 89.0 and 79.4 (d, J_{P-P} = 24.7 Hz). Anal. Calcd for $C_{40}H_{36}P_2Ru$: C, 70.67; H, 5.34. Found: C, 69.12; H, 5.44.

Reaction of 1′a and 1′b with C_6H_5C≡CLi: Formation of 5′a and 5′b. A 50-mg (0.80-mmol) sample of **1′a** (diastereomeric purity 98%) dissolved in 5 mL of toluene was treated with a large excess of C_6H_5C≡CLi (0.8 mmol) in THF for 24 h. The resulting solution was cautiously hydrolyzed with H_2O, and the separated organic phase was dried on Na_2SO_4. The solvent was removed under vacuum, and the residue was dissolved in C_6D_6. ^1H and ^{31}P NMR showed exclusive formation of **5′a** having a diastereomeric purity higher than 98%. Analogously **1′b** (diastereomeric purity 96 ± 2%) gave formation of **5′b** (diastereomeric purity 97 + 2%).

Reaction of 5′a and 5′b with HPF_6: Formation of 2′a and 2′b. A 0.030-g (0.044-mmol) sample of **5′a** (diastereomeric purity 96 ± 2%) was dissolved in 20 mL of CH_2Cl_2 and treated with an excess of HPF_6·Et_2O. The solvent was removed under reduced pressure, and the crude reaction product was dissolved in CD_2Cl_2. The filtered solution was analyzed by ^1H and ^{31}P NMR spectroscopy and showed quantitative formation of **2′a** (diastereomeric purity 96 ± 2%). Analogously from **5′b** (diastereomeric purity 97 ± 2%) **2′b** was exclusively formed with a diastereomeric purity of 98 ± 2%.

X-ray Data Collection, Structure Determination, and Refinement. The refined cell constants and other relevant crystal data for the two compounds (R_{Ru},R_C)-[(η-C_5H_5)Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}{$C(OCH_3)CH_2C_6H_5$}]PF_6 (**3′b**) and (S_{Ru},R_C)-[(η-C_5H_5)Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}(C=$CHCH_3$)]PF_6 (**6′a**) are presented in Table V together with details of intensity measurements. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer. All the data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied by measuring the intensities of two reflections with χ near to 90° for different ψ values (ψ = 0–360° every 10°). The structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least squares. All the nonphenyl group atoms were treated anisotropically in both cations, and in the final refinement the hydrogen atoms were located in their ideal positions (C–H = 0.95 Å) (after each cycle but not refined). The absolute configuration was tested by refining both enantiomers for each compound. In both cases the lower R and R_w values were associated with the previously known[16] R configuration of the asymmetric carbon atom of the diphosphine ligand.

In both compounds the [PF_6] anion was slightly disordered, and we decided to use a model of 12 half fluorine atoms refined isotropically in compound **3′b** and of 6 anisotropic fluorine atoms in compound **6′a**. The final difference Fourier maps were flat in both cases, showing only residual peaks not exceeding 0.5 e/Å^3 near the PF_6^- anions.

All the computations were performed on a PDP 11/34 computer using the Enraf-Nonius structure determination package (SDP). Bond distances and angles are reported in Tables III and IV. The final positional and thermal parameters and computed and observed structure factors for the two compounds are given in the supplementary material.

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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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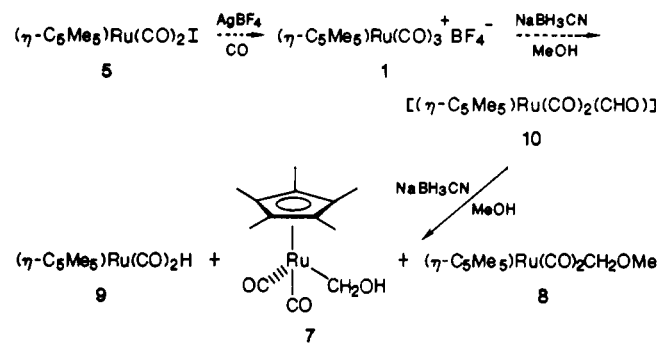
The transition-metal complexes—$(\eta\text{-}C_5Me_5)Ru(CO)_2CH_2OH$ (7), $(\eta\text{-}C_5Me_5)Ru(CO)_2CHO$ (10), and $(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)CHO$ (11)—were synthesized and studied as models for intermediates thought to be involved in the reduction of CO to organic oxygenates by transition-metal 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.

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