were averaged to obtain 1365 unique structure amplitudes; they gave R (internal) of 0.138 before, and 0.046 after, absorption correction.

The crystal structure was successfully solved in the space group $C2/m$ and refined by full-matrix least squares, minimizing the function $\sum w(|F_o| - |F_c|)^2$. The atomic scatting factors and the anomalous dispersion corrections were taken from ref 26. The positions of the platinum atoms were obtained from a Patterson function and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. Hydrogen atoms were not located in electron density maps nor included in structure factor calculations. An allowance was made for anisotropic thermal vibrations of all non-hydrogen atoms. In the final difference electron density map the function values were in the range ±3 e A^{-3}; the extreme values, associated with the positions of platinum and iodine atoms, are likely to reflect residual absorption effects.

The final atomic coordinates are shown in Table III. The anisotropic thermal parameters of atoms and the observed and calculated structure amplitudes are listed in supplementary material.

(26) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, United Kingdom 1974; Vol. IV, Tables 2.2B and 2.3.1.

All calculations were performed on a GOULD SEL 32/27 minicomputer, using the locally developed GX program system.[27]

Acknowledgment. We thank the S.E.R.C. (Great Britain) and the University of Glasgow for help in purchasing the computer and diffractometer, NSERC (Canada) for financial support (R.J.P.) and for a graduate scholarship (S.S.M.L.), and Mr. D. Srokowski for able experimental assistance.

Registry No. **1a**, 88228-39-1; **1b**, 91491-48-4; **1c**, 79870-63-6; **2**, 96412-20-3; **3a**, 89144-05-8; **3b**, 96412-21-4; **4b**, 91491-49-5; **5a**, 96412-23-6; **5c**, 96412-22-5; **7**, 96427-22-4; [{PtIMe$_3$}$_4$], 18253-26-4; MeI, 74-88-4.

Supplementary Material Available: Anisotropic thermal parameters of atoms (Table IV) and final $|F_o|$ and $|F_c|$ values (Table V) (16 pages). Ordering information is given on any current masthead page.

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Stereochemistry of Some Ligand Substitution and Insertion Reactions in Pseudotetrahedral Ruthenium(II) Complexes

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Pseudotetrahedral (S_{Ru},R_C)-**1** and (R_{Ru},R_C)-(η-C_5H_5)Ru(prophos)Cl, 1′ (where prophos is (*R*)-1,2-propanediylbis(diphenylphosphine)), react with CH_3MgBr or C_2H_5MgBr to give the alkylation products (S_{Ru},R_C)-**2** and (R_{Ru},R_C)-(η-C_5H_5)Ru(prophos)R, **2′** (R = CH_3, **a**; R = C_2H_5, **b**), with stereospecific retention of configuration at the ruthenium atom. With C_2H_5MgBr also a competitive formation of the corresponding hydrides (S_{Ru},R_C)-**3** and (R_{Ru},R_C)-(η-C_5H_5)Ru(prophos)H, **3′**, takes place. Hydride formation is the only reaction observed when **1** or 1′ is reacted with *sec*-C_4H_9MgBr and, according to NOE experiments, takes also place with retention of configuration. Under the conditions of their formation (or even under more severe conditions) **2b** and **2b′** do not thermally decompose to **3** or **3′**. Hydride formation is therefore not a consequence of alkylation followed by β-hydrogen elimination but must arise from a different reaction pathway whose possible nature is discussed. Hydrides **3** and **3′** react with CH_2N_2 in the presence of catalytic amounts of $Pd(CH_3COO)_2$ to give the methyl derivatives **2a** and **2a′** with retention of configuration. Stereospecific retention of configuration is also observed in the formation of **3** and **3′** when **1** and 1′ are treated with CH_3ONa. By contrast, the reaction of **1** and 1′ and that of (S_{Ru},R_C)-**4** and (R_{Ru},R_C)-[(η-C_5H_5)Ru(prophos)(CH_3CN)]PF_6, **4′**, with HCOONa is stereoselective; in the first case **3** and **3′** were obtained in a 20:80 and in the second one in a 40:60 molar ratio. **1** and 1′ form from the hydrides **3** and **3′** when treated with $CDCl_3$ or CCl_4 in a stereoselective reaction. Predominant inversion of configuration is observed in the reaction of **4** and **4′** with $(C_6H_5)_4AsCl$ to give **1** and 1′.

Soon after the first reports on homogeneous asymmetric reactions catalyzed by transition-metal complexes containing chiral ligands, the possibility was recognized that the metal can become a chirality center during catalysis.[2,3] The possible role of chiral metals in those enantioselective transformations has been discussed[4] and sometimes probably recognized.[5] Furthermore, it has been recently shown that in the stoichiometric cyclopropanation of styrene by chiral diastereomeric ethylideneiron complexes the chirality at the metal plays an overwhelming (if not exclusive) role with respect to that of the phosphine ligand in determining the stereochemical outcome of the reaction.[6]

Therefore the search for the rationalization and improvement of results of homogeneous asymmetric catalysis implies not only a better identification of the catalytic species[7] but also a more detailed knowledge of the stere-

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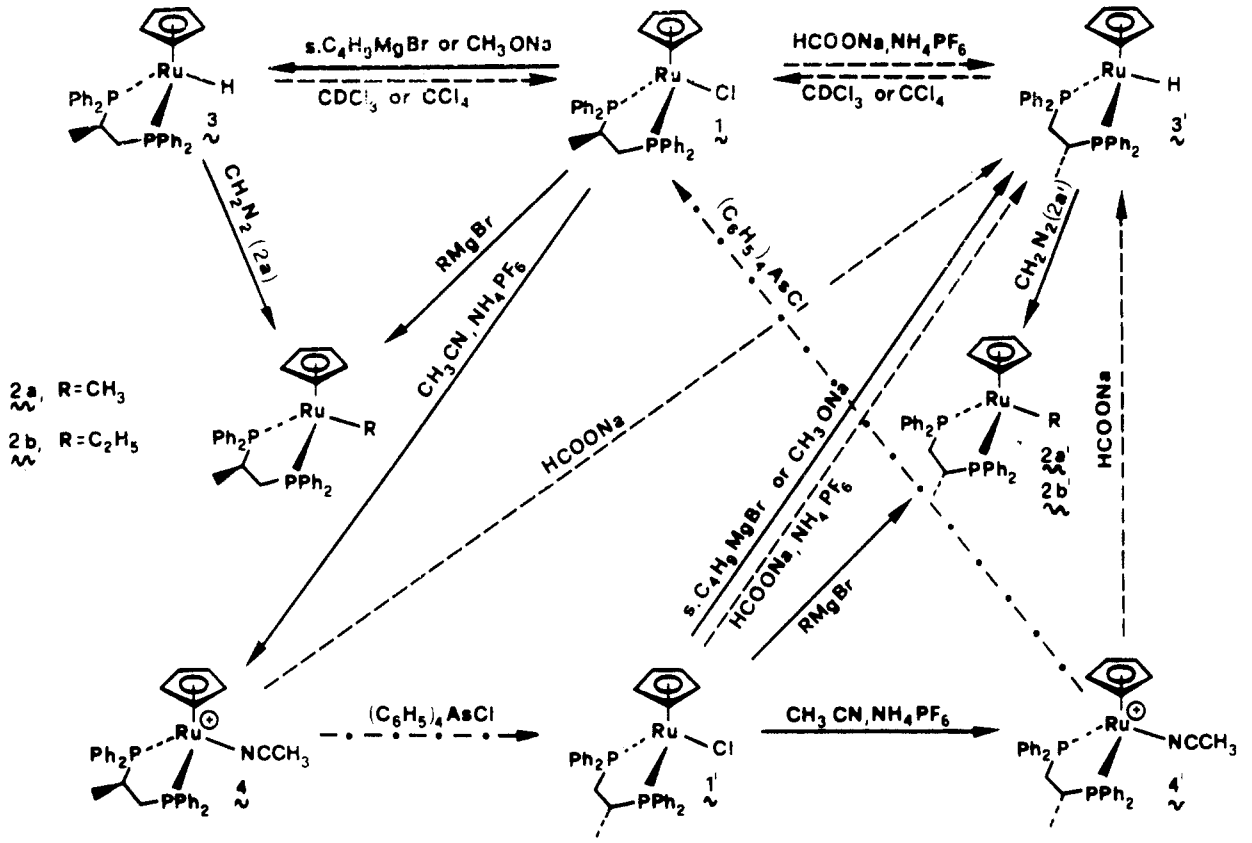
Scheme I[a]



[a] Full lines for the arrows indicate stereospecific retention of stereochemistry, dashed lines stereoselective reactions, and dotdashed lines prevailing inversion of configuration.

ochemistry of reactions which occur at the level of the transition metal and which can be recognized as possible steps in catalytic cycles.

This paper presents the results of our investigation on the stereochemical aspects of some substitution and addition reaction involving pseudotetrahedral diastereomeric ruthenium complexes, containing the (*R*)-1,2-propanediylbis(diphenylphosphine) (prophos)[8] ligand. In fact, stereochemical investigations on complexes containing chiral ligands actually used in homogeneous asymmetric catalysis are rare;[9] (*R*)-prophos was successfully employed in asymmetric hydrogenation[8] and with appreciable results in asymmetric cross-coupling reactions.[10]

A preliminary account of some of these results has recently appeared.[11]

Results

As starting material for our stereochemical investigation, we have used the recently reported[12] (S_{Ru},R_C)-(η-C_5H_5)-RuCl (prophos), **1**, and (R_{Ru},R_C)-(η-C_5H_5)RuCl (prophos), **1'**,[13] as well as (S_{Ru},R_C)-[(η-C_5H_5)Ru(CH_3CN)(prophos)]-PF_6, **4**, and (R_{Ru},R_C)-[(η-C_5H_5)Ru(CH_3CN)(prophos)]PF_6, **4'**.[15] These latter diastereomeric complexes were stereospecifically[16] obtained by substitution of the chloro ligand in **1** and **1'** at room temperature with a large excess of acetonitrile in methanolic solution in the presence of ammonium hexafluorophosphate as the halogen scavenger.[15] The retention of configuration at the ruthenium atom[15,17] for this substitution reaction has been demonstrated through the crystal structure determination of **4**.

Scheme I gives a survey of the reactions we have examined. The reactions were monitored through contemporary ^1H and ^{31}P NMR spectroscopy. Reactions carried out on preparative scale are described in the Experimental Section.

(a) Reactions with Grignard Reagents. The reaction of **1** and **1'** at room temperature in toluene with an ether solution of CH_3MgBr causes quantitative stereospecific formation of the corresponding methyl derivatives **2a** and **2a'**, respectively (Table I).

The retention of configuration at the ruthenium atom was ascertained through the crystal structure determination of **2a**.[11] In the analogous reaction of **1** and **1'** with C_2H_5MgBr, carried out under similar conditions, two different products arise. This is not due to loss of stereospecificity of the alkylation reaction. In fact, together with the stereospecific formation of the ethyl derivatives **2b** and **2b'** a rather extensive (50–60%) stereospecific production of the hydrido complexes **3** and **3'** takes place. The chemoselectivity of the alkylation reaction can be

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Table I. Some ^1H and ^{31}P NMR Data for Complexes 1–4 and 1′–4′[a]

compd	δ(Cp)	δ(H, CH_3, or CH_3CN)	J_{P_A}[b]	J_{P_B}[b]	δ(P_1)[b]	δ(P_2)[b]	$J_{P_1-P_2}$
(η-C_5H_5)Ru(prophos)Cl (1)	4.30				86.4	61.3	30.2
(η-C_5H_5)Ru(prophos)CH_3 (2a)	4.66	−0.49	5.7	6.5	100.0	74.1	35.2
(η-C_5H_5)Ru(prophos)C_2H_5 (2b)	4.66	0.95			99.1	72.3	36.4
(η-C_5H_5)Ru(prophos)H (3)	4.70	−13.04	29.4	37.5	98.1	77.2	30.0
[(η-C_5H_5)Ru(prophos)($NCCH_3$)]PF_6 (4)	4.65	1.46	1.1	1.1	87.3	63.1	32.9
(η-C_5H_5)Ru(prophos)Cl (1′)	4.26				80.9	74.1	36.7
(η-C_5H_5)Ru(prophos)CH_3 (2a′)	4.66	−0.21	4.8	6.4	93.6	85.0	32.2
(η-C_5H_5)Ru(prophos)C_2H_5 (2b′)	4.58	0.95			88.3	81.6	37.1
(η-C_5H_5)Ru(prophos)H (3′)	4.71	−12.90	32.0	32.0	104.3	85.7	22.9
[(η-C_5H_5)Ru(prophos)($NCCH_3$)]PF_6 (4′)	4.49	1.71	1.1	1.1	88.1	75.7	25.6

[a] Solvents: C_7D_8 for 1 and 2; C_6D_6 for 3; CD_2Cl_2 for 4. ^1H chemical shifts in ppm with respect to internal Me_4Si; ^{31}P chemical shifts in ppm with respect to external H_3PO_4. J values in Hz. [b] We have assigned neither the ^{31}P signals nor the relative coupling constants (through double-resonance experiments); therefore the same phosphorus atoms were differently labeled (1 and 2 or A and B).

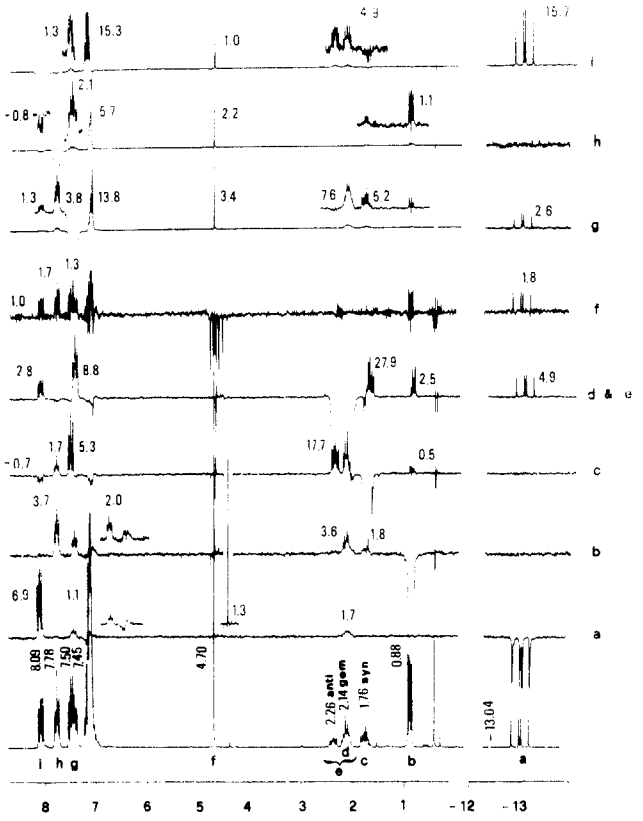

Figure 1. 200-MHz spectrum of (S_{Ru},R_C)-(η-C_5H_5)Ru(prophos)H, 3 (bottom trace), and NOE difference spectra from saturation of the regions indicated by the corresponding labels (solvent C_6D_6).

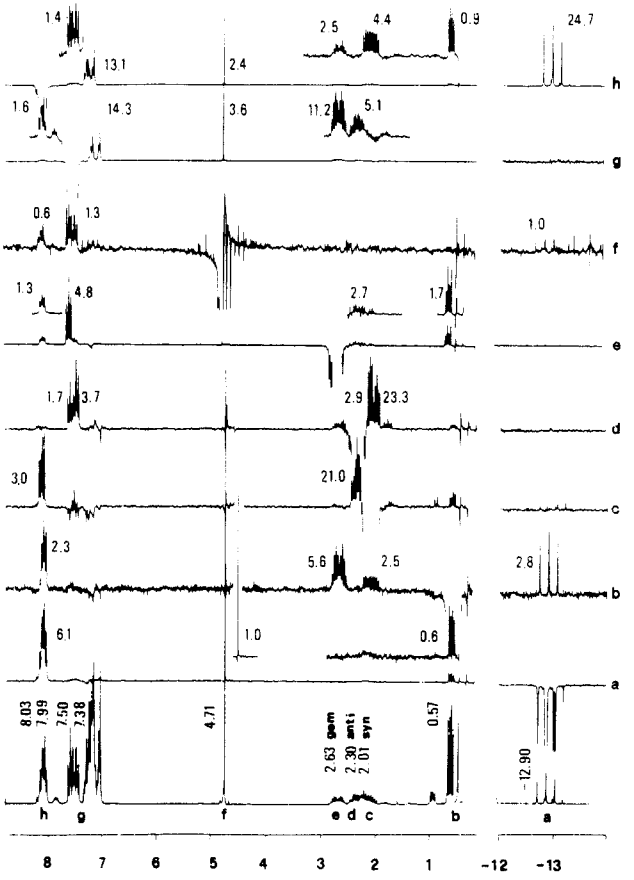

Figure 2. 200-MHz spectrum of (R_{Ru},R_C)-(η-C_5H_5)Ru(prophos)H, 3′ (bottom trace), and NOE difference spectra from saturation of the regions indicated by the corresponding labels (solvent C_6D_6).

improved by working at lower temperature (−80 °C). Under these conditions about 80% of **2b** or **2b′** and 20% of **3** or **3′** are formed. The composition of the reaction mixture does not change, however, when left for 1 month at room temperature or when heated at 90 °C for 15 h. Analogously[19] to (η-C_5H_5)Ru(diphos)-*n*-C_4H_9 (diphos is 1,2-ethanediylbis(diphenylphosphine)), **2b** and **2b′**, therefore, do not decompose thermally to **3** and **3′**. **1** and **1′** do not undergo any alkylation when reacted with *sec*-C_4H_9MgBr at room temperature. In this case, the stereospecific formation of diastereomeric hydrido complexes **3** and **3′** is quantitative. We have not attempted to carry out the reaction at lower temperature. In fact, the reaction mixture obtained at −80 °C from the complex (η-C_5H_5)-RuCl(chiraphos)[19] (chiraphos is (*S*,*S*)-2,3-butanediylbis-(diphenylphosphine))[20] and an excess of *sec*-C_4H_9MgBr shows after 2 h in the ^{31}P and ^1H NMR spectra only the presence of the corresponding hydride complex (~40% conversion) ((η-C_5H_5)Ru(chiraphos)H) and of the unreacted starting material.[21]

We were not able to obtain crystals of **3** and **3′** to perform the determination of the structure by X-ray crystallographic analysis. For this type of compounds, furthermore, the CD spectra are not useful for stereochemical assignment[12] (see Supplementary Material). Thus, the stereochemical assignment of **3** and **3′** was accomplished through nuclear Overhauser effect (NOE) experiments (reported in Figures 1 and 2) by means of NMR differential spectroscopy. The bottom trace gives the reference spectrum, while the other traces are perturbed spectra

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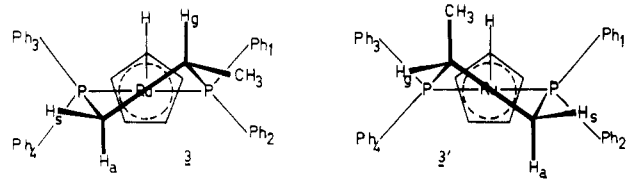

Figure 3. Assignment of the configuration at the ruthenium atom for **3** and **3′** based on NOE experiments.

subtracted from the reference spectrum. The strongly negative signals show the saturated region; the numbers give the percent enhancements and are obtained from the multiplier of the reference spectrum which result in exact matchings with the perturbed spectra. Errors are estimated at about 0.5%.

The irradiation of hydride dd at δ −13.04 of **3** (Figure 1) induces a 1.7% enhancement of the multiplet at δ 2.14 (trace a); the reciprocal perturbation (trace d and e) gives a 4.9% NOE on the hydride. This is the bis(phosphine) backbone proton resonance which gives the greatest NOE (3.6%) from saturation of the methyl dd at δ 0.88 (trace b). This proton is therefore geminal (H_{gem}) to the methyl group, which is consequently in the equatorial orientation. The complex **3** is the S_{Ru},R_C diastereomer (Figure 3). The absolute assignments of the methylenic resonances at δ 1.76 and 2.26 (the latter is split by coupling with ^{31}P) cannot follow from saturation of the methyl group, which is gauche toward the two methylenic protons, nor from perturbation of the H_{gem} resonance, which is too close. The assignment is still possible through inspection of the NOE effects on the ortho aromatics protons. The saturation of the hydride (trace a) identifies the Ph_1 and Ph_3 resonances and that of the methyl (trace b) the Ph_2 and Ph_4 resonances. Ph_1, Ph_2, Ph_3, and Ph_4 are therefore at δ 7.45, 7.78, 8.09, and 7.50, respectively. The methylenic resonance at δ 1.76, which causes positive and negative enhancements of the Ph_4 and Ph_3 resonances, respectively (trace c), is in roughly linear arrangement with these rings and is to be identified with H_{syn}. For exclusion, the doublet of multiplets at δ 2.26 is H_{anti}; because of the spectral proximity, irradiation in this region causes also the saturation of H_{gem}, with NOE enhancements of both Ph_1 and Ph_3 (traces d and e). The assignments are confirmed by irradiations of the ortho multiplets (traces g–i).

In the case of complex **3′** (Figure 2), the saturation of the methyl dd in the bis(phosphine) ligand at δ 0.57 (trace b) induces a 2.8% NOE enhancement of the hydride t at δ −12.90 and 5.6 and 2.5% NOE of the bis(phosphine) proton resonances at δ 2.63 and 2.01. No NOE is observed for the backbone proton resonance at δ 2.30. Because of spin-rotational relaxation, the reciprocal perturbations (traces c and e) give reduced but still observable NOE's of the methyl group. These results allow us to assign the multiplets at δ 2.63, 2.30, and 2.01 to the protons H_{gem}, H_{anti}, and H_{syn}, respectively (Figure 3). More important, they imply that **3′** is the R_{Ru},R_C diastereomer, with a significant population of the conformer having the methyl in close proximity to the hydride (Figure 3). No NOE is observed between the hydride and the H_{syn} methylenic proton (traces a and c). The assignment of the Ph_1, Ph_2, Ph_3, and Ph_4 ortho resonances to the multiplets at δ 8.03, 7.38, 7.99, and 7.50, respectively, is based on the same arguments exposed for the other isomer.

4 and **4′** were each reacted in tetrahydrofuran with excess of an etheral solution of CH_3MgBr at −50 °C for 5 h.[24] The reaction mixture was heated up at room temperature and the solvent eliminated under vacuum. NMR analysis (^{31}P) of the reaction products in C_6D_6 shows the formation of the methyl derivatives **2a** and **2a′** in seemingly similar amounts from either **4** or **4′**. However this accounts only for 3–5% of the total reaction products, which have not been identified yet. Similarly, very complex reaction mixtures (which have not been analyzed in detail) were obtained from **4** and **4′** and *sec*-C_4H_9MgBr. In this case formation of the hydrido complexes **3** and **3′** could not be recognized.

(b) Other Reactions Leading to Hydride Formation. The hydrides **3** and **3′** were also stereospecifically obtained by reacting **1** or **1′** with methanolic CH_3ONa.[25] According to the aforementioned stereochemical assignment, this reaction also takes place with retention of configuration at the ruthenium atom.

By contrast, either **1** or **1′** gives the same mixture of **3** and **3′** in a molar ratio of about 20:80 when reacted with an excess of HCOONa[26] in methanol in the presence of ammonium hexafluorophosphate. Thus, this last reaction is stereoselective.

Similarly stereoselective is the reaction of either **4** or **4′** in methanol with an excess of HCOONa. As a matter of fact, in each case the same product mixture **3**/**3′** in a molar ratio of aboout 40:60 was obtained.

(c) Reactions with Chlorinating Agents. Pure **3** or **3′** react with $CDCl_3$[27,28] in about 20 h to give a mixture of **1** and **1′** in a molar ratio of 80:20. Similarly **1** and **1′** are formed in a molar ratio of 60:40 in the analogously stereoselective and practically instantaneous reaction with CCl_4. Byproducts are $CHDCl_2$ and $CHCl_3$, respectively. No epimerization of the starting materials under the reaction conditions used was noticed during the reaction with $CDCl_3$.

At room temperature **4** reacts slowly (2 days, ~50% conversion) with a large excess of $(C_6H_5)_4AsCl$ in dichloromethane solution, yielding a mixture of **1** and **1′** in a molar ratio of 35:65. A **1**/**1′** molar ratio of 65:35 was instead obtained in the similar reaction of **4′**. A prevailing inversion of configuration at the ruthenium atom therefore takes place. No epimerization of **4** and **4′** during the reaction has been noticed.

(d) Reaction of the Hydride Complexes with Diazomethane. **3** and **3′** in toluene did not react with an ethereal solution (large excess) of diazomethane.[29] Starting materials were recovered unchanged. However, the presence of a trace amount of palladium acetate[30] causes reaction. The reaction is not very chemoselective; however, about 50% of **2a** and **2a′** was stereospecifically formed from **3** and **3′**, respectively. The other reaction products were not identified.

Discussion

The determination of the absolute configuration at the ruthenium atom for the complexes **1**, **2a**, and **4** followed from X-ray analysis as previously reported,[11,12,15] whereas that of the hydride complexes **3** (and **3′**) followed from nuclear Overhauser effect experiments.[22]

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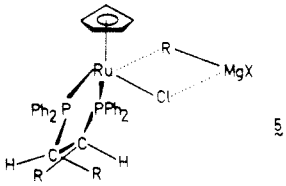
(29) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

(30) Suda, M. *Synthesis* **1981**, 714.

On the other hand, an indirect proof for the assignment of the configuration at ruthenium for **3** and **3′** arises from the stereospecific (even though not very chemoselective) reaction of **3** and **3′** with diazomethane to give **2a** and **2a′**, respectively; this would imply retention of configuration at the ruthenium atom. Indeed, the nature of the reaction of **3** and **3′** with the carbene arising from the palladium-catalyzed decomposition of diazomethane[30] appears in principle similar to that of the reactions of **1** or **1′** with $SnCl_2$ to yield the trichlorostannato derivatives. We have, in fact, recently demonstrated that this reaction is also stereospecific and occurs with retention of configuration at the ruthenium atom.[31]

Since the chemical yield of **2a** and **2a′** starting from **4** and **4a′** and CH_3MgBr was very low, we feel discussion on these reactions unwarranted. The retention of configuration at the ruthenium atom in the alkylation reactions (we assume, in fact, for these reactions the same stereochemistry as for the methylation) of **1** and **1′** with Grignard reagents was not unexpected. It is indeed fully consistent with the generally accepted[19] four-membered transition state (or intermediate) **5**, which would precede the metathesis of the alkyl groups and chlorine ligand.



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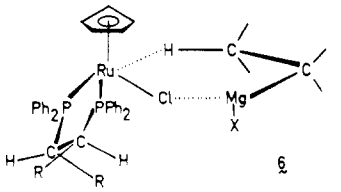
By contrast, the retention of the configuration at the ruthenium atom in the formation of the hydrides **3** and **3′** from **1** and **1′** by reaction with Grignard reagents having available β-hydrogens is more puzzling. Two different reaction mechanisms appeared in principle possible for that reaction. The first one would imply the formation of an alkylruthenium derivative, dissociation of a phosphorus atom from the bis(phosphine), β-elimination of a hydrogen atom from the alkyl group, and formation of the hydride complex after dissociation of the olefin as found for $(\eta\text{-}C_5H_5)Ru(PPh_3)_2R$ complexes.[19] For such a mechanism inversion of configuration at ruthenium or epimerization (depending on the stability of tricoordinate intermediate arising from olefin dissociation prior to chelation) should be expected. The second reaction path postulates that the cyclopentadienyl ligand assumes a η^3-allyl–ene binding mode,[32,33] so that the β-hydrogen elimination from the coordinated alkyl group can take place without phosphorus dissociation of the bis(phosphine). This mechanism would produce the hydride with the observed retention of configuration at the ruthenium atom. However, it can be ruled out in view of the stability of the ethyl complexes **2b** and **2b′** toward heating.

Also for the reaction of ketones with Grignard reagents there is the dichotomy of behavior: alkylation vs. reduction. This last reaction is assumed to arise from a six-membered transition state.[34] A similar intermediate or transition state, **6**, which would fully explain our observations, was indeed recently considered.[19]

The same retention of configuration observed in the formation of the hydrides by reaction of **1** and **1′** with



6

CH_3ONa could imply a similar six-center reaction intermediate. In this case, however, even if we can exclude β-hydrogen elimination via phosphorus dissociation from a methoxy intermediate, the possibility of a change in the bonding mode of the cyclopentadienyl ligand cannot be ruled out.

The stereoselective formation of the hydrides in the reaction of either **1** or **1′** with HCOONa makes a concerted hydride migration of the type previously discussed unlikely. A different extent of stereoselectivity is observed in the similar reaction of **4** and **4′** with HCOONa to give also the hydrido complexes. It is possible that in both reactions intermediate formato complexes are formed. In this case, stereoselectivity should originate in the formation of those intermediates which are expected to decompose stereospecifically rather than stereoselectively.[18] However, further investigations are necessary in order to rationalize the stereochemical outcome of both reactions.[18]

The order of reactivity of CCl_4 and $CDCl_3$ with **3** or **3′** is that expected for a reaction in which a charge transfer from electron-rich **3** and **3′** to the halo compound acceptor[27] would take place. Radical intermediates[28] arising from a variety of mechanisms can, in fact, provide a rationale both for the stereoselectivity and for the different extent of stereoselectivity observed in the above reactions with CCl_4 and $CDCl_3$.

The prevalent inversion of configuration that takes place in the reaction of **4** and **4′** with $(C_6H_5)_4AsCl$ provides, in principle, the interesting possibility to interchange **1** and **1′**. This stereochemistry can arise from a S_N2-type or even from a S_N1-type mechanism.[34] Further kinetic investigation could help to distinguish between the two possibilities.

Conclusions

Stereochemical investigations similar to those reported in this paper (i.e., methylation[36] or tin dichloride insertion[37]) had already been carried out on analogous complexes containing a monodentate phosphine ligand. The stereochemistry of the reaction, however, was not defined, and considerably lower degrees of stereospecificity than those in our case were observed.

Our particular interest in alkylation reactions with Grignard reagents stems from our precedent work on catalyzed cross-coupling reactions between organometallic reagents and different types of electrophiles.[10] A large limitation to this reaction of very broad applicability[38] arises from a competitive reduction instead of alkylation of the electrophile.[28] This reduction is generally ascribed to the transalkylation of the transition-metal compound which eventually undergoes hydride formation via β-elimination.[39] Our investigations show that another pathway for such reduction can be envisaged. A more detailed knowledge of the factors causing either mechanism could considerably extend the scope of the cross-coupling reaction.

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Experimental Section

All reactions and manipulations were carried out under an atmosphere of N_2. The solvents were dried and degassed before use.

^1H and ^{31}P $\{^1H\}$ NMR spectra were recorded on WP60, WP200SY, WH90, and AM300WB Bruker spectrometers. In the case of $^{31}P\{^1H\}$ NMR spectra, 85% H_3PO_4 was used as external standard, with the convention that increasing frequency is positive. Absorption and CD spectra were obtained by using a Cary 14 spectrophotometer and a JASCO J-40As dichrograph, respectively. Complexes 1 and 1′ were prepared as previously described.[12]

NOE Measurements. The usual pulse sequence for differential NOE experiments was adopted;[40] as a unique modification, a multiplet is saturated with the least decoupling power by a 5-s cyclic perturbation of all multiplet lines.[41] The percent enhancements are obtained from the coefficients of the reference spectrum, which result in exact matching with the perturbed spectrum. Errors are estimated about 0.5%.

Preparation of Acetonitrile Derivatives 4 and 4′. A mixture of 0.15 g (0.25 mmol) of 1 or 1′, 0.2 g (1.2 mmol) of NH_4PF_6, and 1 mL of CH_3CN was reacted in 10 mL of CH_3OH for a few hours. After removal of the solvent, the crude product was dissolved in CH_2Cl_2 and the solution filtered. Addition of *n*-hexane causes the precipitation of yellow crystals of pure 4 or 4′ (yields 90%). 4: ^1H NMR (CD_2Cl_2) δ CH_3, 1.19 (dd, 3 H, J_{P-H} = 11.9 Hz, J_{H-H} = 5.7 Hz), CH_3CN, 1.46 (t, 3 H, J_{P-H} = 1.1 Hz), CH_2CH, 2.10–2.81 (m, 3 H), C_5H_5, 4.65 (s, 5 H), C_6H_5, 7.46 (m, 20 H); ^{31}P NMR (δ from H_3PO_4) 67.1 and 87.3 (d, J_{P-P} = 32.9 Hz). Anal. Calcd for $C_{34}H_{34}F_6P_3NRu\cdot 2CH_2Cl_2$: C, 46.27; H, 4.10; N, 1.50. Found: C, 46.68; H, 4.14; N, 1.48.

4′: ^1H NMR (CD_2Cl_2) δ CH_3, 0.77 (dd, 3 H, J_{P-H} = 14.0 Hz, J_{H-H} = 6.6 Hz), CH_3CN, 1.71 (t, 3 H, J_{P-H} = 1.1 Hz), CH_2CH, 2.54–3.10 (m, 3 H), C_5H_5, 4.49 (s, 5 H), C_6H_5, 7.47 (m, 20 H); ^{31}P NMR (δ from H_3PO_4) 75.7 and 88.1 (d, J_{P-P} = 25.6 Hz). Anal. Calcd for $C_{34}H_{34}F_6P_3NRu$: C, 53.41; H, 4.48; N, 1.83. Found: C, 53.78; H, 4.46; N, 1.80.

Preparation of Methyl Derivatives 2a and 2a′. A 50-mL Schlenk tube was charged with 200 mg of 1 (or of 1′) (diastereomeric purity >98%) and 5 mL of toluene. Then 1 mL of CH_3MgBr (2 M in ether) was slowly added, and the reaction mixture was stirred for 22 h. The solvent was removed under vacuum. The residue was dissolved in 5 mL of toluene, the extract filtered on Celite, and the solvent removed under vacuum. This operations were repeated twice. The resulting toluene solution was concentrated (~1 mL). Slow diffusion of pentane causes crystallization of **2a** (or **2a′**) which was filtered and dried; yield 95–100 mg (49%), spectroscopically pure (^1H and ^{31}P NMR). The mass spectrum showed for both diastereomers the molecular ion at *m/e* 594 and fragments at *m/e* 579 (100%), 352, and 393, all of which contain ruthenium.

2a: ^1H NMR (C_6D_6) δ CH_3, −0.49 (dd, 3 H, J_{H-P} = 5.7 and 6.5 Hz), CH_3, 0.96 (ddd, 3 H, J_{H-H} = 7.3, J_{H-P_A} = 5.2, J_{H-P_B} = 0.8 Hz), CH_2CH, 2.08–2.92 (m, 3 H), C_5H_5, 4.66 (s, 5 H), C_6H_5 7.8–8.4 (m, 20 H); ^{31}P NMR (δ from H_3PO_4) 100.0 and 73.1 (d, J_{P-P} = 35.2 Hz).

2a′: ^1H NMR (C_6D_6) δ CH_3, −0.21 (dd, 3 H, J_{P-H} = 4.8 and 6.4 Hz), CH_3 0.86 (dd, 3 H, J_{P-H} = 6.3 Hz, J_{H-H} = 7.7 Hz), CH_2CH, 2.0–2.6 (m, 3 H), C_5H_5 4.66 (s, 5 H), C_6H_5, 7.0–7.8 (m, 20 H); ^{31}P NMR (δ from H_3PO_4) 93.6 and 85.0 (d, J_{P-P} = 32.2 Hz).

Preparation of Ethyl Derivatives 2b and 2b′. The reactions were carried out as the previous one with C_2H_5MgBr instead of CH_3MgBr at ~50 °C. The recovered products (yield 30–50%) were contaminated by variable amounts of the hydrides **3** and **3′** (detected through ^1H and ^{31}P NMR) and were identified through mass and NMR spectroscopy.

For both diastereomers a low intensity parent ion was recognizable at *m/e* 606; fragments at *m/e* 579 (100%) (possibly overlapped with a fragment at *m/e* 580 due to **3** and **3′**) 352, 393, and 459 (all of which contained ruthenium) were also present.

2b: ^1H NMR (C_7D_8) δ CH_2, −0.15 (m, 2 H), CH_3, 0.82 (ddd, 3 H, J_{H-H} = 7.2, J_{H-P_A} = 5.2, J_{H-P_B} = 0.9 Hz), CH_3, 0.95 (t, 3 H, J_{H-H} = 6.8 Hz), CH_2CH, 1.80–2.60 (m, 3 H), C_5H_5, 4.66 (s, 5 H), C_6H_5, 7.0–8.0 (m, 20 H); ^{31}P NMR (δ from H_3PO_4) 99.1 and 72.3 (d, J_{P-P} = 36.4 Hz).

2b′: ^1H NMR (C_7D_8) δ CH_2, −0.18 (m, 2 H), CH_3, 0.52 (dd, 3 H, J_{H-H} = 7.9, J_{H-P} = 6.4 Hz), CH_3 0.95 (t, 3 H, J_{H-H} = 6.8 Hz), CH_2CH, 1.80–2.60 (m, 3 H), C_5H_5, 4.58 (s, 5 H), C_6H_5, 7.0–8.0 (m, 20 H); ^{31}P NMR (δ from H_3PO_4) 88.3 and 81.6 (d, J_{P-P} = 37.1 Hz).

Preparation of Hydrides 3 and 3′. (a) Reaction of 1 and 1′ with Methanolic CH_3ONa. A mixture of 0.15 g (0.244 mmol) of 1 or 1′ and 10 mL of a 0.2 M solution of CH_3ONa in anhydrous methanol was stirred for 4 h at room temperature. During this time the color turns yellow. The solvent was eliminated under vacuum, and the stereochemistry of the reaction was determined through ^1H and ^{31}P NMR spectroscopy on the crude product. Pure **3** and **3′** were obtained through recrystallization from benzene/methanol (yield 80%). Both diastereomers show in the mass spectrum the parent ion at *m/e* 580 (100%) and other fragments containing ruthenium at *m/e* 352, 460, 393, 502, and 536.

3: ^1H NMR (C_6D_6) δ Ru–H, −13.04 (dd, 1 H, J_{P-H} = 29.4 Hz, J_{P-H} = 37.5 Hz), CH_3, 0.88 (dd, 3 H, J_{P-H} = 10.1 Hz, J_{H-H} = 6.4 Hz), CH_2CH, 1.76, 2.14, 2.26 (m, 3 H), C_5H_5, 4.70 (s, 5 H), C_6H_5 7.15–8.09 (m, 20 H); ^{31}P NMR (δ from H_3PO_4) 77.2 and 98.1 (d, J_{P-P} = 30.0 Hz). Anal. Calcd for $C_{32}H_{32}P_2Ru$: C, 66.31; H, 5.56. Found: C, 65.34;, H, 5.34.

3′: ^1H NMR (C_6D_6) δ Ru–H, −12.90 (t, 1 H, J_{P-H} = 32.0 Hz), CH_3, 0.57 (dd, 3 H, J_{P-H} = 12.5 Hz, J_{H-H} = 6.5 Hz), CH_2CH, 2.01, 2.30, 2.63 (m, 3 H), C_5H_5, 4.71 (s, 5 H), C_6H_5, 7.15–8.03 (m, 20 H); ^{31}P NMR (δ from H_3PO_4) 85.7 and 104.3 (d, J_{P-P} = 22.9 Hz). Anal. Found: C, 65.19; H, 5.34.

(b) Reaction of 1 and 1′ with HCOONa. A mixture of 0.15 g (0.244 mmol) of 1 or 1′ and 0.05 g (0.31 mmol) of NH_4PF_6 in 10 mL of anhydrous methanol was stirred for a few minutes. Then, 0.05 g (0.73 mmol) of solid HCOONa was added and the mixture stirred until the color turns yellow. The solvent was removed under reduced pressure and the stereochemistry tested on the crude product through ^1H and ^{31}P NMR spectroscopy.

3 and **3′** were obtained pure by recrystallization from benzene/methanol.

(c) Reaction of 1 and 1′ with *sec*-C_4H_9MgBr. 1 and 1′ (20 mg) were each reacted in NMR tubes in 0.5 mL of C_7D_8 with 0.2 mL of *sec*-C_4H_9MgBr (1.7 N) for 4 h. ^1H and ^{31}P NMR spectra reveal quantitative and exclusive stereospecific formation of **3** and **3′**, respectively.

Reaction of 3 and 3′ with CH_2N_2. A 20-mL Schlenk tube was charged with 50 mg of either **3** and **3′**, 1 mg of $Pd(OAc)_2$, and 2 mL of toluene. The solution was cooled at 0 °C and treated with a large excess of an ether solution of CH_2N_2. After a 4-h reaction time, the solvent was eliminated in vacuo. The residue was dissolved in C_6D_6 (~0.08 mL) and analyzed by ^1H and ^{31}P NMR after filtration. In each case stereospecific formation of **2a** and **2a′**, respectively, was recognized, in about 50% yield.

Reaction of 3 and 3′ with $CDCl_3$ and CCl_4. About 0.015 g (0.03 mmol) of **3** or **3′** was dissolved in $CDCl_3$ in a NMR tube. The reaction was monitored by recording from time to time the ^1H NMR spectra at room temperature.

The same procedure was used for the reaction of **3** and **3′** with CCl_4. In this case the complexes were dissolved in C_6D_6 and an excess of CCl_4 was added.

Reaction of 4 and 4′ with HCOONa. 4 and 4′ 0.1 mg (0.13 mmol) were treated for 24 h with an excess (50 mg, 0.73 mmol) of HCOONa in 10 mL of methanol. Then, the solvent was removed, the crude product dissolved in C_6D_6, and the solution filtered directly in a NMR tube. The stereochemistry of the reactions was determined by recording the ^1H NMR spectra.

Reaction of 4 and 4′ with Ph_4AsCl. A mixture of 0.15 g (0.2 mmol) of 4 or 4′ and 0.23 mg (0.55 mmol) of Ph_4AsCl was stirred for 2 days at room temperature in 10 mL of CH_2Cl_2. During this time the color turns from yellow to orange. After the solvent was removed under vacuum, the mixture was dissolved in CD_2Cl_2 and filtered off. The ^1H NMR spectra showed that at this time the conversion was about 50% and determined the stereochemistry of the reaction.

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a gift of $RuCl_3$ and Prof. H. Lehmkuhl for suggestions concerning NOE experiments.

Registry No. 1, 79681-92-8; 1′, 79732-92-6; **2a**, 85153-18-0; **2a′**, 85201-32-7; **2b**, 96151-62-1; **2b′**, 96193-47-4; **3**, 88898-37-7; **3′**, 88929-95-7; **4**, 90502-92-4; **4′**, 90581-29-6; (η-C_5H_5)RuCl(chiraphos), 79681-91-7; (η-C_5H_5)RuH(chiraphos), 96151-63-2; $CHDCl_2$, 1665-01-6.

Supplementary Material Available: CD spectra of **2a** and **2a′** (Figure 4), **3** and **3′** (Figure 5), and **4** and **4′** (Figure 6) (3 pages). Ordering information is given on any current masthead page.

Activation of Vinylidenebis(diphenylphosphine) through Metal Complexation

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Vinylidenebis(diphenylphosphine) (vdpp) was found to give an insoluble 1:2 complex, (vdpp)·$(AuCl)_2$ (1), but a soluble 1:1 complex, (vdpp·$AuCl)_2$ (2), when treated with (CO)AuCl in the appropriate molar ratio. The crystal structure determination of (vdpp·$AuCl)_2$·$CHCl_3$ revealed a dimer with a centrosymmetric eight-membered ring skeleton composed of two P,P-bridging vdpp ligands, and trigonally coordinated Au(I) centers, with the two AuP_2Cl planes parallel to each other. The vinylidene groups are not engaged in metal bonding but have become strongly activated through the vdpp–metal coordination. Methanol is added at 20 °C to give the AuCl complex of 1,1-bis(diphenylphosphino)-2-methoxyethane (6). This addition is reversible, and the CH_3OH is lost quantitatively at 150 °C, with recovery of **2**. 1:1 complexes were also prepared from CuCl, AgCl, $AgOCOCH_3$, and $AgBF_4$ (**3**, **4a–c**), but the vdpp ligands in none of these products is sufficiently activated to give similar addition reactions. Elemental analyses, osmometric molecular mass data, and ^1H, ^{13}C, and ^{31}P NMR, IR, and mass spectra were used for a preliminary characterization of the compounds. The X-ray data for **2** are as follows: $(C_{26}H_{22}AuClP_2)_2$·$CHCl_3$, a = 9.920 (2) Å, b = 11.545 (2) Å, c = 12.272 (2) Å, α = 90.40 (1)°, β = 88.25 (2)°, γ = 109.17 (1)°, d_{calcd} = 1.723 g cm^{-3} for Z = 1, space group $P\bar{1}$; 4339 observed reflections, R = 0.033, R_w = 0.042.

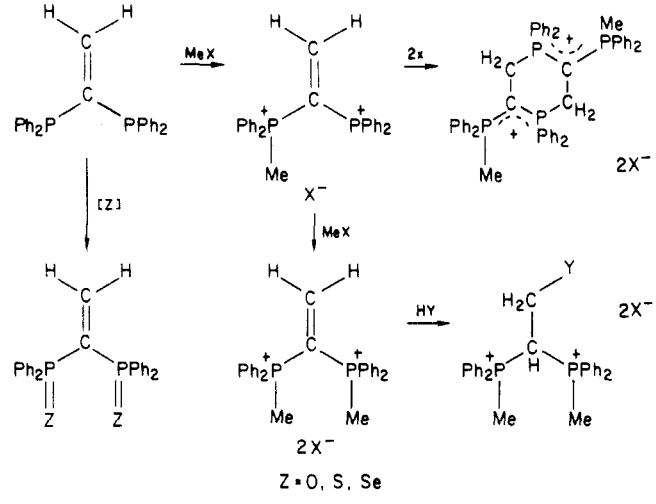
Introduction

A plethora of mono- or polydentate tertiary phosphines have been designed, synthesized, and introduced as ligands to metals and metal clusters in order to meet steric and electronic specifications suitable for application to stoichiometric or catalytic reactions.[1-3] These ligand molecules may either be prepared independently and then be integrated into a coordination sphere or constructed in a template synthesis at the metal center(s). For the latter purpose, organophosphorus compounds with versatile functional groups are of prime importance. It is therefore surprising that in this context the potentially reactive phosphino olefins have received little attention. Geminally phosphine-substituted olefins in particular are still rare species and have appeared in the literature only very recently.[4-6]

In initial studies carried out in this laboratory it was found that the prototype molecule vinylidenebis(diphenylphosphine), for which convenient syntheses are available,[4,5] can be strongly activated by monoquaternization with an alkyl halide. In the absence of a suitable nucleophile, dimerization occurs to give cyclic semiylide salts in quantitative yield at room temperature.[6] Double alkylation leads to bis(phosphonium) salts whose C=C bond is sufficiently electrophilic to add even weak components like alcohols, thiols, phosphines, or amines.[6-10] A similar activation is induced by oxidation of the phosphines with oxygen or sulfur (Scheme I).

These results made investigations highly desirable in which the effects of (phosphine)metal complexation on the olefinic double bond is probed. A large variety of mono- or binuclear complexes are possible candidates as acceptor centers, and therefore almost any degree of activation could

Scheme I



† X-ray structure analysis.

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