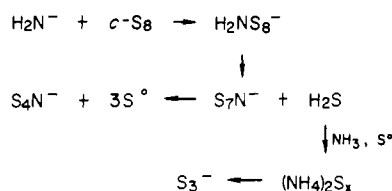


mation of the radical anion, S_3^- , is favored in dilute solutions in which it is undoubtedly formed by dissociation or disproportionation of polysulfides, e.g., S_4^{2-} or S_6^{2-} .⁸ The lack of an ESR signal for S_3^- in more concentrated solutions (10^{-1} M)³ is probably due to dimerization of the radical anions.⁸

In order to explain the formation of the anionic species identified by Raman spectroscopy in this investigation, we propose the following scheme.



The initial step in the cleavage of $c\text{-S}_8$ by nucleophiles (e.g., CN^- , S^{2-} , or Ph_3P)²⁸ is ring opening, and we suggest a similar step for the reaction of $c\text{-S}_8$ with the nucleophile NH_2^- formed by self-ionization of ammonia. Further degradation of the intermediate chain species, H_2NS_8 , by NH_2^- could produce intermediates of the type proposed by Sato and co-workers, i.e., H_2NS_x^- ($x = 1, 2$),⁶ but there is no direct evidence for these species from our spectroscopic studies. We propose that H_2NS_8^- loses H_2S to give the binary sulfur-nitrogen anion S_7N^- , which is known to rearrange to form S_4N^- .¹⁰ Support for this suggestion comes from the observation that S_7NH is formed, albeit in low yield, by the hydrolysis of blue solutions formed by passing ammonia into solutions of sulfur in HMPA.⁷ In the presence of ammonia and sulfur, the H_2S eliminated will form ammonium polysulfides and hence, by dissociation or disproportionation, the radical anion S_3^- .^{8,13,19}

Finally, it seems reasonable to conclude that the S_4N^- ion is one of the reactive nucleophiles in reactions of sulfur-ammonia solutions with organic substrates. Since salts of S_4N^- have recently been prepared and isolated,¹² the nucleophilic behavior of this anion can now be tested.

Acknowledgment. We thank Dr. J. Bojes for a gift of $\text{PPN}^+\text{S}_4\text{N}^-$ and the NSERC (Canada) for financial support.

Registry No. S_8 , 10544-50-0; NH_3 , 7664-41-7; S_3^- , 12597-04-5; S_4N^- , 74273-17-9.

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Enantioselective Displacement Reaction of PPh_3 by Chiral Diphosphines in $(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_2)_2$

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It is believed that chiral complexes containing optically active ligands in which the metal is a chirality center are important in determining the stereochemical course of homogeneous asymmetric reactions catalyzed by transition-metal complexes.¹⁻³ Optically active organometallic compounds of the above type were identified more than a decade ago.⁴

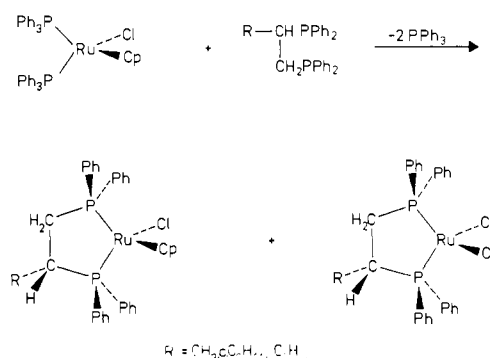
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Table I. ^1H and ^{31}P NMR Data for the Complexes Examined in Toluene- d_8 as the Solvent

complex	δ			$J_{\text{P}_1\text{P}_2}$, Hz	
	$\eta^5\text{-C}_5\text{H}_5^a$	P_1^b	P_2^b		
$\eta^5\text{-CpRuCl}(\text{PPh}_3)_2$	4.05	38.8			
$\eta^5\text{-CpRuCl}(\text{dpe})$	4.55 ^c	79.7			
$\eta^5\text{-CpRuCl}(\text{chiraphos})$	4.29 ^d	84.6	66.5	39.3	
$\eta^5\text{-CpRuCl}(\text{prophos})$ {	d_1^e	4.26	80.9	74.1	30.2
	d_2	4.30	86.4	61.3	36.7
$\eta^5\text{-CpRuCl}(\text{phephos})$ {	d_1	4.18	83.9	66.4	35.7
	d_2	4.13	90.2	58.1	40.0
$\eta^5\text{-CpRuCl}(\text{cyphos})$ {	d_1	4.30	71.0	67.4	36.8
	d_2	4.31	90.0	61.9	36.8

^a $(\text{CH}_3)_4\text{Si}$ as the internal standard. ^b H_3PO_4 85% as the external standard; downfield is positive. ^c In CD_2Cl_2 (see ref 7). ^d In CD_2Cl_2 . ^e $d = \text{diastereomer}$.

Scheme I



However, there are not many examples of kinetic control of the asymmetric induction in the formation of such organo-transition-metal compounds.³

It has recently been reported that 1,2-bis(diphenylphosphino)ethane (dpe) is able to displace triphenylphosphine from $(\eta^5\text{-cyclopentadienyl})\text{chlorobis}(\text{triphenylphosphine})\text{ruthenium(II)}$ (**1**) in boiling benzene^{5,6} or toluene.⁷ In view of our interest in the use of chiral homologues of dpe in asymmetric reactions such as hydroformylation⁸ and cross-coupling^{9,10} and our search for the mode of transmission of the chiral information from the ligand to the substrate, we have studied the displacement reaction of triphenylphosphine from **1** by (+)-(*R*)-1,2-bis(diphenylphosphino)propane (prophos),¹¹ by (-)-(*R*)-1-phenyl-1,2-bis(diphenylphosphino)ethane (phephos),¹² and by (-)-(*S*)-1-cyclohexyl-1,2-bis(diphenylphosphino)ethane (cycphos).¹³ Furthermore, the reaction of **1** with dpe and with (-)-(*2S,3S*)-2,3-bis(diphenylphosphino)butane (chiraphos)¹⁴ has also been investigated as a comparison.

The reactions were carried out in NMR tubes either under vacuum or under nitrogen, with equimolecular amounts of both reagents in toluene- d_8 as the solvent. Products were monitored

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by ^1H and ^{31}P NMR spectroscopy, and the NMR parameters of the chelate complexes and those of **1** are reported in Table I.

In the case of prophos, phephos, and cycphos, because of the nonequivalence of the two phosphorus atoms and because of the pseudotetrahedral structures of **1**,¹⁵ two diastereomers are expected to form (Scheme I), which have different configurations at the ruthenium atom. After about 2-h reaction time at 80 °C, the ^1H NMR spectrum of the reaction mixture shows that the signal of the η^5 -cyclopentadienyl protons of **1** has completely disappeared. Two new signals for these protons in nearly a 1:1 ratio appear in the case of prophos, phephos, and cycphos; however, only one signal appears in the case of dpe and chiraphos. In the ^{31}P NMR spectrum, the signal of **1** at +38.8 ppm and that at -13.4 ppm of free dpe completely disappear and the signal of free triphenylphosphine and a singlet of chelating dpe at +79.7 ppm appear. For chiraphos, there are two doublets in the resonance region of complexed chelate ($J_{\text{PP}} = 39.3$ Hz). These results are in keeping with the pseudotetrahedral structure of the complexes and with the fact that, for chiraphos, the two phosphorus atoms of the chelate ligand in the complex are diastereotopic due to the chirality centers present in the ligand. In the spectra of prophos, cycphos, and phephos two pairs of doublets are present in the range of resonances of the complexed ligands, supporting the formation of two diastereomers for each ligand.

The ratio of the diastereomers formed from prophos, phephos, and cycphos, calculated on the basis of the relative intensities of the cyclopentadienyl signals in the ^1H NMR spectra, remains unchanged, even after the reaction mixture has been heated for 48 h at 80 °C.

It is noteworthy that for prophos, phephos, and cycphos, when the reactions are carried out at room temperature, the ^{31}P NMR spectra of the mixtures show that one diastereomer is predominantly formed (d_1 in Table I). A more quantitative evaluation, based on the intensities of the signals of the cyclopentadienyl protons, gives ratios (d_1/d_2) of 80/20 for prophos, 87/13 for phephos, and 88/12 for cycphos, with about 25% conversion of **1** into the chelate complexes (reaction time 5 days). Thus asymmetric induction is rather high under these conditions.

The displacement reactions do not go to completion after 26 days. During this time the differences in the concentrations of the two diastereomers became smaller ($d_1/d_2 \sim 65/35$ for prophos and 73/27 for phephos). Apparently a slow epimerization at the ruthenium atom takes place.

The stepwise nature of the displacement reaction is easily recognized when the reactions are carried out at temperatures lower than 80 °C. When an equimolar solution of dpe and **1** is heated for 4 h at 50 °C, the ^{31}P NMR spectrum shows, in addition to the relatively small signal of free dpe, a doublet centered at -13.5 ppm ($J_{\text{PP}} = 27.2$ Hz), which is attributed to the noncoordinated phosphorus atom of dpe. A similar intermediate has been proposed for the reaction between dpe and $(\eta^5\text{-C}_5\text{H}_5)\text{OsBr}(\text{PPh}_3)_2$.⁵ Only a very small amount of the chelate complex is formed. A very complex pattern of signals is present in the region 38–43 ppm, due to complexed triphenylphosphine and the coordinated phosphorus atom of dpe, which acts as a monodentate ligand.¹⁶ When the ligand is prophos, after 5 days' reaction time at room temperature, two new doublets appear in the region of the chemical shifts of noncomplexed phosphorus atoms ($\delta_1 = -17.2$, $J_{\text{PP}} = 17.6$ Hz; $\delta_2 = +2.86$, $J_{\text{PP}} = 23.5$ Hz). These signals are attributed to the two types of uncoordinated monodentate prophos. There

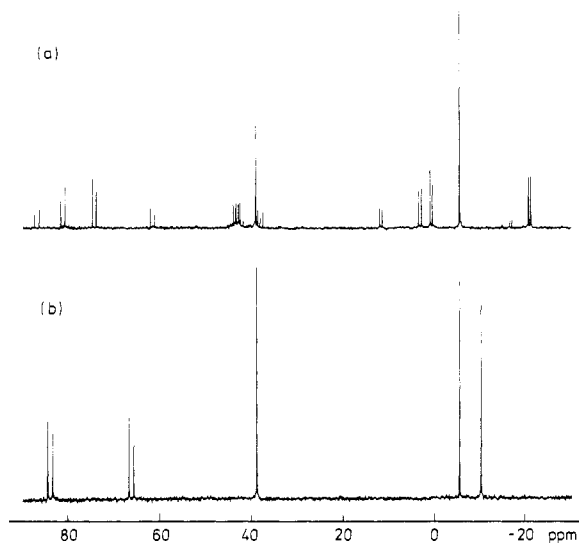
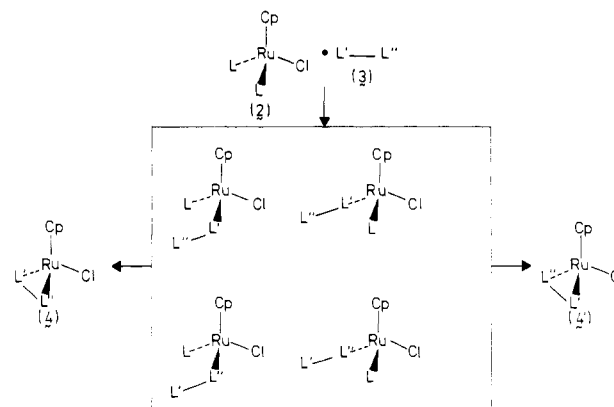


Figure 1. ^{31}P NMR spectra of the reaction mixtures of **1** with (a) (*R*)-prophos after 12 days at room temperature and (b) (*S,S*)-chiraphos after 4 h at 50 °C.

Scheme II



is also a four-line system centered at +11.3 ppm (the assignment of which is, at the moment, uncertain) and a complex pattern between +37 and +45 ppm (Figure 1a). In the case of phephos there are no new doublets in the region of the free ligand; however, two four-line systems at about +5.5 and +10.6 ppm appear in addition to the common complex pattern between +41.5 and +43.5 ppm. Analogously in the case of cycphos, a four-line system at about -4.1 ppm and the complex pattern between +41 and +42 ppm appear. In the case of chiraphos, only the signals due to the free ligand and to the complexed chelate ligand are present (Figure 1b).

The formation of chelate complexes appears to be more favored in the case of chiraphos in comparison with the other diphosphines used. This can be explained by considering that cyclization reactions become easier when the number of substituents on the moiety to be cyclized is increased. This explanation can be understood on the basis of the Thorpe–Ingold effect,¹⁷ which has already been found to play an important role in the formation of chelate transition-metal complexes.¹⁸

The displacement reaction becomes slower when the conversion is increased. Considering that **1** is an 18-electron complex,¹⁹ the decrease in the rate of reaction suggests that the displacement of triphenylphosphine takes place via a dissociative of the triphenylphosphine ligand. A dissociative

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mechanism has been indeed evidenced²⁰ in the phosphine substitution in $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)_2$ by trimethylphosphine leading to $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PMe}_3)(\text{PPh}_3)$. For the three unsymmetrical chelates a stepwise displacement should result in four different intermediates (Scheme II). At present it is not clear whether the first step occurs with a large enantioselectivity and which step is responsible for the high kinetic asymmetric induction observed.

Work is in progress to address the above questions and to separate the diastereomeric complexes that will be used in a stereochemical investigation.

Experimental Part

The solvents used were dried and degassed before use. (*R*)-prophos,¹¹ (*R*)-phephos,¹² (*S*)-cycphos,¹³ (*S,S*)-chiraphos,¹⁴ and $(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2$ ²¹ were prepared according to methods described in the literature. ¹H NMR spectra were recorded at 90 MHz on a WH 90 Bruker spectrometer using $(\text{CH}_3)_4\text{Si}$ as the internal standard. ³¹P NMR spectra were recorded at 24.28 MHz with ¹H complete decoupling; 85% H_3PO_4 was used as the external standard, with the convention that increasing frequency is positive.

General Procedure for NMR Analysis of Exchange Reactions. A mixture of 30.5 mg (42.0 μmol) of **1** and the equimolecular amount of the appropriate diphosphine was dissolved in toluene-*d*₆ directly in a NMR tube under inert atmosphere. In some cases the tube was sealed under vacuum. The ¹H and ³¹P NMR spectra were recorded from time to time at room temperature. The exchange reaction between **1** and (*S,S*)-chiraphos was also carried out on a preparative scale.

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}((S,S)\text{-chiraphos})$. We used a procedure similar to that described for the analogous complex containing dpe.⁵ A mixture of **1** (1 g; 1.38 mmol) and (*S,S*)-chiraphos (0.59 g; 1.38 mmol) was refluxed in 100 mL benzene for 3 h. The volume was reduced to 20 mL, and heptane was added until an orange precipitate formed. The crude product was recrystallized from CH_2Cl_2 /heptane; mp 255 °C dec. Anal. Calcd for $\text{C}_{33}\text{H}_{33}\text{ClP}_2\text{Ru}$: C, 63.11; H, 5.30; Cl, 5.64. Found: C, 61.75; H, 5.44; Cl, 5.70. ¹H NMR (CD_2Cl_2): δ 0.85 (dd, 3 H, CH_3 ; $J_{\text{PH}} = 11.2$ Hz, $J_{\text{HH}} = 6.7$ Hz), 1.00 (dd, 3 H, CH_3 ; $J_{\text{PH}} = 11.0$ Hz, $J_{\text{HH}} = 6.5$ Hz), 1.90–2.22 (complex m, 1 H, CH), 2.50–2.85 (complex m, 1 H, CH), 4.29 (1, 5 H, C_5H_5), 6.96–8.05 (complex m, 20 H, C_6H_5).

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Registry No. **1**, 32993-05-8; $\eta^5\text{-CpRuCl}(\text{dpe})$, 71397-10-9; $\eta^5\text{-CpRuCl}(\text{chiraphos})$, 79681-91-7; $\eta^5\text{-CpRuCl}(\text{prophos})$, isomer *d*₁, 79681-92-8; $\eta^5\text{-CpRuCl}(\text{prophos})$, isomer *d*₂, 79732-92-6; $\eta^5\text{-CpRuCl}(\text{phephos})$, isomer *d*₁, 79681-93-9; $\eta^5\text{-CpRuCl}(\text{phephos})$, isomer *d*₂, 79732-93-7; $\eta^5\text{-CpRuCl}(\text{cycphos})$, isomer *d*₁, 79681-94-0; $\eta^5\text{-CpRuCl}(\text{cycphos})$, isomer *d*₂, 79733-76-9.

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Reaction of $\text{SF}_5\text{C}\equiv\text{CCF}_3$ with $\text{Ni}(\text{CO})_4$

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Interest in transition-metal-acetylene chemistry originated with the report by Reppe in 1948 of the Ni(II)-catalyzed cyclization of acetylene to benzene.¹ Since that time, work

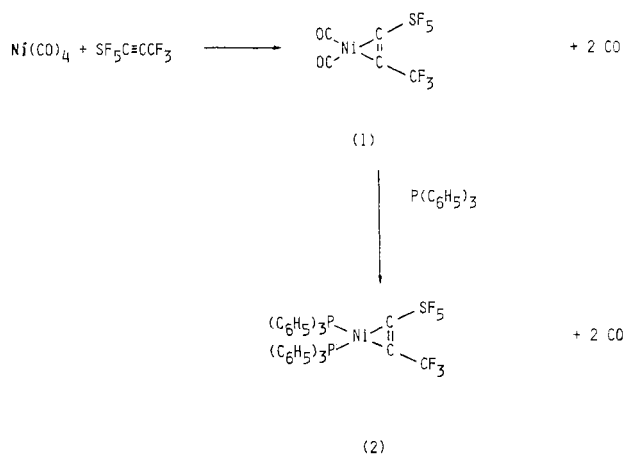


Figure 1. Reaction scheme for $\text{Ni}(\text{CO})_4$ and $\text{SF}_5\text{C}\equiv\text{CCF}_3$.

in this area has expanded to include studies of the catalytic effects of numerous transition-metal complexes, most notably those in group 8, on the reactions of a variety of acetylene derivatives.² For these purposes, nickel tetracarbonyl has frequently been used as a convenient source of nickel in a low oxidation state. We have investigated the reaction between nickel tetracarbonyl and pentafluoro[(trifluoromethyl)acetylenyl]sulfur as a possible means of cyclizing, and perhaps polymerizing, the acetylene.

Pentafluoro[(trifluoromethyl)acetylenyl]sulfur and nickel tetracarbonyl react at room temperature, with periodic removal of CO at -196 °C, to produce a yellow liquid (**1**) identified as $\text{Ni}(\text{CO})_2(\text{SF}_5\text{C}_2\text{CF}_3)$ (Figure 1). The reaction can be followed conveniently by mixing the reactants in a gas-phase infrared cell as described in the Experimental Section. The product appears to be stable in the presence of small quantities of CO but decomposes to form CO, SF_4 , $\text{CF}_3\text{C}\equiv\text{C}\equiv\text{CF}_3$, and a brown residue upon continued removal of CO.

The gas-phase infrared spectrum of **1** contains two intense bands (2140 , 2100 cm^{-1}) and a third weaker band (2060 cm^{-1}) in the terminal CO stretching region as expected for a nickel dicarbonyl compound. In addition, two moderately intense bands are seen at 1890 and 1865 cm^{-1} , which are assigned to the C=C stretching vibration. The ¹⁹F NMR spectrum contains a poorly resolved, irregular quartet at -75.5 ppm, a smaller singlet at -75.2 ppm, and a quintet, also poorly resolved and irregular, at 55.6 ppm.

Compound **1** reacts with an ether solution of triphenylphosphine at -78 °C to form a bright yellow solid (**2**) identified as $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{SF}_5\text{C}_2\text{CF}_3)$ and a noncondensable gas (presumably CO). The infrared spectrum of **2** contains no absorptions in the CO stretching region but does have a band of moderate intensity at 1750 cm^{-1} , which is assigned to $\nu(\text{C}=\text{C})$. This represents a decrease of a little more than 100 cm^{-1} in comparison to $\nu(\text{C}=\text{C})$ for **1** and is consistent with a greater amount of $\text{Ni } d \rightarrow \pi^* \text{C}=\text{C}$ interaction in **2**. Such an effect is consistent with the stronger σ -donor and weaker π -acceptor abilities of $\text{P}(\text{C}_6\text{H}_5)_3$, which place a higher electron density on the nickel atom in comparison to CO. The proton NMR spectrum in methylene-*d*₂ chloride contains a multiplet in the phenyl region with a τ value of 2.78 for the most intense peak. In contrast to **1**, the fluorine spectrum contains the expected AB_4 pattern in the SF_5 region with $\delta_{\text{A}} = -82.3$ and $\delta_{\text{B}} = -77.2$ for the most intense peaks in each of the patterns, and

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(2) See for example: Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1 and references therein.