

mechanism has been indeed evidenced<sup>20</sup> 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,<sup>11</sup> (*R*)-phephos,<sup>12</sup> (*S*)-cycphos,<sup>13</sup> (*S,S*)-chiraphos,<sup>14</sup> and  $(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2$ <sup>21</sup> were prepared according to methods described in the literature. <sup>1</sup>H NMR spectra were recorded at 90 MHz on a WH 90 Bruker spectrometer using  $(\text{CH}_3)_4\text{Si}$  as the internal standard. <sup>31</sup>P NMR spectra were recorded at 24.28 MHz with <sup>1</sup>H complete decoupling; 85%  $\text{H}_3\text{PO}_4$  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  $\mu\text{mol}$ ) of **1** and the equimolecular amount of the appropriate diphosphine was dissolved in toluene-*d*<sub>6</sub> directly in a NMR tube under inert atmosphere. In some cases the tube was sealed under vacuum. The <sup>1</sup>H and <sup>31</sup>P 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.<sup>5</sup> 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  $\text{CH}_2\text{Cl}_2$ /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. <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  0.85 (dd, 3 H,  $\text{CH}_3$ ;  $J_{\text{PH}} = 11.2$  Hz,  $J_{\text{HH}} = 6.7$  Hz), 1.00 (dd, 3 H,  $\text{CH}_3$ ;  $J_{\text{PH}} = 11.0$  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,  $\text{C}_5\text{H}_5$ ), 6.96–8.05 (complex m, 20 H,  $\text{C}_6\text{H}_5$ ).

**Acknowledgment.** We thank P. Pino, P. S. Pregosin, and L. M. Venanzi for reading and commenting on the manuscript. We are also grateful to Dr. D. P. Riley for sending us a sample of cycphos and a description for the method of preparation<sup>13</sup> prior to publication.

**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*<sub>1</sub>, 79681-92-8;  $\eta^5\text{-CpRuCl}(\text{prophos})$ , isomer *d*<sub>2</sub>, 79732-92-6;  $\eta^5\text{-CpRuCl}(\text{phephos})$ , isomer *d*<sub>1</sub>, 79681-93-9;  $\eta^5\text{-CpRuCl}(\text{phephos})$ , isomer *d*<sub>2</sub>, 79732-93-7;  $\eta^5\text{-CpRuCl}(\text{cycphos})$ , isomer *d*<sub>1</sub>, 79681-94-0;  $\eta^5\text{-CpRuCl}(\text{cycphos})$ , isomer *d*<sub>2</sub>, 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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Received June 23, 1981

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

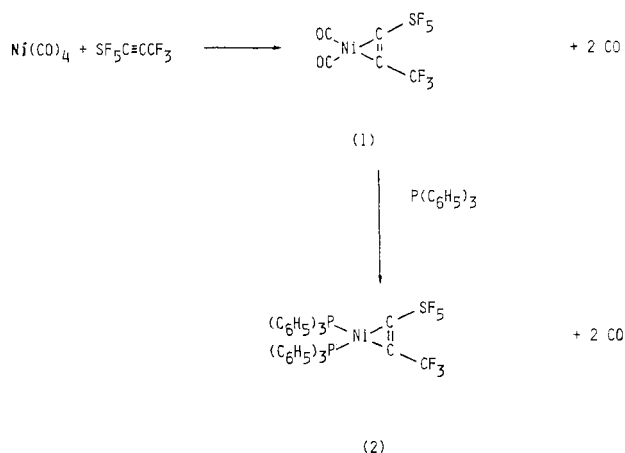


Figure 1. Reaction scheme for  $\text{Ni}(\text{CO})_4$  and  $\text{SF}_5\text{C}\equiv\text{CCF}_3$ .

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.<sup>2</sup> 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,  $\text{SF}_4$ ,  $\text{CF}_3\text{C}\equiv\text{C}\equiv\text{CF}_3$ , and a brown residue upon continued removal of CO.

The gas-phase infrared spectrum of **1** contains two intense bands ( $2140$ ,  $2100$   $\text{cm}^{-1}$ ) and a third weaker band ( $2060$   $\text{cm}^{-1}$ ) in the terminal CO stretching region as expected for a nickel dicarbonyl compound. In addition, two moderately intense bands are seen at  $1890$  and  $1865$   $\text{cm}^{-1}$ , which are assigned to the  $\text{C}\equiv\text{C}$  stretching vibration. The <sup>19</sup>F 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  $1750$   $\text{cm}^{-1}$ , which is assigned to  $\nu(\text{C}=\text{C})$ . This represents a decrease of a little more than 100  $\text{cm}^{-1}$  in comparison to  $\nu(\text{C}\equiv\text{C})$  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  $\sigma$ -donor and weaker  $\pi$ -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*<sub>2</sub> chloride contains a multiplet in the phenyl region with a  $\tau$  value of 2.78 for the most intense peak. In contrast to **1**, the fluorine spectrum contains the expected  $\text{AB}_4$  pattern in the  $\text{SF}_5$  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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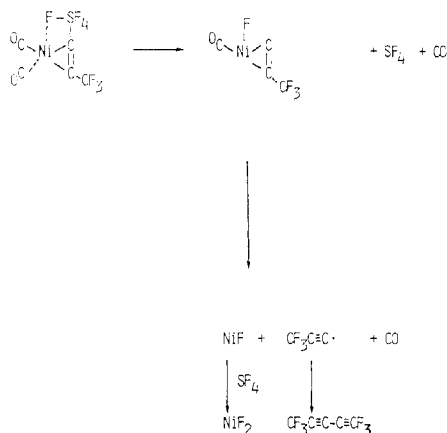


Figure 2. Proposed decomposition path for  $\text{Ni}(\text{CO})_2(\text{SF}_5\text{C}_2\text{CF}_3)$ .

$J_{\text{F}_A-\text{F}_B} = 126$  Hz. In the CF region, a multiplet (sextet,  $\delta = 53.2$ ,  $J = 6.4$  Hz) is observed.

Our results show that  $\text{SF}_5\text{C}\equiv\text{CCF}_3$  reacts with  $\text{Ni}(\text{CO})_4$  to form a product whose spectroscopic and chemical properties are consistent with the formulation  $\text{Ni}(\text{CO})_2(\text{SF}_5\text{C}_2\text{CF}_3)$  as shown in Figure 1. This is analogous to the reaction of hexafluorobutene with  $\text{Ni}(\text{CO})_4$  at 50–60 °C to form  $\text{Ni}(\text{CO})_2(\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)$  (**3**).<sup>3</sup> Although both compounds are moderately stable at room temperature in the presence of either excess CO for **1** or hexafluorobutene for **3**, they decompose to give very different products. For example, **1** eliminates CO,  $\text{SF}_4$ , and  $\text{CF}_3\text{C}\equiv\text{C}-\text{C}\equiv\text{CCF}_3$ , suggesting an interaction between the nickel atom and the  $\text{SF}_5$  group as shown in Figure 2, whereas  $\text{Ni}(\text{CO})_2(\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)$  forms the cluster complex  $\text{Ni}_4(\text{CO})_{14}[\mu_3(\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)]_3$ . The triphenylphosphine derivative of **1** is stable at ambient conditions, showing no tendency to decompose in this fashion. This could be attributed to the nickel atom being a comparatively weaker Lewis acid toward the fluorine lone pairs as a result of its bonding to the more basic triphenylphosphine groups in **2**. In neither system do we find evidence for the cyclization or polymerization of  $\text{SF}_5\text{C}\equiv\text{CCF}_3$ , which was our primary objective.

### Experimental Section

Vacuum-system operations were carried out in a Pyrex system equipped with greaseless Kontes glass/Teflon stopcocks. Routine infrared spectra were recorded on a Perkin-Elmer 467 spectrophotometer using a 10-cm glass cell equipped with 25-mm KBr windows. NMR spectra were obtained by using a JEOL JNM-FX60Q spectrometer operating at 59.75 MHz for  $^1\text{H}$  and 56.20 MHz for  $^{19}\text{F}$ . Chemical shifts are reported relative to  $(\text{CH}_3)_4\text{Si}$  and  $\text{CFCl}_3$  for proton and fluorine spectra, respectively. Mass spectra were recorded with a CVC time-of-flight spectrometer operating at 70 eV. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Pentafluoro[(trifluoromethyl)acetylenyl]sulfur was prepared according to published procedures.<sup>4</sup>

**Infrared Study of  $\text{Ni}(\text{CO})_4 + \text{SF}_5\text{C}\equiv\text{CCF}_3$ .** Nickel tetracarbonyl (0.10 mmol) and  $\text{SF}_5\text{C}\equiv\text{CCF}_3$  (0.11 mmol) were condensed into the cold finger of a gas-phase infrared cell. The mixture was subjected to several freeze-thaw cycles, which resulted in the formation of a yellow liquid in the cell. The gas-phase spectrum of the vapor above the liquid contained the following bands: 2360 (br, w), 2180 (br, w), 2140 (vs), 2100 (vs), 2060 (vs), 1890 (m), 1865 (s), 1260 (vs), 1245 (vs), 1200 (vs), 940 (vs), 910 (vs), 885 (vs), 840 (vs), 765 (s), 735 (PQR, w), 720 (m), 675 (s), 650 (m), 610 (vs), 590 (m), 515 (w), 490 (m), 455 (m), 425 (w)  $\text{cm}^{-1}$ . Noncondensable gases were removed, and a second spectrum was run, which revealed a considerable decrease in the intensities of bands at 2360, 2180, 2060, and 425  $\text{cm}^{-1}$  and a moderate increase in the PQR band at 735  $\text{cm}^{-1}$ . The mass spectrum

of these materials in the gas phase contained peaks arising from  $\text{SF}_5\text{C}\equiv\text{CCF}_3$ , CO,  $\text{CO}_2$ ,  $\text{CF}_3\text{C}\equiv\text{C}-\text{C}\equiv\text{CCF}_3$ , and possibly  $\text{SF}_4$  (a strong peak at 89 amu for  $\text{SF}_3^+$  suggested the presence of  $\text{SF}_4$ ; this would be consistent with assigning the PQR band at 735  $\text{cm}^{-1}$  in the infrared spectrum to  $\text{SF}_4$ ).<sup>5</sup> The materials that were volatile at -78 °C were removed, leaving a yellow liquid whose gas-phase spectrum contained bands at 2140 (vs), 2100 (vs), 2060 (m), 1890 (m), 1865 (s), 1255 (vs), 1240 (vs), 1180 (vs), 945 (s), 910 (s), 885 (vs), 850 (vs), 765 (s), (740, 730, 720) (s), 675 (s), 645 (m), 610 (s), 585 (m), 575 (m), 520 (w), 490 (m), and 455 (m)  $\text{cm}^{-1}$ .

**NMR Study of  $\text{Ni}(\text{CO})_4 + \text{SF}_5\text{C}\equiv\text{CCF}_3$ .** Nickel tetracarbonyl (0.48 mmol) and  $\text{SF}_5\text{C}\equiv\text{CCF}_3$  (0.71 mmol) were condensed into an NMR tube and warmed to room temperature. The mixture was subjected to several freeze-thaw cycles at -196 °C to remove noncondensable gases (presumably CO) produced in the formation of a yellow liquid. Fluorotrichloromethane (0.98 mmol) was added to the mixture, and the tube was sealed off. The spectra are discussed in the text.

**Synthesis of  $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{SF}_5\text{C}_2\text{CF}_3)$ .** Nickel tetracarbonyl (0.74 mmol) and  $\text{SF}_5\text{C}\equiv\text{CCF}_3$  (0.97 mmol) were condensed into one part of a two-sided reactor connected by the side arm of a glass/Teflon stopcock. The second part of the reactor contained an evacuated solution of  $\text{P}(\text{C}_6\text{H}_5)_3$  (2.11 mmol in 1 mL of dry diethyl ether). After removal of the noncondensable gases from the  $\text{Ni}(\text{CO})_4\text{-SF}_5\text{C}_2\text{CF}_3$  mixture with several freeze-thaw cycles at -196 °C, the mixture was cooled to -78 °C, and excess  $\text{SF}_5\text{C}_2\text{CF}_3$  (0.27 mmol) was removed, leaving a yellow liquid. The triphenylphosphine-ether solution was then transferred into the section containing the yellow liquid, and a yellow solid formed immediately. The noncondensable gases were removed, and the ether was distilled out of the reactor upon warming. The solid was dissolved in  $\text{CH}_2\text{Cl}_2$ , followed by precipitation at -78 °C and washing with hexane to yield 136.4 mg (23%) of a yellow powder identified as  $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{SF}_5\text{C}_2\text{CF}_3)$  (**2**). The compound melted at 137 °C with decomposition. Anal. Calcd for  $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{SF}_5\text{C}_2\text{CF}_3)$ : C, 58.31; H, 3.76; Ni, 7.31. Found: C, 59.65; H, 3.97; Ni, 7.50. Molecular weight: calcd, 803; found (in  $\text{CH}_2\text{Cl}_2$ ), 828. The infrared spectrum of **2** in a KBr pellet contained the following bands: 3060 (w), 1750 (m), 1480 (m), 1430 (m), 1310 (w), 1245 (m), 1215 (vs), 1110 (vs), 1025 (w), 1000 (w), 900 (m), 825 (vs), 745 (s), 690 (s), 655 (w), 630 (w), 590 (w), 510 (s), 495 (s), 455 (w), 420 (w)  $\text{cm}^{-1}$ . The NMR spectra in methylene- $d_2$  chloride are discussed in the text.

**Registry No.** **1**, 79681-89-3; **2**, 79681-90-6;  $\text{Ni}(\text{CO})_4$ , 13463-39-3;  $\text{SF}_5\text{C}\equiv\text{CCF}_3$ , 69923-35-9.

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### Crystal and Molecular Structure of Dimethyl- $\mu$ -cyclopentadienyl-aluminum Polymer

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Received June 18, 1981

The chemistry, structures, and bonding associated with cyclopentadienylmetal derivatives are of major interest because of the ability of this organic moiety to form derivatives with  $\eta^1$ -,  $\eta^2$ -,  $\eta^3$ -, and  $\eta^5$ -bound cyclopentadienyl groups and often include two or more types of cyclopentadienyl groups bound

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