Reactions of Electrophiles with a Metal–Hydride Complex. Reduction of CS_2 by $Cp^*Rh(PMe_3)H_2$ To Produce the Bridging Methanedithiolate Complex $Cp^*Rh(PMe_3)(SCH_2S)$

William D. Jones* and Anthony D. Selmeczy

Department of Chemistry, University of Rochester, Rochester, New York 14627

Received August 13, 1991

The title complex $Cp^*Rh(PMe_3)(SCH_2S)$ (**3**) was prepared by the reaction of $Cp^*Rh(PMe_3)H_2$ with CS_2. No reaction was observed with CO_2 at ambient or elevated temperatures and pressures. Reaction with OCS gave the known compounds $Cp^*Rh(PMe_3)(CO)$ (**4**) and $Cp^*Rh(CO)_2$ (**5**) plus $S{=}PMe_3$. Kinetic measurements show a first-order dependence on $[CS_2]$ and a small dependence on solvent polarity. Activation parameters for the reaction with CS_2 were also measured, consistent with an associative transition state. The molecular structure of **3** was determined by a single-crystal X-ray diffraction study. **3** crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.594$ (5) Å, $b = 21.546$ (7) Å, $c = 9.050$ (4) Å, $\beta = 95.73$ (4)°, and $Z = 4$.

Introduction

There is considerable interest in the reduction of CO_2 by metal complexes to activate this otherwise highly unreactive molecule.[1] Insertions of CO_2 into metal–hydride bonds to produce formate complexes are rare.[2] Much use has been made, however, of the heterocumulenes OCS and CS_2 as more reactive models for CO_2 activation. There have been numerous accounts of CS_2 insertion into metal–hydride bonds to give dithioformate complexes[3] and several instances of CS_2 reacting with polynuclear systems to give bridging methanedithiolate compounds.[4] A few systems have also been reported in which sulfhydryl ligands react with CH_2Cl_2 or acetone to give a four-membered metallocycle methanedithiolate complex.[5] Only one example to date, however, has been reported in which a metal dihydride has converted a carbon disulfide molecule to a methanedithiolate moiety in the form of a metallocycle.[6] We report here the second example of such a reaction using the dihydride $Cp^*Rh(PMe_3)H_2$.

Scheme I

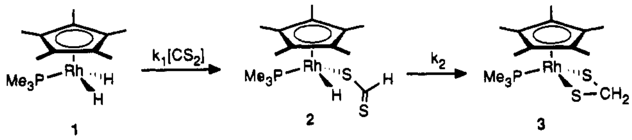


Table I. Rate Data for the Reaction of **1** with CS_2 at 25 °C[a]

$[CS_2]$, M	solvent	k_{obs}, s^{-1}
0.037	THF	0.000 878 (2)
0.037	THF	0.000 788 (2)
0.052	THF	0.001 05 (1)
0.052	THF	0.001 08 (1)
0.104	THF	0.001 74 (1)
0.104	THF	0.002 13 (1)
0.200	THF	0.004 03 (3)
0.200	THF	0.003 88 (3)
0.052	C_6H_6	0.000 699 (1)
0.052	hexanes	0.000 081 (2)

[a] [**1**] = 0.000 44 M.

Results

The dihydride $Cp^*Rh(PMe_3)H_2$ (**1**) (Cp^* = permethylcyclopentadienyl) is prepared as a light tan oil by reacting $Cp^*Rh(PMe_3)Cl_2$ with $PPNBH_4$ (bis(triphenylphosphine)nitrogen(1+) tetrahydroborate) overnight in THF. Addition of excess CS_2 in C_6D_6 causes a color change from colorless to dark red over the course of 20 min. ^1H and ^{31}P spectra show no starting material remaining, and a single new product is obtained in 59% isolated yield (Scheme I). The new product is formulated as $Cp^*Rh(PMe_3)(SCH_2S)$ (**3**) and exhibits ^1H resonances at δ 1.572 (Cp^*, d, J = 3 Hz), 1.379 (PMe_3, d, J = 10 Hz), 5.730 (SCH*H*S, dt, J = 7.3, 2.3 Hz), and 5.025 (SC*H*HS, dd, J = 7.3, 5.6 Hz). The ^{31}P spectrum shows a doublet centered at δ 5.039 with a coupling constant of 159 Hz, indicative of Rh in the +3 oxidation state.[7] The IR spectrum shows a strong band at 1261 cm^{-1} assigned to ν(C–S).

At early reaction times an intermediate can be observed by NMR spectroscopy. A ^1H NMR spectrum obtained immediately after injection of the CS_2 shows new resonances at δ 1.646 (Cp^*, s), 1.034 (PMe_3, d, J = 11.5 Hz), a new hydride at −11.432 (dd, J = 43, 16.5 Hz), and a low-field resonance at 11.949 (SC(S)*H*, s). The ^{31}P spectrum shows a resonance at δ 1.836 (d, J = 148 Hz) consistent with Rh^{III}. This intermediate is formulated as the S-bound [1,2] insertion product $Cp^*Rh(PMe_3)(SC(S)H)H$ (**2**) on the basis of the above data. This species is only observed for several minutes, after which complete conversion to **3** is achieved.

---

[1] For reviews on the subject, see, for example: (a) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135. (b) Sneedon, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, Stone, Abel, Eds.; Pergamon Press; Oxford, U.K., 1982, Vol. 8, Chapter 50.4.

[2] (a) Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *22*, L 35. (b) Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 3529. (c) Darensbourg, D. J.; Rokiki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223. (d) Darensbourg, D. J.; Rokiki, A. *J. Am. Chem. Soc.* **1982**, *104*, 349. (e) Slater, S. G.; Lusk, R.; Schumann, B. F.; Darensbourg, M. Y. *Organometallics* **1982**, *1*, 1662.

[3] For reviews on the subject, see: (a) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *101*, 161. (b) Yaneff, P. V. *Coord. Chem. Rev.* **1977**, *101*, 183. (c) Morandini, F.; Consiglio, G.; Sironi, A. *Gazz. Chim. Ital.* **1987**, *117*, 61.

[4] (a) Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 1306. (b) Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 546.

[5] See, for example: (a) Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwangert, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456. (b) Rakowski DuBois, M.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064. (c) Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 3710. (d) McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329. (e) Klein, D. P.; Kloster, G. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 2022.

[6] Okuda, J. *Z. Naturforsch.* **1990**, *45B*, 753.

[7] Klingert, B.; Werner, H. *Chem. Ber.* **1983**, *116*, 1450.

0276-7333/92/2311-0889$03.00/0

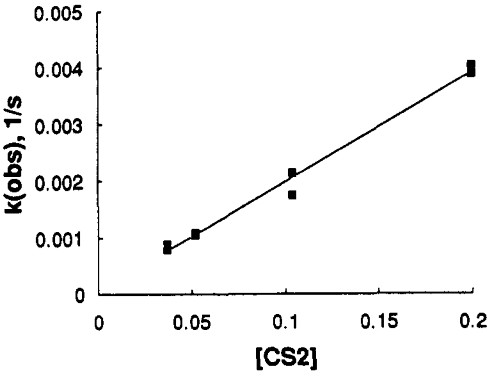


Figure 1. Plot of k_{obs} vs $[CS_2]$ for the reaction of $Cp^*Rh(PMe_3)H_2$ with CS_2 at 25 °C.

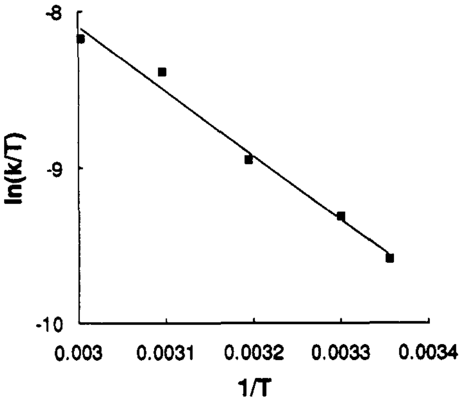


Figure 2. Eyring plot for the reaction of $Cp^*Rh(PMe_3)H_2$ with CS_2.

Table II. Rate Data for the Reaction of 1 with CS_2 at Different Temperatures[a]

temp, K	k_1, s^{-1}	temp, K	k_1, s^{-1}
298	0.0204 (1)	323	0.0737 (1)
303	0.0273 (1)	333	0.0938 (1)
313	0.0406 (1)		

[a] $[CS_2]$ = 0.052 M; [1] = 0.00044 M.

Table III. Intramolecular Distances (Å) and Angles (deg) for $Cp^*Rh(PMe_3)(SCH_2S)$

	distance		angle
Rh-S1	2.361 (1)	S1-Rh-S2	73.58 (5)
Rh-S2	2.376 (2)	S1-Rh-P1	93.43 (5)
Rh-P1	2.265 (1)	S2-Rh-P1	87.43 (5)
S1-C1	1.832 (4)	Rh-S1-C1	90.9 (1)
S2-C1	1.821 (4)	Rh-S2-C1	90.7 (1)
		S1-C1-S2	101.9 (2)

The kinetics of this reaction were studied in detail. Rates were measured by monitoring the appearance of product 3 by UV-visible spectroscopy at λ = 320 nm for at least 5 half-lives. Pseudo-first-order kinetics were obtained with varying excess concentrations of CS_2 (Table I) using THF solvent. Data were fit assuming a single-exponential rise with constant offset A_0 (see Experimental Section). Plotting $[CS_2]$ vs k_{obs} gives a straight line indicating first-order dependence on $[CS_2]$ (Figure 1). The slope of the line in Figure 1 gives $k_1 = 0.0193\ (8)\ M^{-1}\ s^{-1}$.

With the mechanistic scheme shown in Scheme I the rate law in eq 1 can be derived. Two limiting cases are possible: (i) $k_1[CS_2] \gg k_2$ and (ii) $k_2 \gg k_1[CS_2]$ which simplify to the expressions given in eqs 2 and 3, respectively.

$$\text{rate} = \frac{d[3]}{dt} = [1]_0 \frac{k_1k_2[CS_2]}{k_2 - k_1[CS_2]}(e^{-k_1[CS_2]t} - e^{-k_2t}) \quad (1)$$

$$\text{rate} = [1]_0k_2e^{-k_2t} \quad (2)$$

$$\text{rate} = [1]_0k_1[CS_2]e^{-k_1[CS_2]t} \quad (3)$$

The first-order dependence on $[CS_2]$ indicates that regime ii is in fact the case under the conditions employed in the UV-visible kinetic experiments. The observation of intermediate 2 at early reaction times (<3 min) in the NMR experiments is consistent with this scheme, since these experiments used higher CS_2 concentrations, thus satisfying $k_1[CS_2] \cong k_2$ at the early stages of the reaction and allowing a rapid buildup of 2.

The activation parameters were determined for the reaction by measuring the rate over a 35-deg temperature range (Table II). An Eyring plot of ln (k/T) vs $1/T$ gives $\Delta H^‡$ = 8.2 (5) kcal mol^{-1} and $\Delta S^‡$ = −39 (2) eu (Figure 2). The large negative value for $\Delta S^‡$ is consistent with the associative mechanism proposed above. The small positive $\Delta H^‡$ value shows little bond breaking in the transition state. Mechanistic implications are discussed below.

A single-crystal X-ray determination was performed for complex 3. An ORTEP drawing is shown in Figure 3. Structural features of the $Cp^*Rh(PMe_3)(SCH_2S)$ molecule are not unusual. The methylene group is bent out of the S-Rh-S plane by roughly 18° toward the Cp* ring, as was seen earlier in a similar iridium complex.[5e] The S-C-S bond angle is 104.82°, indicating almost perfect tetrahedral geometry at C1. Carbon-sulfur distances are typical of C-S single bonds (1.832 and 1.821 Å). The bite angle of the methanedithiolate is slightly acute (73.58°), and the Rh-S-C angle is nearly 90°. Selected bond lengths and angles are given in Table III. A complete listing of bond lengths, angles, and thermal parameters is available in the supplementary material.

The reaction of 1 with CS_2 prompted the examination of other similar substrates. No reaction was observed between 1 and CO_2 (1 atm) at room temperature. Attempts to react 1 with CO_2 were unsuccessful under conditions of 1 atm and 80 °C (benzene reflux) overnight. The solution darkened considerably due to decomposition, and only starting material was detected by ^1H and ^{31}P spectroscopy. Elevated pressures of CO_2 (100 psi) at 65 °C for 24 h yielded no identifiable products.

It was anticipated that reaction with carbonyl sulfide (OCS) might proceed via insertion of the C-S bond into the metal hydride to give either a mono- or disubstituted product,[8] but this was not observed. When a large excess of OCS is condensed into a solution of 1 in C_6D_6, a slow reaction takes place, resulting initially in the formation of a single metal-containing species, as determined by ^1H and ^{31}P NMR spectroscopy. The ^1H NMR spectrum shows only two new peaks corresponding to the new material at δ 1.970 (Cp*, d, J = 1.7 Hz) and 1.051 (PMe_3, d, J = 9.1 Hz). No peaks assignable to a new hydride, aldehyde, or reduced OCS metallocycle are seen, and free H_2 is observed at δ 4.459. The ^{31}P NMR spectrum shows a single metal-containing compound at δ −5.16 (d, J = 190 Hz) and the presence of S=PMe, at δ 27.81. The large coupling constant reflects a change in the oxidation state of rhodium from +3 to +1. The new product is assigned as the carbonyl adduct $Cp^*Rh(PMe_3)(CO)$ (4) on the basis of comparison with an authentic sample. This species disappears over several days if excess OCS is present, showing only a singlet in the ^{31}P spectrum corresponding to $SPMe_3$, and a new metal product is detected via ^1H NMR (δ 1.73, s) and IR spectroscopy. Some free C_5Me_5H is also observed. The final metal product is established as $Cp^*Rh(CO)_2$ (5)

---

(8) Mishra, A.; Agarwala, U. C. *Inorg. Chim. Acta* **1988**, *145*, 191.

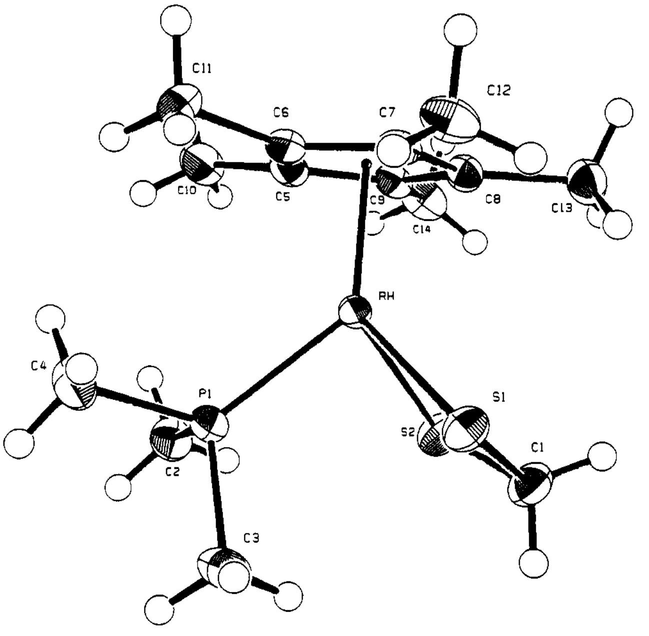
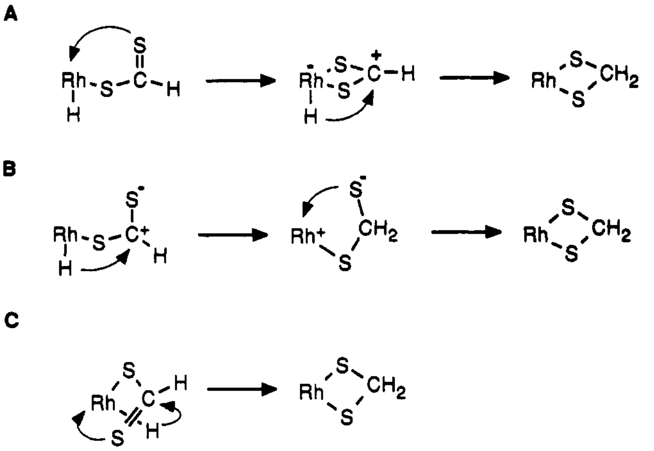


Figure 3. ORTEP drawing of $Cp^*Rh(PMe_3)(SCH_2S)$ with ellipsoids drawn at the 50% level.

Scheme II

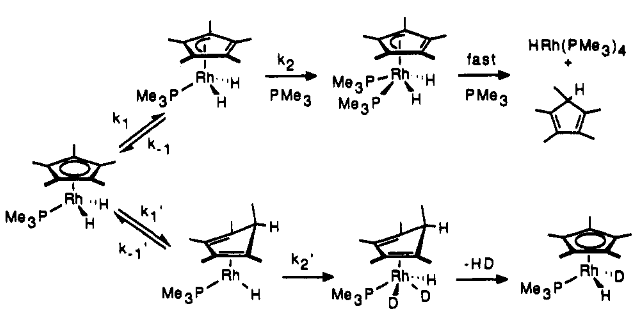


by comparison with an authentic sample. Exclusive formation of 4 can be achieved by reacting 1 with a slight excess of OCS and freeze/pump/thaw degassing the sample thoroughly when no starting material remains. In this case little or no formation of 5 occurs and conversion to 4, C_5Me_5H, and $S{=}PMe_3$ is observed (as determined by ^1H and ^{31}P NMR spectroscopy).

Discussion

Although single insertions of CS_2 into metal–hydride bonds are common, the reduction of CS_2 to methanedithiolate has only been seen previously in the reaction of Cp_2MoH_2 with CS_2.[7b] No intermediates were detected in this case, however. In the present study, the initial reaction to form intermediate 2 is typical of insertions of unsaturated compounds into metal hydrides, but the subsequent step(s) are not. Several mechanisms can be envisioned for this transformation (Scheme II, A–C). In path A, the dithioformate sulfur acts as a nucleophile, attacking the metal center and forming a carbocation. A coordinatively unsaturated metal center is required to allow attack of the sulfur atom at rhodium. This might be achieved by an $\eta^5 \rightarrow \eta^3$ ring slip or hydride to ring migration to give an $(\eta^4\text{-}C_5Me_5H)Rh^I$ species. A [1,3] hydride shift would then give the observed product. Alternatively, a [1,3] hydride shift from rhodium to carbon might occur, followed by fast trapping of the Rh^+ center by thiolate (path B). A third possibility is that of a [1,2] intramolecular insertion of the coordinated thioaldehyde into the Rh–H bond (path C). Multiple insertions of CS_2 to give bis(dithioformate) derivatives might be expected but are not observed.

Scheme III



In an attempt to determine whether an ionic intermediate such as a charge-transfer complex is involved, the rate of the reaction was measured in THF, benzene, and hexanes (Table I). Comparison of these rates shows a slight decrease as the polarity of the solvent is diminished. Under the dilute pseudo-first-order conditions used in the kinetics experiments, the rate-determining step is the bimolecular reaction with CS_2, not the subsequent rearrangement to give the methanedithiolate complex. Thus an initial charge-transfer complex appears unlikely, but the nature of the steps subsequent to CS_2 coordination and insertion cannot be probed by this kinetic data.

Previous work by Jones et al.[9] provided evidence for competing hydride migration and ring slip mechanistic pathways in the reaction of $Cp^*Rh(PMe_3)H_2$ with D_2 and with PMe_3 (Scheme III). Saturation kinetics were observed in the reaction with PMe_3, giving a limiting value for $k_1 < 5 \times 10^{-6}\ s^{-1}$. The reaction with D_2, however, used concentrations of D_2 too low to produce saturation behavior. A pseudo-first-order plot of $[D_2]$ vs k_{obs} gave a value for $k_1'k_2'/k_1' \cong 3 \times 10^{-3}\ M^{-1}\ s^{-1}$. It was proposed that the reaction with PMe_3 proceeds via an $\eta^5 \rightarrow \eta^3$ ring slip pathway due to the absence of a kinetic isotope effect using an equimolar mixture of $Cp^*Rh(PMe_3)H_2/Cp^*Rh(PMe_3)D_2$, while the reaction with D_2 was believed to undergo a hydride-to-ring migration based on stepwise formation of $Cp^*Rh(PMe_3)HD$ and $Cp^*Rh(PMe_3)D_2$. Exchange of $P(CD_3)_3$ for $P(CH_3)_3$ in the starting material was slower than the reaction with PMe_3 to give $HRh(PMe_3)_4$, thus ruling out phosphine loss as the initial step.

Comparison of the rate of the CS_2 reaction with these previous studies allows us to rule out the pathway that 1 undergoes with PMe_3, since the limiting rate k_1 is far too slow. Thus an $\eta^5 \rightarrow \eta^3$ ring slip does not appear to be the initial step leading to coordination of free CS_2. If we assume a small value for K_{eq} (k_1'/k_{-1}') in the reaction with H_2 ($K_{eq} \cong 0.05$) then a limiting value for $k_2 \leq 0.06\ M^{-1}\ s^{-1}$ is obtained, which is consistent with the k_1 measured for the reaction with CS_2. We therefore cannot rule out a hydride-to-ring migration as a preequilibrium step. A concerted mechanism involving a four-membered transition state is also possible.

Conclusion

In conclusion, we have shown that dihydride 1 reacts with CS_2 to produce the methanedithiolate complex 3 and with OCS to give the known complexes $Cp^*Rh(PMe_3)(CO)$

---

[9] Jones, W. D.; Kuykendall, V. L.; Selmeczy, A. D. *Organometallics* **1991**, *10*, 1577.

(4) and Cp*Rh$(CO)_2$ (5). The insertion product 2 is observed at early reaction times. The reaction with CS_2 may proceed via an initial hydride-to-ring migration or may involve a concerted pathway through a four-membered transition state. No reaction with CO_2 was observed at ambient or elevated pressures and temperatures. This is only the second example reported to date for reduction of CS_2 to methanedithiolate and may be of interest concerning reduction processes involving sulfur-containing compounds. We are currently studying this and other related reactions as models for potential homogeneous HDS systems.

Experimental Section

All manipulations were performed under an inert atmosphere of nitrogen or on a high-vacuum line with the use of Schlenk techniques. Benzene, THF, and hexanes were distilled from purple solutions of benzophenone ketyl. CS_2 was purchased from Aldrich Chemical Co. and distilled before use. OCS and CO_2 were obtained from Matheson and were used as received. $PPNBH_4$ was prepared using the method of Bau.[10] The complexes Cp*Rh(PMe_3)(CO) and Cp*Rh$(CO)_2$ were prepared as described by Werner.[11] The complex Cp*Rh$(PMe_3)H_2$ was prepared as described elsewhere.[12]

^1H (400 MHz), ^{31}P (162 MHz), and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AMX-400 spectrometer. ^1H NMR shifts were measured relative to residual ^1H resonances in deuterated solvent: C_6D_6 (δ 7.15). ^{31}P NMR spectra were reported in units of δ (chemical shifts are referred to external 10% H_3PO_4 at δ 0.0 ppm). ^{13}C NMR shifts were measured relative to the C_6D_6 triplet (δ 128). C_6D_6 was purchased from MSD Isotopes Chemical Division and was vacuum-distilled from potassium–benzophenone prior to use.

Reaction of Cp*Rh$(PMe_3)H_2$ with CS_2. Cp*Rh$(PMe_3)H_2$ (0.026 mmol) was dissolved in 0.7 mL of C_6D_6, and the solution was placed in a NMR tube. The solution was subjected to three freeze/pump/thaw degas cycles. A 30-mL aliquot of CS_2 (0.29 mmol) was injected under an inert atmosphere. ^1H and ^{31}P NMR spectra recorded within 5 min showed the presence of both Cp*Rh(PMe_3)(SC(S)H)H (2) and Cp*Rh$(PMe_3)(SCH_2S)$ (3). ^1H and ^{31}P NMR spectra obtained after 20 min showed only 3. Spectroscopic data for 2: ^1H NMR (C_6D_6) δ −11.432 (dd, J = 43, 16.5 Hz, 1 H), 1.035 (d, J = 11.5 Hz, 9 H), 1.646 (s, 15 H), 11.949 (s, 1 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 1.836 (d, J = 148 Hz). Spectroscopic data for 3: ^1H NMR (C_6D_6) δ 1.379 (d, J = 10 Hz, 9 H), 1.572 (d, J = 3 Hz, 15 H), 5.025 (dd, J = 7.3, 5.6 Hz, 1 H), 5.730 (dt, J = 7.3, 2.3 Hz, 1 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 98.522, 53.972, 15.262 (d, J = 30 Hz), 9.402; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 5.038 (d, J = 159 Hz); IR (KBr) 2962, 2904, 1261, 1095, 1022, 802 cm^{-1}. Anal. Calcd for $RhPS_2C_{14}H_{26}$: C, 42.86; H, 6.68; P, 7.89. Found: C, 42.24; H, 7.15; P, 7.12.

Kinetic Studies of Cp*Rh$(PMe_3)H_2$ + CS_2. All kinetic experiments were carried out using a 0.01 M standard solution of Cp*Rh$(PMe_3)H_2$ in THF. In a typical experiment, 20 μL of the standard solution was injected into a 0.1-mm quartz cell and diluted to 0.45 mL with THF ([1] = 4.4×10^{-4} M). A 1.0–5.4-μL aliquot of CS_2 was then injected into the cell under inert atmosphere and the contents shaken thoroughly. The sample was then immediately placed in a temperature-regulated UV–visible cell at 25 °C, and absorbances were measured every 10 s at λ = 320 nm for at least 5 half-lives. Data were fit to the equation $A_t = (A_{final} - A_0)(1 - e^{-kt}) + A_0$ by varying k. For 1, λ_{max} = 292 nm; for 3, λ_{max} = 320 nm.

Reaction of Cp*Rh$(PMe_3)H_2$ with OCS (2 equiv). Cp*Rh$(PMe_3)H_2$ (0.052 mmol) was dissolved in C_6D_6, and the solution was placed in a NMR tube. The solution was subjected to three freeze/pump/thaw degas cycles. OCS (36 Torr) was introduced into a 50-mL ampule (0.10 mmol) and condensed into the tube. The reaction was monitored by ^1H and ^{31}P NMR spectroscopy for 5 days. Spectroscopic data for 4: ^1H NMR (C_6D_6) δ 1.051 (d, J = 9.2 Hz, 9 H), 1.970 (d, J = 1.7 Hz, 15 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −5.160 (d, J = 190 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 199.47 (dd, J = 88.26 Hz), 97.65, 20.28 (d, J = 29 Hz), 11.47; IR (KBr) 2961, 2918, 1927, 1262, 1098, 1024, 802 cm^{-1}.

Table IV. Summary of Crystallographic Data for Cp*Rh$(PMe_3)(SCH_2S)$

Crystal Parameters	
chemical formula	$RhP_1S_2C_{14}H_{26}$
fw	392.359
cryst syst	monoclinic
space group (No.)	$P2_1/n$ (14)
Z	4
a, Å	8.594 (5)
b, Å	21.546 (7)
c, Å	9.050 (4)
β, deg	95.73 (4)
vol, $Å^3$	1667.32
ρ_{calc}, g cm^{-3}	1.563
cryst dimens, mm	0.15 × 0.19 × 0.75
temp, °C	−75
Measurement of Intensity Data	
diffractometer	Enraf-Nonius CAD4
λ(Mo Kα radiation, graphite monochromatized), Å	0.71073
scan type	$2\theta/\omega$
takeoff angle, deg	2.6
total bkgd time	(scan time)/2
scan rate, deg min^{-1}	2–16.5
scan range, deg	0.7 + 0.35 tan θ
2θ range, deg	4–40
data collcd	$+h,+k,\pm l$
no. of data collcd	3234
no. of unique data $F^2 > 3\sigma(F^2)$	2730
no. of params varied	163
μ, cm^{-1}	13.275
systematic absences	$0k0$, k odd $h0l$, $h + l$ odd
abs corr	differential
range of trans factors	0.957–1.037
equiv data	$0kl = 0k\bar{l}$
agreement between equiv data (F_o)	0.019
$R(F_o)$	0.0264
$R_w(F_o)$	0.0383
goodness of fit	1.818

Reaction of Cp*Rh$(PMe_3)H_2$ with OCS (60 equiv). Cp*Rh$(PMe_3)H_2$ (0.052 mmol) was dissolved in C_6D_6, and the solution was placed in a NMR tube. The solution was subjected to three freeze/pump/thaw degas cycles. OCS (100 Torr) was introduced into a high-vacuum line (approximate volume 600 mL; 3.2 mmol) and condensed into the tube. The reaction was monitored by ^1H and ^{31}P NMR spectroscopy for 24 h. The solution became dark red. After 24 h, in addition to 5, free Cp*H was detected by ^1H NMR spectroscopy (C_6D_6) at δ 2.405 (q, 1 H, J = 7.6 Hz), 1.786 (s, 6 H), 1.729 (s, 6 H), and 0.978 (d, 3 H, J = 7.6 Hz), and $SPMe_3$ at δ 1.033 (d, J = 13 Hz). Spectroscopic data for 5: ^1H NMR (C_6D_6) 1.735 (s); IR (KBr) 2964, 2921, 2017, 1959, 1948, 1261, 1092, 1022, 951, 804 cm^{-1}.

Reaction of Cp*Rh$(PMe_3)H_2$ with CO_2 (1 atm). Cp*Rh$(PMe_3)H_2$ (0.052 mmol) was dissolved in C_6D_6, and the solution was placed in a NMR tube. The solution was subjected to three freeze/pump/thaw degas cycles. CO_2 (700 Torr) was introduced into the sample on a high-vacuum line. No reaction was observed at 23 °C. The sample was heated at 80 °C for 24 h, during which time considerable darkening occurred due to some decomposition. No reaction was observed by ^1H or ^{31}P NMR spectroscopy.

Reaction of Cp*Rh$(PMe_3)H_2$ with CO_2 (7 atm). Cp*Rh$(PMe_3)H_2$ (0.026 mmol) was dissolved in THF, and the solution was placed in a glass-lined bomb apparatus. CO_2 (100 psi) was introduced into the bomb and the mixture heated at 60 °C for 24 h. The residue in the bomb was dissolved in C_6D_6. No identifiable products were detected by ^1H or ^{31}P NMR spectroscopy.

Preparation of S=PMe_3. PMe_3 (250 μL, 2.4 mmol) and sulfur (75 mg, 2.4 mmol) were heated to 90 °C for 1 h. A white crystalline

---

(10) Kirtley, S. W.; Andrews, M. A.; Bau, R.; Grynkewich, G. W.; Marks, T. J.; Tipton, D. L.; Whittlesey, B. L. *J. Am. Chem. Soc.* 1977, *99*, 7154.

(11) Werner, H.; Klingert, B. *J. Organomet. Chem.* 1981, *218*, 395.

(12) Jones, W. D.; Kuykendall, V. L. *Inorg. Chem.* 1991, *30*, 2615.

Organometallics **1992,** *11,* 893–900

solid was formed. Yield: 223 mg of S=PMe$_3$ (2.06 mmol, 86%). ^{1}H NMR (C$_6$D$_6$): 1.0482 (d, J = 13 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$): 27.81 (s).

X-ray Structure of Cp*Rh(PMe$_3$)(SCH$_2$S). A single crystal of the complex (crystal dimensions 0.15 × 0.18 × 0.75 mm) was mounted, and cell constants were obtained from 25 centered reflections with values of χ between 0 and 70°. A quadrant of data was collected in accord with the parameters given in Table IV. The Molecular Structure Corporation TEXSAN analysis software package was used for data reduction and solution.[13] A standard Patterson map solution of the structure to locate the rhodium, followed by expansion of the structure with the program <<DIRDIF, revealed all non-hydrogen atoms. After isotropic refinement, an absorption correction was applied using the program DIFABS. Full-matrix least-squares anisotropic refinement of the non-hydrogen atoms with hydrogens attached to carbon in idealized positions was carried out to convergence. Selected distances and angles are given in Table III.

Acknowledgment. We thank the U.S. Department of Energy (Grant DE-FG02-86ER13569) for their support of this work.

Supplementary Material Available: Complete tables of final positional and thermal parameters, non-hydrogen bond distances and angles, and least-squares planes (7 pages); a listing of calculated and observed structure factors (18 pages). Ordering information is given on any current masthead page.

---

[13] $R_1 = \{\sum||F_o| - |F_c||\}/\{\sum|F_o|\}$; $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}/\{\sum wF_o^2\}$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{1/2}$ for the non-poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

Synthesis and Spectroscopic Characterization of Linear Mono-, Bi-, and Trimetallic Bis(methyldiphenylphosphine)nickel Complexes Having 1,4-Tetrafluorophenylene Bridges[1,2]

Robert McDonald, K. Craig Sturge, Allen D. Hunter,* and Lonni Shilliday

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received August 15, 1991

The synthesis and spectroscopic characterization of a series of linear mono-, bi-, and trimetallic complexes containing (MePh$_2$P)$_2$Ni units and bridging and/or terminal fluoroaryl groups is reported. The mononickel complexes (MePh$_2$P)$_2$Ni(1,4-C$_6$F$_4$X)Br and (MePh$_2$P)$_2$Ni(1,4-C$_6$F$_4$X)$_2$ (X = H, F, Br) may be prepared via reaction of (MePh$_2$P)$_2$NiBr$_2$ with 1 or 2 equiv, respectively, of 1,4-C$_6$F$_4$XLi. The "arene-poor" di- and trinickel complexes [(MePh$_2$P)$_2$NiBr]$_2$(μ-1,4-C$_6$F$_4$) and [(MePh$_2$P)$_2$Ni]$_3$(μ-1,4-C$_6$F$_4$)$_2$Br$_2$ are obtained via reaction of 1 equiv of 1,4-C$_6$F$_4$Li$_2$ or (MePh$_2$P)$_2$Ni(1,4-C$_6$F$_4$Li)$_2$, respectively, with 2 equiv of (MePh$_2$P)$_2$NiBr$_2$, while [(MePh$_2$P)$_2$Ni]$_3$(μ-1,4-C$_6$F$_4$)$_2$Cl$_2$ is obtained in an analogous reaction from (MePh$_2$P)$_2$NiCl$_2$. The "arene-rich" di- and trinickel compounds [(MePh$_2$P)$_2$Ni(1,4-C$_6$F$_4$H)]$_2$(μ-1,4-C$_6$F$_4$) and [(MePh$_2$P)$_2$Ni]$_3$(μ-1,4-C$_6$F$_4$)$_2$(1,4-C$_6$F$_4$H)$_2$ may then be prepared from the reaction of their respective "arene-poor" precursors with 2 equiv of 1,4-C$_6$F$_4$HLi. The ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR spectroscopic data for each oligomer unambiguously establishes its chain length and repeat unit structure (trans geometry about nickel and 1,4-substitution about C$_6$F$_4$) and suggests that there is significant electronic communication down the oligomer backbones in the polymetallic complexes. Evidence is also presented which suggests that *cis*-(MePh$_2$P)$_2$Ni(1,4-C$_6$F$_4$Br)$_2$ is a kinetic intermediate in the synthesis of the trans isomer.

Introduction

Over the last several years there has been growing interest in the preparation and characterization of organometallic polymers having transition metals in the polymer backbone. Such materials are of interest because of their substantial potential for practical applications in the areas of one-dimensional conductivity[3] and nonlinear optical behavior.[4] Complexes in which the transition-metal centers are joined by organic fragments capable of π conjugation (e.g. $-C{\equiv}CC_6H_4C{\equiv}C-$, $-NC_4H_4N-$, $-CNC_6H_4NC-$)[5,6] are expected to display these useful properties due to conjugation of the π-symmetry orbitals on the metal centers and the organic ligands. These ma-

---

(1) One-Dimensional Organometallic Materials. 1.

(2) Parts of this work have been presented orally: (a) Hunter, A. D.; Li, J.; McDonald, R.; Guo, X. 74th Canadian Chemical Conference, Hamilton, Ontario, June 1991; Abstr. *585* NM-H1. (b) Hunter, A. D. Polymers for Alberta's Future, Edmonton, Alberta, June 14, 1991.

(3) See, for example: (a) Carter, F. L. *Molecular Electronic Devices*; Marcel Dekker: New York, 1982. (b) Carter, F. L. *Molecular Electronic Devices II*; Marcel Dekker: New York, 1987. (c) Mort, J.; Pfister, G. *Electronic Properties of Polymers*; John Wiley & Sons: New York, 1982.

(4) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; John Wiley and Sons: New York, 1991; pp 134–143.

(5) (a) Ogawa, H.; Onitsuka, K.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *Organometallics* **1988**, *7*, 2257–2260. (b) Takahashi, S.; Morimoto, H.; Murata, E.; Kataoka, S.; Sonogashira, K.; Hagihara, N. *J. Polym. Sci. Polym. Chem. Educ.* **1982**, *20*, 565–573. (c) Sonogashira, K.; Ohga, K.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1980**, *188*, 237–243. (d) Takahashi, S.; Murata, E.; Sonogashira, K.; Hagihara, N. *J. Polym. Sci. Polym. Chem. Educ.* **1980**, *18*, 661–669. (e) Takahashi, S.; Ohyama, Y.; Murata, E.; Sonogashira, K.; Hagihara, N. *J. Polym. Sci. Polym. Chem. Educ.* **1980**, *18*, 349–353. (f) Takahashi, S.; Kariya, M.; Yatake, T.; Sonogashira, K.; Hagihara, N. *Macromolecules* **1978**, *11*, 1063–1066. (g) Sonogashira, K.; Kataoka, S.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *160*, 319–327. (h) Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 673–674. (i) Davies, S. J.; Johnson, B. F. G.; Lewis, J.; Khan, M. S. *J. Organomet. Chem.* **1991**, *401*, C43–45. (j) Johnson, B. F. G.; Kakkar, A. K.; Khan, M. S.; Lewis, J.; Dray, A. E.; Wittmann, F.; Friend, R. H. *J. Mater. Chem.* **1991**, *1*, 485. (k) Johnson, B. F. G.; Kakkar, A. K.; Khan, M. S.; Lewis, J. *J. Organomet. Chem.* **1991**, *409*, C12–14. (l) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187–188. (m) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188–190. (n) Marder, T. B.; Lesley, G.; Yuan, Z.; Fyfe, H. B.; Chow, P.; Stringer, G.; Jobe, I. R.; Taylor, N. J.; Williams, I. D.; Kurtz, S. K. In *Materials for Nonlinear Optics: Chemical Perspectives*; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991; p 605.

0276-7333/92/2311-0893$03.00/0