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Reactions of Dihydridotetrakis(tertiary phosphine)ruthenium(II) Complexes with Carbon Dioxide, Carbon Disulfide and Sulfur Dioxide

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Carbon dioxide reacts with $RuH_2(PPh_3)_4$ to give its insertion product, hydridoformatotris(triphenylphosphine)-ruthenium(II). The reversibility of the CO_2 insertion has been demonstrated. Insertion products of carbon disulfide and adducts of sulfur dioxide with ruthenium also have been obtained by the reactions of carbon disulfide and sulfur dioxide with various ruthenium dihydride complexes, RuH_2L_4 (L=PPh_3, PPh_2H, PPh_2Me, $PPhMe_2$). These compounds were characterized by IR and NMR spectroscopy, elemental analysis and chemical reactions.

Since the first reports on the reactions of a hydrido-(dinitrogen)cobalt complex with carbon dioxide to yield a cobalt formate complex[1,2] the reactions of CO_2 with transition metal alkyls and hydrides have been attracting increasing attention.[3] As an extension of our preliminary communication[4] we now report the reactions of tertiary phosphine-coordinated ruthenium dihydride complexes (RuH_2L_4) with carbon dioxide and its analogs, carbon disulfide and sulfur dioxide.

Results and Discussion

Reaction of Dihydridotetrakis(phosphine)ruthenium(II) with Carbon Dioxide. The reaction of $RuH_2(PPh_3)_4$ (I) with carbon dioxide in toluene proceeds readily at room temperature to give a diamagnetic complex $RuH(O_2CH)(PPh_3)_3$(toluene) (II) in a high yield.[a]

$$\underset{\text{(I)}}{RuH_2(PPh_3)_4} + CO_2 \xrightarrow{\text{toluene}} \underset{\text{(II)}}{RuH(O_2CH)(PPh_3)_3(\text{toluene})} + PPh_3$$

Complex II is an air-sensitive yellow solid which is stable in a nitrogen atmosphere but decomposes in air in about 1 day releasing 1 mol of carbon dioxide per ruthenium. The IR spectrum of II is in agreement with its formulation as a hydrido-formato complex. Table 1 tabulates relevant IR absorption bands of the hydridoformato complex II with assignments based on comparison with IR spectra of other known formates, $Rb(O_2CH)$[6] and $Co(O_2CH)(PPh_3)_3$.[1]

The reactions of CO_2 with other phosphine-coordinated complexes of a general formula RuH_2L_4 (L=PPh_2H,[7] PPh_2Me,[8] $PPhMe_2$[9]) also have been examined. However, none of these complexes other than I reacted with CO_2 in toluene even at 110 °C and only starting dihydrido complexes were recovered. Presumably, a predissociation of one of the four phosphine ligands from the coordinatively saturated complexes is required for accommodating a coordination site for the reactant to enter into the reaction. Examination of $^{31}P\{^1H\}$-NMR of RuH_2L_4 complexes in polar solvents such as pyridine revealed that complex I is completely dissociated to $RuH_2(PPh_3)_3$(solvent) and PPh_3 whereas other phosphine-coordinated complexes are not dissociated in the polar solvents.[10] In non-polar solvents the dissociation of PPh_3 from I is much less extensive and the dissociative process may constitute a rate determining step as we previously observed in polymerization of vinyl compounds by PPh_3-coordinated complexes.[11,12]

Acidolysis of II in the solid state with sulfuric acid liberated carbon monoxide and hydrogen in addition to carbon dioxide. Complex II readily loses CO_2 on various chemical treatments. Reaction of II with alkyl halides released carbon dioxide and alkanes and gave a quantitative yield of hydridohalotris(triphenylphosphine)ruthenium.[13]

$$\underset{\text{(II)}}{(HCOO)RuH(PPh_3)_3(\text{toluene})} + RX \longrightarrow HRuX(PPh_3)_3 + RH + CO_2 + \text{toluene}$$

(RX=MeI, EtBr, EtI)

TABLE 1. MAIN IR BANDS OF FORMATO COMPLEXES

Assignment	IR bands (cm^{-1})		
	$Rb(O_2CH)$[6]	$(HCO_2)RuH(PPh_3)_3$	$(HCO_2)Co(PPh_3)_3$[1]
C–H stretch	2801 w	2895 w, 2805 w	2795 w, 2700 w
asym OCO stretch	1592 s	1553 s	1620 s
asym OCO deformation	1381	1365 m, 1347 m	
sym OCO stretch	1370 s	1310 s	1300 s
sym OCO deformation	774 s	795 s	
out of plane deformation	1066 vw		
M–H stretch		1996 m	

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[a] Vol'pin *et al.* first reported the reaction claiming that $Ru(OMe)H(PPh_3)_3 \cdot CO_2$ was obtained.[3a] However, subsequent to our communication[4] the complex was reformulated as $RuH(OOCH)(PPh_3)_3$ and its molecular structure with an octahedral configuration containing the formato group as a bidentate ligand has been established by X-ray analysis.[5]

Complex II is thermally fairly stable, and thermolysis of II takes place in two steps. At *ca.* 140 °C II releases about one mol of CO_2 per II leaving a ruthenium hydride complex having a ν(Ru-H) band at 2080 cm^{-1}. The second decomposition takes place at 200 °C, which is very close to the decomposition point of $RuH_2(PPh_3)_4$, and at the temperature hydrogen and a small amount of carbon monoxide are liberated.

The formate Complex II can be also obtained by reactions of carbon dioxide with $RuH_4(PPh_3)_3$ and $RuH_2(N_2)(PPh_3)_3$.[14,15]

A salient feature of the formate complex is the ready release of carbon dioxide in solution. Bubbling of H_2 and N_2 through benzene solutions containing II displaces readily carbon dioxide giving $RuH_4(PPh_3)_3$ and $RuH_2(N_2)(PPh_3)_3$, respectively. Addition of PPh_3 to the benzene solution containing II also liberated CO_2 giving Complex I.

$$RuH(OOCH)(PPh_3)_3 + H_2 \rightleftharpoons RuH_4(PPh_3)_3 + CO_2$$

$$RuH(OOCH)(PPh_3)_3 + N_2 \rightleftharpoons RuH_2(N_2)(PPh_3)_3 + CO_2$$

$$RuH(OOCH)(PPh_3)_3 + PPh_3 \rightleftharpoons \underset{\text{(I)}}{RuH_2(PPh_3)_4} + CO_2$$

Addition of triphenylphosphite and tributylphosphine to II also led to liberation of CO_2 and toluene. The reversibility of the reactions among $RuH_2(PPh_3)_4$, $RuH_4(PPh_3)_3$ and $RuH_2(N_2)(PPh_3)_3$ have been previously demonstrated.[14,15]

Reaction of RuH_2L_4 with Carbon Disulfide. As extension of the reaction of RuH_2L_4 with carbon dioxide the reaction with its isoelectronic compound toward RuH_2L_4 have been examined. Insertion reactions of CS_2 into transition metal-alkyl bonds are known;[16] several examples of CS_2 insertion into transition metal-hydrogen bond have been reported.[16d,17]

In the interium since we started this line of work the reactions of I and $RuH_4(PPh_3)_3$ with CS_2 to afford $Ru(S_2CH)_2(PPh_3)_2$ have been reported by Harris *et al.*[18] We describe here the reactions of CS_2 with RuH_2L_4 including other phosphine ligands (L=PPh_3, PPh_2H, PPh_2Me, $PPhMe_2$).

In contrast to the reaction of CO_2 with RuH_2L_4, where the CO_2 insertion into only one of the two Ru–H bonds in I was observed, the CS_2 insertion into both of the Ru–H bonds proceeds smoothly at room temperature in all of the RuH_2L_4 type complexes examined to afford bis(dithioformato) type complexes. Negligible amounts of hydrogen were evolved in the reactions. One might observe the formation of HCSSH if one molecule of CS_2 should be inserted into one of the two Ru–H bonds to be followed by abstraction of hydrogen from the remaining Ru–H bond. Examination of the volatile reaction products by NMR excluded the formation of HCSSH in the reaction. This was further supported by failure of the formation of silver dithioformate by treating the volatile matters with silver nitrate.

Table 2 shows yields, physical and chemical properties, and analytical data of the isolated bis(dithioformato) complexes obtained by the reactions of RuH_2L_4 with CS_2.

The thermal stability of the dithioformate complex appears to depend on the phosphine ligand. Less basic ligands such as triphenylphosphine and diphenylphosphine gave more stable complexes than more basic ligands such as diphenylmethylphosphine and phenyldimethylphosphine. Pyrolysis of the dithioformate complex containing triphenylphosphine releases carbon disulfide and triphenylphosphine sulfide. Liberation of CS_2 was observed in the pyrolysis of other phosphine-coordinated complexes and the release of a small amount of hydrogen was noted in the pyrolysis of $Ru(S_2CH)_2(PPh_2H)_4$.

Acidolysis of $Ru(S_2CH)_2(PPh_3)_2$ (III) with concentrated sulfuric acid released CS_2 and SO_2. Hydrogen chloride and methyl iodide did not react with (III) at room temperature.

Table 2 includes IR bands which are not observed in the RuH_2L_4 type complexes. Known dithioformate and dithiobenzoate complexes[16] show ν (CS_2) bands in the range of 900—1100 cm^{-1} whereas CS_2-coordinated complexes and carbon-bonded metal dithio acid type (M-CSSR) complexes have ν(CS_2) bands at much higher frequencies. Therefore the strong new bands in the range of 900—1100 cm^{-1} may be assigned to ν(CS_2) bands of the dithio formate group. The dithioformate group can act as a bidentate as well as a monodentate ligand. In $Ru(S_2CH)_2(PPh_3)_2$ the ν(CS_2) band appears at the lowest frequency among the four dithioformate complexes shown in Table 2. This may well arise from its octahedral configuration having two bidentate

TABLE 2. REACTIONS OF RuH_2L_4 WITH CS_2

Reactant	$RuH_2(PPh_3)_4$	$RuH_2(PPh_2H)_4$	$RuH_2(PPh_2Me)_4$	$RuH_2(PPhMe_2)_4$
Product	$Ru(S_2CH)_2(PPh_3)_2$	$Ru(S_2CH)_2(PPh_2H)_4$	$Ru(S_2CH)_2(PPh_2Me)_3$	$Ru(S_2CH)_2(PPhMe_2)_3$
Color	red-orange	yellow	brown	red
Yield	*ca.* 80%	*ca.* 80%	*ca.* 20%	*ca.* 20%
Dec.pt.	196—200°C	200—203°C	138°C	140°C
Pyrolysis product	CS_2	CS_2+(H_2)	CS_2	CS_2
Analysis	Found (Calcd)	Found (Calcd)	Found (Calcd)	Found (Calcd)
	C, 59.2 (58.5)	C, 60.3 (60.0)	C, 57.8 (57.5)	C, 45.4 (46.6)
	H, 4.0 (4.1)	H, 4.6 (4.7)	H, 4.8 (4.8)	H, 5.5 (5.3)
	S, 17.3 (16.4)	S, 12.2 (12.8)	S, 15.9 (15.0)	S, 20.7 (19.2)
IR	910 cm^{-1} (s)	1016 cm^{-1} (s)	1090 cm^{-1} (w)	990 cm^{-1} (s)
(new peaks)	918 (sh)	950 (sh)	1022 (s)	960 (s)
	786 (m)		995 (s)	

dithioformate groups. Conversely the strong $\nu(CS_2)$ absorption band at 1016 cm^{-1} in $Ru(S_2CH)_2(PPh_2H)_4$ may be ascribed to the monodentate dithioformate group in the octahedral complex, and the strong bands in $Ru(S_2CH)_2(PPh_2Me)_3$ and $Ru(S_2CH)_2(PPhMe_2)_3$ may be due to the presence of two modes of coordination of the two dithioformate ligands in these complexes. All the dithioformate complexes showed a weak band at 1510 cm^{-1} which disappears on drying them in vacuum for a long period. This band may be due to the presence of an S-bonded CS_2 molecule which has a weak interaction with the ruthenium complex. A similar band has been observed in the IR spectrum of $PtMe(I)(CS_2)(PPh_3)_2$.[16d]

Reaction of RuH_2L_4 with Sulfur Dioxide. We have examined further the reactions of RuH_2L_4 type complexes with sulfur dioxide. The reactions of SO_2 with various organometallic compounds have been recently reviewed.[19] The reactions of SO_2 with $RuH_2(PPh_2H)_4$ and $RuH_2(PPh_2Me)_4$ in toluene gave light yellow complexes without evolution of hydrogen, whereas a considerable amount of hydrogen was evolved in the reactions of SO_2 with $RuH_2(PPh_3)_4$ and $RuH_2(PPhMe_2)_4$. We tentatively formulate the sulfinate structures $Ru(SO_2H)(PPh_2H)_3$ and $Ru(SO_2H)(PPh_2Me)_3$ for the products obtained without evolution of hydrogen and SO_2-coordinated structures $Ru(SO_2)_2(PPh_3)_2$ and $Ru(SO_2)(PPhMe_2)_3$ for those obtained with evolution of hydrogen. The latter complexes liberated only SO_2 on acidolysis and pyrolysis whereas the PPh_2H-coordinated complex released H_2 in addition to SO_2 on pyrolysis. No infrared band due to ν(Ru–H) was observed in these complexes. The complexes which may have the sulfinate structure showed a broad NMR signal in the region of δ 5. Formulation of the reaction product of $RuH_2(PPh_3)_4$ with SO_2 as $Ru(SO_2)_2(PPh_3)_2$ has been previously proposed by Eliades *et al.*[18a]

Experimental

All the reactions were carried out under nitrogen or in a vacuum. Infrared spectra were recorded as KBr disks on a Hitachi model EPI-G3 spectrometer. NMR spectra were measured on JNM-PS-100 and JNM-MH-60. Elemental analyses were performed with Yanagimoto CHN Autocorder Type MT2. Gas chromatograms were recorded by using Shimadzu type GC-5A. Solvents were purified by usual methods under nitrogen. Carbon dioxide gas was dried by passing it through a $CaCl_2$ column and carbon disulfide was dried with CaH_2. Sulfur dioxide was obtained on reaction of Cu with concd H_2SO_4 and dried by passing through a concd H_2SO_4 bubbler. RuH_2L_4 (L=PPh_3,[18] PPh_2H,[7] PPh_2Me,[8] and $PPhMe_2$[9]) were synthesized by the methods previously reported.

Hydrido(formato)tris(triphenylphosphine)(toluene)ruthenium(II) (II), $RuH(O_2CH)(PPh_3)_3$(toluene). When carbon dioxide was brought in contact with or bubbled into the toluene solution of I at room temperature, a yellow precipitate was formed in about 1 day. The precipitate was washed with hexane a few times and dried in a vacuum; yield, *ca.* 80%. Anal. Calcd for $RuH(O_2CH)(PPh_3)_3$(toluene): C, 72.6; H, 5.4%. Found: C, 72.8; H, 5.2%.

Attempts of recrystallization led only to decomposition of the formate complex with liberation of CO_2. Reactions of $RuH_2(N_2)(PPh_3)_3$ or $RuH_4(PPh_3)_3$ with carbon dioxide gave the same product.

Reaction of $RuH(O_2CH)(PPh_3)_3$(toluene) (II). i) Acidolysis. Acidolysis of II (159.0 mg, 0.155 mmol) by *ca.* 5 ml of concd sulfuric acid released carbon monoxide (0.08 mmol) and hydrogen (0.03 mmol) at room temperature.

ii) Reaction of II with Alkyl Halide. The reaction of II (162.6 mg, 0.158 mmol) with methyl iodide (*ca.* 2 ml) gave methane (0.15 mmol) and carbon dioxide (0.13 mmol). The resultant complex is considered to be hydridoiodotris(triphenylphosphine)ruthenium $RuHI(PPh_3)_3$ on the basis of IR spectrum showing a ruthenium-hydrogen stretching band at 2020 cm^{-1}. Because a quaternary salt of triphenylphosphine with methyl iodide was also produced in this reaction, the complete purification was not feasible, but in case of the reaction of II with ethyl bromide $RuHBr(PPh_3)_3$ was isolated. Pyrolysis of II (148.5 mg, 0.145 mmol) liberated carbon dioxide (0.15 mmol) at *ca.* 200 °C. Formation of a small amount of benzene was observed.

iv) Reaction of II with Triphenylphosphite. When complex (II) (625.7 mg, 0.610 mmol) was treated with triphenylphosphite (*ca.* 2 ml), toluene was released as identified by gas chromatography in a yield of 52 mg (0.56 mmol, 93%). Hydrogen and carbon dioxide were also evolved. By the reaction of II with tributylphosphine CO_2 and toluene were released.

v) Reaction of II with Hydrogen, Nitrogen and Triphenylphosphine. An excess of hydrogen was brought in contact with a benzene solution of II to precipitate white needles in a few hours. Carbon dioxide was detected in the gas phase. The white needles were washed with hexane a few times and dried in a vacuum, dec. pt. 135°; ν(Ru–H) 1950 cm^{-1}.[14] No particular attempt was made for purification of the complex by recrystallization, but the analytical value was close to that of $RuH_4(PPh_3)_3$. Found: C, 71.8; H, 5.2%. Calcd for $RuH_4(PPh_3)_3$: C, 72.8; H, 5.5%.

Bubbling of nitrogen into the heterogeneous solution of II gave $RuH_2(N_2)(PPh_3)_3$ with the liberation of CO_2; the formation of the dinitrogen complex was confirmed on the basis of its IR spectrum with a $\nu(N_2)$ band at 2143 cm^{-1}. Addition of excess triphenylphosphine into the benzene solution of II liberated carbon dioxide at room temperature forming $RuH_2(PPh_3)_4$. The formation of $RuH_2(PPh_3)_4$ was confirmed by its infrared spectrum with a ν(Ru–H) band at 2080 cm^{-1}.

Reactions of RuH_2L_4 with Carbon Disulfide. The reactions of CS_2 with RuH_2L_4 type complexes were carried out in a similar manner. Excess CS_2 was introduced by a trap-to-trap distillation method to a flask containing RuH_2L_4. The suspension became homogeneous in an hour at room temperature and a yellow or red precipitate was deposited which was washed with hexane a few times and dried *in vacuo* (yield-50—80%). No detectable amount of gas was evolved in the reaction. The product was recrystallized from dichloromethane and ether, or from toluene except for $Ru(S_2CH)_2(PPh_3)_2$ which reacted with dichloromethane.

Pyrolysis of $Ru(S_2CH)_2(PPh_3)_2$ (0.1954 g, 0.251 mmol) at 200 °C liberated carbon disulfide (0.023 mmol, 9%) and triphenylphosphine sulfide. The carbon disulfide was identified by IR and mass spectroscopy and gas chromatography. Triphenylphosphine sulfide was identified on the basis of IR spectrum, ν(P=S) 1105 cm^{-1}, and elemental analysis (Calcd for $C_{18}H_{15}PS$: S, 10.9%; Found: S, 10.8%).

Reactions of RuH_2L_4 with SO_2. The reactions of SO_2 with RuH_2L_4 type complexes were performed by allowing SO_2 gas to contact with toluene solutions containing the hydrido complexes at room temperature. In the reactions of RuH_2-

$(PPh_3)_4$ and $RuH_2(PPhMe_2)_4$ hydrogen evolution (30—40%) was observed. The precipitate was washed with hexane and dried *in vacuo*, and recrystallized from dichloromethane and ether.

$Ru(SO_2)_2(PPh_3)_2$, mp (dec.) 243—251 °C; new IR (KBr disc) peaks not present in $RuH_2(PPh_3)_4$: 1270 (s), 1138 (s), 650 (w), 570 cm^{-1} (w). Found: C, 57.2; H, 4.3; S. 7.4%. Calcd for $Ru(SO_2)_2(PPh_3)_2$: C, 57.4; H, 4.0; S, 7.4%.

$Ru(SO_2)(PPhMe_2)_3$ (tentative formula), mp (dec.) 270—280 °C; new IR (KBr disc) peaks not present in $RuH_2(PPhMe_2)_4$: 1210 (s), 1140 (s), 1010 (m), 652 (m), 610 (w), 455 cm^{-1} (w). Considerable difficulty was encountered in purification due to the formation of $PPhMe_2$–SO_2 adduct. Found: C, 45.7; H, 5.5; S, 5.1%. Calcd for $Ru(SO_2)(PPhMe_2)_3$: C, 49.7; H, 5.7; S. 5.5%.

$Ru(SO_2H)(PPh_2Me)_3$ (tentative formula), mp (dec.) 212—215 °C; IR (KBr disc) not present in $RuH_2(PPh_2Me)_4$: 1260 (m), 1138 (s), 1122 (s), 640 (m), 565 cm^{-1} (w). Found: C, 56.0; H, 4.8; S, 6.8%. Calcd for $Ru(SO_2H)_2(PPh_2Me)_3$: C, 56.3; H, 5.0; S, 7.7%.

$Ru(SO_2H)_2(PPh_2H)_3$ (tentative formula), mp, 146 °C; dec. 226 °C; new IR (KBr) peaks not present in $RuH_2(PPh_2H)_4$: 1238 (m), 1130 (s), 650 (m), 545 cm^{-1} (sh). Found: S, 8.0%. Calcd for $Ru(SO_2H)_2(PPh_2H)_3$: S, 8.1%.

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