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Preliminary communication

Reactions of hydrido complexes of ruthenium and rhodium with carbon dioxide involving reversible insertion

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SUMMARY

The complexes $[RuH_2(PPh_3)_4]$ and $[RhH(PPh_3)_4]$ in toluene react (reversibly) with carbon dioxide to give $[Ru(OOCH)H(PPh_3)_3(PhMe)]$ and $[Rh_2H_2(CO_2)(PPh_3)_6(PhMe)]$, respectively.

Following the recent upsurge of interest in the reaction of nitrogen with transition metal complexes, the corresponding reactions involving carbon dioxide are of growing interest. After the first reports of carbon dioxide insertion, into the Co–H bond of $CoH(N_2)(PPh_3)_3$ [1,2], a few examples of such insertion into other transition metal–hydrogen bonds have been reported[3]. Vol'pin recently reported that $RuH_2(PPh_3)_4$ [4,5], I gave $HRu(CO_2)(OMe)(PPh_3)_3$ on reaction with CO_2 [6], but our studies have shown that quite different products are formed, as described below. The corresponding reaction with a rhodium complex is also described.

(1) Reaction of $RuH_2(PPh_3)_4$*, I, with* CO_2

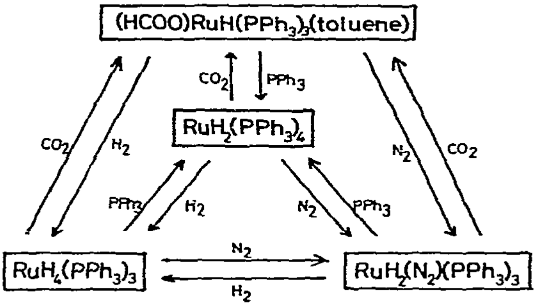
When carbon dioxide was brought in contact with or bubbled into the toluene solution of I at room temperature, a yellow precipitate (complex II) was formed in about 1 day. The complex II was identified as $(HCOO)RuH(PPh_3)_3$(toluene), (nc). IR: $\nu(OCO_{asym.})$ 1553 cm^{-1}; $\nu(OCO_{sym.})$ 1310 cm^{-1}; ν(Ru–H) 1996 cm^{-1}; ν(C–H of $HCOO^-$), 2895, 2805 cm^{-1}. (Anal. Found: C, 72.7; H, 5.3. $C_{62}H_{55}O_2P_3Ru$ calcd.: C, 72.6; H, 5.4%.)

Acidolysis of II by sulfuric acid releases carbon monoxide and hydrogen, showing that II is a formate complex of ruthenium. A noteworthy feature of the complex is the ready release of CO_2 on various chemical treatments of the complex. Thus on treatment of II with alkyl halides, carbon dioxide and alkanes were released, with the formation of hydridohalotris(triphenylphosphine)ruthenium[7].

$$(HCOO)RuH(PPh_3)_3(toluene) + RX \rightarrow HRuX(PPh_3)_3 + RH + CO_2 + toluene$$

Thermolysis of II gave a quantitative amount of carbon dioxide at ca. 140°, and hydrogen, along with a small amount of carbon monoxide, at ca. 200°.

The formate complex II is unstable toward ligands such as triphenylphosphite and tri-n-butylphosphine; thus when II was treated with triphenylphosphite, toluene was released quantitatively, and hydrogen and carbon dioxide were evolved. Hydrogen, nitrogen, or excess triphenylphosphine liberate CO_2, yielding $RuH_4(PPh_3)_3$, $RuH_2(N_2)(PPh_3)_3$, and $RuH_2(PPh_3)_4$, respectively. These reactions are summarized in Scheme 1.



Scheme 1. Reversible insertion of CO_2 into Ru–H bond.

Tetrahydro(triphenylphosphine)ruthenium, $RuH_4(PPh_3)_3$ [4,8] was obtained as white or tan needles from II in benzene by contact with hydrogen in a sealed system at room temperature. Bubbling CO_2 into the toluene solution of the resulted tetrahydro complex of ruthenium again gave II, in which the presence of the formate group was confirmed by IR spectroscopy. Reaction of II with nitrogen or an excess of triphenylphosphine were similarly reversible.

(2) Reaction of $RhH(PPh_3)_4$ [4,9], III, with CO_2

The rhodium hydride complex III in toluene reacted with carbon dioxide at room temperature in about 1 week to give an orange precipitate (complex IV), which was shown to be $Rh_2H_2(CO_2)(PPh_3)_6$(toluene), (nc). IR: $\nu(OCO_{asym.})$ 1460 cm^{-1}; Raman: $\nu(OCO_{sym.})$ 1300 cm^{-1}. (Anal. Found: C, 72.4; H, 5.0. $C_{116}H_{100}O_2P_6Rh_2$ calcd.: C, 72.6; H, 5.5%.)

Acidolysis of IV by sulfuric acid releases only carbon dioxide, that shows that it is not a formate complex, but a carbon dioxide adduct. Treatment of IV with methyl iodide liberates methane and carbon dioxide. Thermolysis of IV released only carbon dioxide up to 220°. Treatment of IV with triphenylphosphite gave carbon dioxide and toluene.

The poor solubility of IV prevented the measurement of the molecular weight, but we propose a dimeric structure for IV on the basis of IR and Raman spectroscopy, and on the diamagnetism and chemical reactions of IV, which release a half mole of CO_2 per rhodium atom. A similar adduct of nickel with a bridging CO_2 was recently reported by Jolly[10]. Although the ν(Rh–H) band was not observed, the hydride structure is presently favored on the basis of the chemical reactions of IV.

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