1540 *J. Org. Chem.* **2000,** *65,* 1540−1543

Notes

A New Rhodium Catalyst: Formation of $[Rh(CO)_4]^+$ in Concentrated Sulfuric Acid and Its Application to Carbonylation of Olefins

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Received October 21, 1999

Introduction

Metal carbonyls have played a very important role in chemistry and the chemical industry.[1] For the typical metal carbonyls such as $Ni(CO)_4$, $Co_2(CO)_8$, $Fe(CO)_5$, and $Mn(CO)_4{}^{3-}$, the average vibrational frequencies, $\nu(CO)$, are considerably lower than the value for free CO, 2143 cm^{-1}, mainly due to the metal-to-CO π-back-bonding.[2] Reactions catalyzed by such metal carbonyls usually require drastic conditions; for example, the Roelen and Reppe reactions, which employ $Co_2(CO)_8$ or $Ni(CO)_4$ to catalyze the carbonylation of olefins to produce aldehydes and alkanoic acids, are operated at high temperature and high pressure.[1]

In the last ca. 10 years, there has been a rapid development in the preparation and structural characterization of homoleptic metal carbonyl cations and their cationic derivatives; this new class of metal carbonyl complexes ranges from group 6 to group 12.[3−5] In contrast to the typical metal carbonyl complexes, the new family of metal carbonyls has a distinguishing characteristic in that the CO vibrational frequencies are considerably raised; they have remarkably reduced π-back-bonding and reactive CO ligands. There have been reports on the use of the metal carbonyl cations as catalysts under mild conditions. Cu(I), Ag(I), Au(I), and Pd(I) carbonyls have been shown to be highly active for the catalytic carbonylation of olefins (the Koch-type reaction) in strong acids under an atmospheric pressure of CO.[6−8] $[Pt(CO_4)][Sb_2F_{11}]_2$ has recently been used for the stereospecific tetramerization of 2-propynol and the polymerization of arylacetylenes.[9]

Rhodium catalysts, most of which work in organic solvents, have been employed in many important reactions, such as the hydrogenation,[10] hydroformylation, and carbonylation of unsaturated compounds.[1] In this paper, we report a new rhodium carbonyl catalyst in concd H_2SO_4, with which olefins react with CO to produce tertiary carboxylic acids in high yields at atmospheric pressure and room temperature. This work extends the family of the cationic metal carbonyl catalysts for carbonylation of olefins from groups 11 and 10 to the group 9 elements.

Results and Discussion

Formation of Rhodium(I) Tetracarbonyl Cation, $[Rh(CO)_4]^+$, in Concentrated H_2SO_4. Very recently, new Rh(I) and Rh(III) carbonyl cations have been generated. The rhodium(I) tetracarbonyl cation, $[Rh(CO)_4]^+$, was prepared by the solvolysis and carbonylation of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ in HSO_3F[11] and isolated by treating $[Rh(\mu\text{-}Cl)(CO)_2]_2$ with $Ag[1\text{-}Et\text{-}CB_{11}F_{11}]$;[12] in both of the cases, Rh retains the oxidation state of +1. $[Rh(CO)_4]^+$ was also prepared by the reductive carbonylation of $Rh(SO_3F)_3$ in HSO_3F.[11] The Rh(III) tricarbonyl complex, $Rh(CO)_3(SO_3F)_3$, was formed by the oxidation of $[Rh(CO)_4]^+$ with $S_2O_6F_2$, one of the strongest oxidizers, in HSO_3F.[11]

We have found a remarkably facile route for the synthesis of $[Rh(CO)_4]^+$ in strong acids. By dissolving $Rh_4(CO)_{12}$ in concd H_2SO_4 under a CO atmosphere at room temperature, a yellow-brown solution was formed, which exhibits no ^1H NMR resonance for a hydride and no Raman band due to $\nu(Rh{-}Rh)$, in contrast with the observation of a resonance at −20 ppm for the hydride[13] and two Raman bands at 199 and 163 cm^{-1} due to $\nu(Ir{-}Ir)$ for $[Ir_4(CO)_{12}H_2]^{2+}$ formed by the dissolution of $Ir_4(CO)_{12}$ in concd H_2SO_4. During the reaction, the CO

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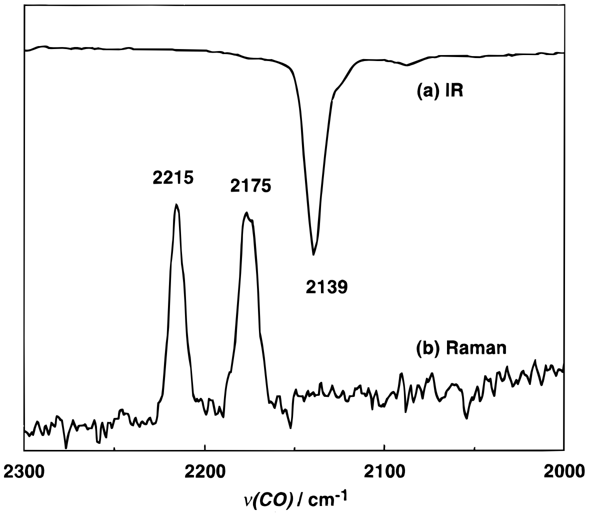

Figure 1. FT-IR (a) and FT-Raman (b) spectra of the rhodium(I) tetracarbonyl cation, $[Rh(CO)_4]^+$, at 0.136 M formed by the dissolution of $Rh_4(CO)_{12}$ in 96% H_2SO_4 solution under a CO atmosphere at room temperature.

uptake of 4 mol and H_2 evolution of 2 mol per mol of $Rh_4(CO)_{12}$ were observed, leading to the formulation of $[Rh(CO)_4]^+$ for the new Rh carbonyl species. Therefore, the dissolution of $Rh_4(CO)_{12}$ in concd H_2SO_4 under a CO atmosphere results in the breaking of the Rh−Rh bonds and the formation of the mononuclear Rh(I) tetracarbonyl cation, $[Rh(CO)_4]^+$, and H_2 according to eq 1; this is the first example of the oxidation of Rh(0) to Rh(I) by H^+. There have been only related reports on the oxidation of the Rh and Ir carbonyl cluster anions, $[Rh_6C(CO)_{15}]^{2-}$ and $[Ir_6(CO)_{15}]^{2-}$, respectively, by H^+, the former giving rise to the formation of $[Rh_{12}C(CO)_{24}]^{2-}$ and H_2,[14] and the latter to the formation of $Ir_6(CO)_{16}$ and H_2.[15]

$$Rh^0{}_4(CO)_{12} + 4CO + 4H^+ \xrightarrow{H_2SO_4} 4[Rh^I(CO)_4]^+ + 2H_2 \qquad (1)$$

It has been found that $[Rh(CO)_4]^+$ is also formed from $Rh_6(CO)_{16}$ instead of $Rh_4(CO)_{12}$, or in HSO_3F or magic acid ($HSO_3F\cdot SbF_5$) instead of concd H_2SO_4.

Figure 1 shows the CO stretching region of the FT-IR and FT-Raman spectra of $[Rh(CO)_4]^+$ in concd H_2SO_4 under a CO atmosphere. An IR band at 2139 cm^{-1} (E_u) and two Raman bands at 2215 (A_{1g}) and 2175 (B_{1g}) cm^{-1} were observed, which are consistent with the square planar structure (D_{4h}) for $[Rh(CO)_4]^+$ formed from $[Rh(\mu\text{-}Cl)(CO)_2]_2$ in HSO_3F[11] or for $[Rh(CO)_4]^+$ with the $[1\text{-}Et\text{-}CB_{11}F_{11}]^-$ anion.[12] It is interesting to compare $[Rh(CO)_4]^+$ with other d^8 ML_4 complexes such as $Ru(CO)_2L_2$ ($L = P^tBu_2Me$), which has a nonplanar structure markedly different from the planar isoelectronic species $Rh(CO)_2L'_2{}^+$ ($L' = TMP = P[2,4,6\text{-}C_6H_2(OMe)_3]_3$).[16] It has been illustrated that π-acceptor ligands are necessary for distorting ML_4 away from a square-planar structure; the different geometries for the two isoelectronic complexes $Ru(CO)_2L_2$ and $Rh(CO)_2L_2{}^+$ are related to the role of the σ lone pair of CO and the effect of π-back-donation and determined by the relative energies of the d orbitals of Ru(0) and Rh(I).[16] The square-planar structure for $[Rh(CO)_4]^+$ hence reflects significantly reduced Rh-to-CO π-back-bonding, which is consistent with the large ν(CO) values.

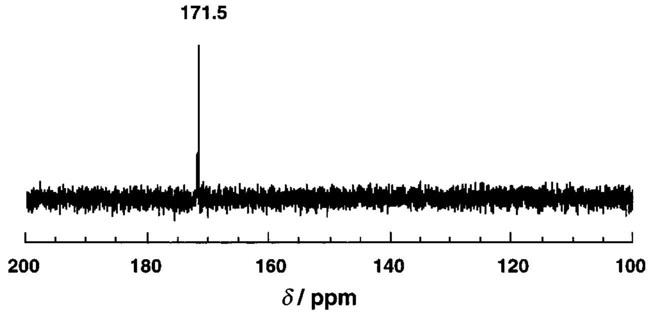

Figure 2. ^{13}C NMR spectrum (100.40 MHz) of the rhodium(I) tetracarbonyl cation, $[Rh(CO)_4]^+$, of natural ^{13}C abundance at 0.136 M formed by the dissolution of $Rh_4(CO)_{12}$ in 96% H_2SO_4 solution under a CO atmosphere at room temperature.

Figure 2 shows the ^{13}C NMR spectrum of $[Rh(CO)_4]^+$ of natural ^{13}C abundance in concd H_2SO_4 at room temperature and 1 atm of CO. The ^{13}C resonance for $[Rh(CO)_4]^+$ at 171.5 ppm, upfield from 184 ppm for free ^{13}CO, is located in the range where those for the monovalent copper,[17] silver,[17] gold,[8b] palladium,[8a] and platinum[5] carbonyl cations are located. Although the coupling of $^{103}Rh-^{13}C$ is expected for $[Rh(CO)_4]^+$, the nonexistence of a split for the ^{13}C resonance suggests a rapid CO exchange process between the Rh(I) carbonyl cations due to the significantly weak Rh−CO bond.

By a brief evacuation, $[Rh(CO)_4]^+$ readily loses CO ligands to give a dark red-brown solution, which exhibits no IR and Raman bands in the CO stretching region and no ^{13}C NMR resonance; its composition and structure remain to be determined. By reintroducing CO into the red-brown solution, the Rh(I) tetracarbonyl cation is reformed. The observations indicate that CO is reversibly coordinated to Rh, suggesting a remarkably weak Rh−CO bond consistent with the above NMR and IR results.

Rhodium(I) Carbonyl Cation-Catalyzed Carbonylation of Olefins. Rhodium catalysts, most of which work in organic solvents, have assumed a very important position in synthetic chemistry. Rh catalysts such as $RhCl(PPh_3)_3$, the so-called Wilkinson's catalyst, have been employed for the homogeneous hydrogenation of unsaturated compounds.[10] Rh-catalyzed carbonylation processes have made a considerable commercial impact as they operate at ambient pressures and temperatures.[1] Rh complexes with phosphines as ligands facilitate the hydroformylation of olefins (Roelen reaction) to be conducted at much lower temperatures and pressures than the original Co catalyst ($HCo(CO)_4$).[18] Catalyst systems based on Rh ($[RhI_2(CO)_2]^-$) represent the most effective way of manufacturing acetic acid under much mild

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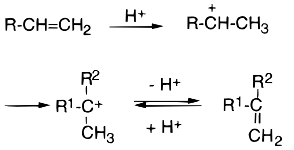
conditions, the selectivity being as high as 99%, whereas the original Fe, Co, and Ni carbonyl catalysts work at high temperature and pressure.[19]

The Koch reaction, another carbonylation, gives tertiary carboxylic acids in strong acids such as H_2SO_4, HF, H_3PO_4, or $BF_3{\cdot}H_2O$, in which no metal catalysts are used but high CO pressure is necessary.[20] We have reported that cationic Cu(I), Ag(I), Au(I), and Pd(I) carbonyl catalysts cause the Koch-type reaction to proceed under much milder conditions.[7,8] This paper reveals that, in the presence of the Rh(I) tetracarbonyl cation, olefins readily react with CO to give *tert*-carboxylic acids in high yields at room temperature and atmospheric pressure.



$$R\text{-}CH{=}CH_2 \xrightarrow{H^+} R\text{-}\overset{+}{C}H\text{-}CH_3 \longrightarrow R^1\text{-}\underset{CH_3}{\overset{R^2}{C^+}} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} R^1\text{-}\underset{CH_2}{\overset{R^2}{C}} \qquad (2)$$

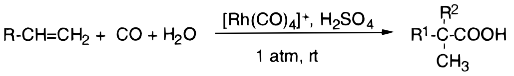
Strong acids and superacids have been used as useful reaction media and catalysts in organic syntheses and industrial processes,[21] including the cationic carbonylation of methane and its substituted derivatives[22] and the formylation of aromatic compounds.[23] In concd H_2SO_4, the olefin is protonated to form a carbocation intermediate, which isomerizes to a *tert*-carbocation via the Wagner-Meerwein rearrangement.[21] There is an equilibrium between the deprotonation of the carbocation and the protonation of the isomerized olefins (eq 2).[24] Polymerization of the olefins and carbocations is another reaction occurring in this system. In the original Koch reaction, the direct reaction of the carbocations with the dissolved CO in the solution leads to the formation of acylium cations, which react with water to give tertiary carboxylic acids. Without the rhodium(I) carbonyl catalyst, olefins are carbonylated to form the carboxylic acids in yields as low as 10% under atmospheric pressure of CO and at room temperature because of the low CO solubility in the solution and the presence of the polymerization as a competing reaction.

Table 1 summarizes the results of the rhodium(I) carbonyl cation-catalyzed carbonylation of olefins at room temperature and atmospheric pressure of CO in 96% H_2SO_4 (eq 3). The addition of the rhodium carbonyl catalyst drastically enhances the rate of carbonylation, which is completed in 1 h, and *tert*-carboxylic acids are formed in high yields. During the reaction, the IR band at 2139 cm^{-1} remains unchanged, indicating that $[Rh(CO)_4]^+$ is the active species for the catalytic carbonylation.

Table 1. Rhodium(I) Carbonyl Cation-Catalyzed Carbonylation of Olefins in Concd H_2SO_4[a]

olefin	*tert*-carboxylic acid	yield[b]/%
1-pentene	2,2-dimethylbutanoic	68
	others	1
1-hexene	2,2-dimethylpentanoic	55
	2-methyl-2-ethylbutanoic	25
	others	1
1-octene	2,2-dimethylheptanoic	41
	2-methyl-2-ethylhexanoic	22
	2-methyl-2-propylpentanoic	10
	others	3
1-decene	2,2-dimethylnonanoic	30
	2-methyl-2-ethyloctanoic	14
	2-methyl-2-propylheptanoic	11
	2-methyl-2-butylhexanoic	5
	others	2
cyclohexene	1-methylcyclopentanecarboxylic	54

[a] $Rh_4(CO)_{12}$/olefin = 0.17 mmol/2.5 mmol, 96% H_2SO_4 5 mL, CO 1 atm, rt. [b] Based on olefin.



$$R\text{-}CH{=}CH_2 + CO + H_2O \xrightarrow[\text{1 atm, rt}]{[Rh(CO)_4]^+,\ H_2SO_4} R^1\text{-}\underset{CH_3}{\overset{R^2}{C}}\text{-}COOH \qquad (3)$$

We recently proposed a complex formed from the metal carbonyl cation and the isomerized olefin as an intermediate for the catalytic carbonylation of olefins in strong acids.[8b] As observed for the Cu(I), Ag(I), and Au(I) carbonyl cations,[6] the Rh−CO bonding in the Rh(I) tetracarbonyl cation in concd H_2SO_4 is so weak that a brief evacuation for only several seconds leads to the evolution of the reversible CO ligands, while an evacuation for 17 h is required to remove the CO ligands from the Pd(I) carbonyl cation, $[Pd_2(CO)_2]^{2+}$.[8a] On the other hand, the conversions of olefins to tertiary carboxylic acids by these cationic metal carbonyl catalysts under atmospheric CO are comparable despite the significant difference in the strength of the M−CO bonding. Therefore, the catalytic activity of the cationic metal carbonyl catalysts is not merely correlated to the ease of the dissociation of the M−CO bonds; it can be concluded that the coordination of the substrate to the metal should be taken into consideration, although the reaction mechanism requires more investigation, such as kinetic, spectroscopic and theoretical studies.

Conclusions

In summary, we have found a remarkably facile route to prepare the rhodium(I) tetracarbonyl cation, $[Rh(CO)_4]^+$, from the neutral Rh carbonyl cluster, $Rh_4(CO)_{12}$, in concd H_2SO_4 solution under a CO atmosphere. This is the first example of the oxidation of Rh(0) to Rh(I) by H^+. In concd H_2SO_4 solution, the Rh(I) tetracarbonyl cation catalyzes the carbonylation of olefins to give *tert*-carboxylic acids in high yields at room temperature and atmospheric pressure of CO.

Experimental Section

Commercial Reagents. $Rh_4(CO)_{12}$ (Strem Chemicals), H_2SO_4 (96%, Kanto Chemical Co.), and CO (Nippon Sanso) were used for the preparation and characterization of the rhodium(I) carbonyl catalyst. Reagents (special grade, Wako Pure Chemical) 1-pentene, 1-hexene, 1-octene, 1-decene, and cyclohexene were used for the carbonylation without further purification.

The preparation of the rhodium(I) tetracarbonyl cation was carried out using a 100-mL three-necked flask connected

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to a gas buret, similar to the equipment used in the previous studies.[8] A mixture of 125 mg (0.17 mmol) of $Rh_4(CO)_{12}$ and 5 mL of 96%H_2SO_4 was vigorously stirred under atmospheric CO, resulting in the formation of a yellow-brown solution. The gas uptake was monitored by the gas buret, and the dihydrogen formed during the reaction was analyzed using a Hitachi M-2000 mass spectrometer and a Yanaco G-3800 gas chromatograph with a column of 13X molecular sieves. The characterization of $[Rh(CO)_4]^+$ was carried out by FT-IR, FT-Raman, and ^{13}C NMR as previously described.[5,8]

The carbonylation of olefins was carried out by a method similar to that described in previous papers.[8] Using a syringe, an olefin was added dropwise into the concd H_2SO_4 solution of $[Rh(CO)_4]^+$. After the reaction was finished, the reaction mixture was poured over ice−water. The products were extracted with *n*-hexane and analyzed by GC, NMR, and IR. Identification of the products in Table 1 was carried out by a comparison of the retention times and "spiking" with the authentic samples prepared by the Cu(I) carbonyl cation-catalyzed carbonylation of olefins.[7]

Acknowledgment. We thank Prof. H. Willner for helpful discussions, Dr. M. Tanaka for valuable help and discussions, and Prof. S. H. Strauss for a preprint of his work prior to publication.

JO991659U