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Palladium(I) Carbonyl Cation-Catalyzed Carbonylation of Olefins and Alcohols in Concentrated Sulfuric Acid

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A new palladium catalyst was found to exhibit high catalytic activity for carbonylation of olefins and alcohols. *cyclo*-Bis(μ-carbonyl)dipalladium(I) cation (**1**) with bridging CO ligands is formed by reductive carbonylation of palladium sulfate, $PdSO_4$, in concentrated H_2SO_4. When an olefin or alcohol is added, complex **1** changes to a new complex (**2**) with terminal CO ligands, and tertiary carboxylic acids are obtained in high yields at room temperature and atmospheric pressure of CO. IR and ^{13}C NMR studies suggest that complex **2** may be tentatively formulated to be $[Pd_2(CO)_2]^{2+}$, in which the terminal CO ligands are chemically equivalent. Complex **1** is a catalyst precursor, and complex **2** functions as an active species for the carbonylation of olefins and alcohols. The catalytic behavior of the palladium carbonyl catalyst supports the recently proposed reaction mechanism involving an olefin−metal−CO complex as an intermediate for the catalytic carbonylation of olefins and alcohols in strongly acidic solution.

Introduction

Recently, the more than 100-year-old chemistry of the metal carbonyls has achieved remarkable developments.[1,2] Many new highly reduced metal carbonyl anions have been obtained through chemical reduction in basic solvents.[3] Our knowledge of relatively stable neutral carbonyl complexes has been dramatically enriched by the synthesis of the first metalloidal and alkaline earth metal carbonyls, $[Cp^*Si(CO)]$[4] and $[Cp^*Ca(CO)]$,[5] respectively, in solution and by the isolation and X-ray structural characterization of the first *f*-block carbonyl complex, $[(C_5Me_4H)_3U(CO)]$.[6] In particular, the focus of much attention for the past years has been a new and very intriguing class of late-metal carbonyl complexes: homoleptic carbonyl cations and their cationic derivatives of the electron-rich metals in groups 8−12 isolated in superacidic media,[7−12] including $[Pd(CO)_4][Sb_2F_{11}]_2$,[9a,e] *cis*-$Pd(CO)_2(SO_3F)_2$,[9b,d] and $[c\text{-}Pd_2(\mu\text{-}CO)_2](SO_3F)_2$.[9c] In contrast to typical metal carbonyl complexes, the new family of metal carbonyls has a distinguishing characteristic in that the CO vibrational frequencies are considerably higher than that of free CO, for which the term *nonclassical metal carbonyl* was previously proposed, and its definition has recently been revised.[13d,e] Although there is an argument on the classification of *classical* and *nonclassical* metal carbonyls,[8h,13b,e] there is no doubt that the metal carbonyl cations have remarkably reduced π-back-bonding. Of great interest is the catalytic activity for carbonylation related to the high reactivity of CO originating from the reduced metal → CO π-back-bonding.[14,15]

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There has been a large number of reports dealing with the carbonylation of olefins, many of which are catalyzed by metal carbonyls.[16] In Roelen[17] and Reppe[18] reactions, the typical metal carbonyls, such as $Co_2(CO)_8$ and $Ni(CO)_4$, are used to catalyze the carbonylation of olefins to produce aldehydes and carboxylic acids, which requires high temperature and high pressure. Another carbonylation, the Koch reaction, 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.[19] We previously reported that the addition of Cu(I) and Ag(I) carbonyl catalysts caused the Koch-type reaction to proceed under much milder conditions—at ambient temperature and pressure.[20] Recently, we have also found that the gold(I) carbonyl cation is an excellent catalyst for carbonylation of olefins, which is the first application of gold(I) carbonyls to organic syntheses.[21]

Starting with the ingenious invention of the industrial process for acetaldehyde production by the air oxidation of ethylene catalyzed by $PdCl_2$ and $CuCl_2$, the so-called Wacker process, remarkable progress has been made in organic synthesis using Pd compounds both as stoichiometric reagents and catalysts.[22,23] Many significant reactions are catalyzed or promoted by Pd(0) and Pd(II) compounds, including oxidative carbonylation of olefins by Pd(II) and hydrocarboxylation of olefins by Pd(0), whereas little is known about the catalytic activities of Pd(I) compounds.[22] Most of the reactions by Pd catalysts are carried out in organic solvents, while a few of them proceed in acidic media such as TFA, HCl, and HBF_4.[24,25]

In this paper, we wish to report a new palladium carbonyl catalyst in concd H_2SO_4, with which olefins and alcohols react with CO to produce tertiary carboxylic acids in high yields at atmospheric pressure and room temperature. Evidence for the formation of a new Pd(I) carbonyl complex without bridging CO ligands is presented. This work extends the family of the highly active metal carbonyl catalysts for carbonylation of olefins from group 11 to group 10 elements. The discovery of the palladium carbonyl catalyst sheds light on the reaction mechanism of the metal carbonyl cation-catalyzed carbonylation in strongly acidic media.

Results and Discussion

Formation of Palladium(I) Carbonyl Cation, $[c\text{-}Pd_2(\mu\text{-}CO)_2]^{2+}$ (1), in Concentrated H_2SO_4. So far, three palladium carbonyl complexes, $[Pd(CO)_4][Sb_2F_{11}]_2$, *cis*-$Pd(CO)_2(SO_3F)_2$, and $[c\text{-}Pd_2(\mu\text{-}CO)_2](SO_3F)_2$, have been prepared in superacidic media and well characterized by Willner et al.[9] The reductive carbonylation of the mixed-valency compound $Pd^{II}Pd^{IV}(SO_3F)_6$ at 25 °C produces almost exclusively *cis*-$Pd(CO)_2(SO_3F)_2$.[9b] When the reaction is carried out in fluorosulfuric acid, an isomer mixture of the composition $Pd(CO)_2(SO_3F)_2$ is obtained.[9d] Single crystals of both *cis*-$Pd(CO)_2(SO_3F)_2$ and $[c\text{-}Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ are obtained by recrystallization of the isomer mixture from fluorosulfuric acid under slightly different conditions.[9c,d] The cyclic and completely planar cation with symmetrically bridging carbonyl ligands, $[c\text{-}Pd_2(\mu\text{-}CO)_2]^{2+}$, has also been recently isolated as the salt of $[Sb_2F_{11}]^-$.[9e] The homoleptic carbonyl cation, $[Pd(CO)_4]^{2+}$, has been isolated with the most weakly coordinating anion $[Sb_2F_{11}]^-$ by the solvolysis of $Pd(CO)_2(SO_3F)_2$ in liquid antimony(V) fluoride in the presence of CO.[9a]

We have found a remarkably facile route for preparing palladium carbonyls suitable for the catalytic carbonylation of olefins and alcohols. The commercial palladium sulfate, $PdSO_4$, is reduced by CO to form the *cyclo*-bis(μ-carbonyl)dipalladium(I) cation, $[c\text{-}Pd_2(\mu\text{-}CO)_2]^{2+}$ (**1**), in concd H_2SO_4 solution at 25 °C (eq 1). The brown color fades away during the CO uptake, and a clear orange-red solution is obtained if the concentration of Pd in 96% H_2SO_4 is below 0.15 M. The CO uptake is 1.5 mol per mole of $PdSO_4$, and hence, the CO/Pd stoichiometric ratio, the number of moles of absorbed CO per mole of Pd, is exactly 1.0, because the reduction of Pd(II) to Pd(I) is accompanied by the oxidation of 0.5 mol of CO to CO_2, which is dissolved in the H_2SO_4 solution. When the concentration of Pd in 96% H_2SO_4 is above 0.15 M, a heterogeneous suspension is formed.

$$PdSO_4 + CO \xrightarrow{H_2SO_4} \underset{\mathbf{1}}{[c\text{-}Pd_2(\mu\text{-}CO)_2]^{2+}} \qquad (1)$$

Complex **1** is also formed in concd H_2SO_4 using palladium oxide, PdO, or palladium acetate, $Pd(CH_3COO)_2$, as the starting material, and the resulting solutions are suitable for the catalytic carbonylation of olefins and alcohols. Carbonyl derivatives of palladium with lower oxidation state tend to be formed in media of lower acidity. For example, the reaction of $PdSO_4$ with CO in the so-called magic acid, HSO_3F/SbF_5 (1:1), resulted in the formation of $[Pd(CO)_4]^{2+}$, while $[Pd(CO)_4][Sb_2F_{11}]_2$, the salt obtained from SbF_5,[9a] was immediately converted into complex **1** when dissolved in concd H_2SO_4. Palladium sulfate is reduced to Pd metal by directly exposing it to CO or by allowing it react with CO in sulfuric acid of concentration below 70%.

Complex **1** in concd H_2SO_4 solution exhibits IR absorption at 1972 cm^{-1} (Figure 1a), which is close to that for the bridging CO groups in solid $[c\text{-}Pd_2(\mu\text{-}CO)_2](SO_3F)_2$.[9c] The unusually high CO stretching frequencies, ν_{CO}, about 200 cm^{-1} higher than for bidentate bridging CO groups in usual transition-metal carbonyl compounds, suggest substantially reduced metal-to-CO π-back-bonding. Complex **1** survives after continuous evacuation for over 24

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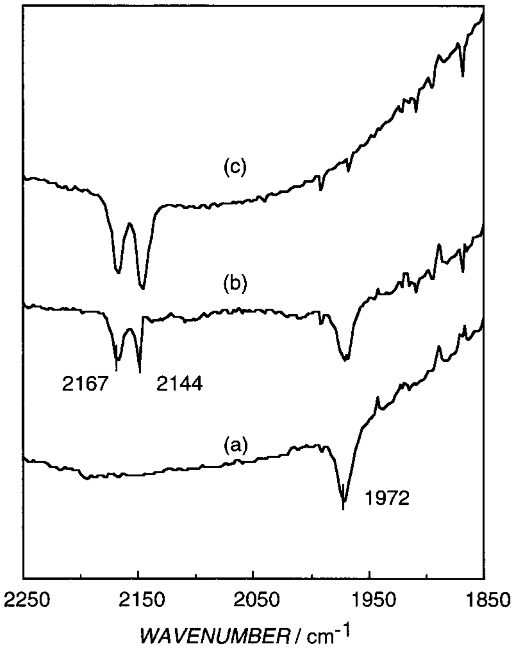


Figure 1. Infrared spectra of palladium(I) carbonyl cations in 96% H_2SO_4 solution at room temperature: (a) *cyclo*-bis(μ-carbonyl)dipalladium(I) cation at 0.1 M; (b) after addition of 1-hexene equimolar to Pd in the solution of (a); (c) after addition of 2.0 mol of 1-hexene per mole of Pd in the solution of (a).

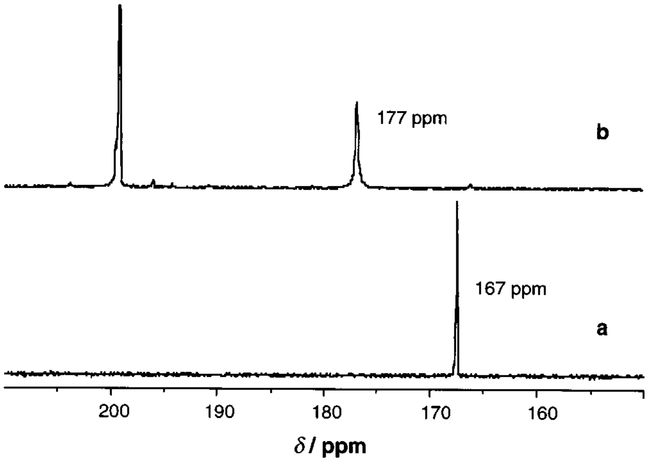


Figure 2. ^{13}C NMR spectra of palladium(I) carbonyl cations in 96% H_2SO_4 solution at room temperature: (a) ^{13}C-enriched *cyclo*-bis(μ-carbonyl)dipalladium(I) cation at 0.1 M; (b) after addition of 5 mol of *tert*-butyl alcohol per mole of Pd in the solution of (a) under ^{13}CO at 1 atm.

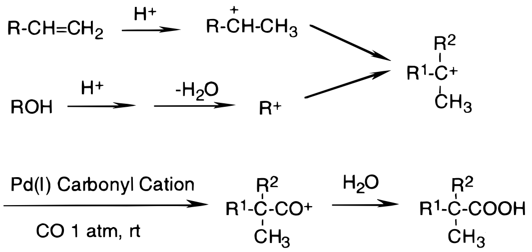
Table 1. Palladium(I) Carbonyl Cation-Catalyzed Carbonylation of Olefins and Alcohols in Concd H_2SO_4[a]

substrate	*tert*-carboxylic acid	yield[b]/%
1-hexene	2,2-dimethylpentanoic	48
	2-methyl-2-ethylbutanoic	23
	others	1
1-octene	2,2-dimethylheptanoic	37
	2-methyl-2-ethylhexanoic	17
	2-methyl-2-propylpentanoic	9
	others	2
1-decene	2,2-dimethylnonanoic	29
	2-methyl-2-ethyloctanoic	15
	2-methyl-2-propylheptanoic	9
	2-methyl-2-butylhexanoic	3
	others	2
cyclohexene	1-methylcyclopentanecarboxylic	52
t-butanol	2,2-dimethylpropanoic	70
	others	2
1-hexanol	2,2-dimethylpentanoic	57
	2-methyl-2-ethylbutanoic	27
	others	2
1-octanol	2,2-dimethylheptanoic	47
	2-methyl-2-ethylhexanoic	23
	2-methyl-2-propylpentanoic	12
	others	2
1-decanol	2,2-dimethylnonanoic	38
	2-methyl-2-ethyloctanoic	20
	2-methyl-2-propylheptanoic	11
	2-methyl-2-butylhexanoic	5
	others	3
cyclohexanol	1-methylcyclopentanecarboxylic	62

[a] $PdSO_4$/substrate = 1.0 mmol/5.0 mmol, 96% H_2SO_4 10 mL, CO 1 atm, rt. [b] Based on substrate.

h or on standing at 60 °C for 3 days, indicating relatively high stability of the bridging CO ligands. Two resonances appear in the ^{13}C NMR spectrum of the ^{13}C-labeled complex **1** in concd H_2SO_4 at ambient temperature and atmospheric pressure of ^{13}CO, a signal at 125 ppm due to $^{13}CO_2$, and an intense resonance at 167 ppm due to $[c\text{-}Pd_2(\mu\text{-}CO)_2]^{2+}$ (Figure 2a). The resonance at 167 ppm remains a singlet even at a temperature down to -10 °C, the freezing point of concd H_2SO_4, excluding a CO exchange process and indicating that the CO ligands are chemically equivalent.

Palladium(I) Carbonyl Cation-Catalyzed Carbonylation of Olefins and Alcohols. Palladium catalysts, most of which work in organic solvents, have assumed a very important position in synthetic chemistry.[22] Many significant reactions are catalyzed or promoted by Pd(0) and Pd(II) compounds, whereas few Pd(I) catalysts have been reported so far to our knowledge. It has been reported that Cu(I), Ag(I), and Au(I) carbonyl cations catalyze the carbonylation of olefins and alcohols in strong acids.[15,20,21] This paper reveals that, in the presence of Pd(I) carbonyl cations, olefins and alcohols react readily with CO to give *tert*-carboxylic acids in high yields at room temperature and atmospheric pressure (eq 2).



(2)

Table 1 summarizes the results of the palladium(I) carbonyl cation-catalyzed carbonylation of olefins and alcohols under atmospheric pressure of CO and at room temperature in 96% H_2SO_4. Strong acids and superacids have been used as useful reaction media and catalysts in organic syntheses and industrial processes,[26] including cationic carbonylation of methane and its substituted derivatives[27] and formylation of aromatic compounds.[28] In concd H_2SO_4, the olefin is protonated, or the alcohol is protonated and dehydrated, to form a carbocation

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intermediate, which isomerizes to a *tert*-carbocation via Wagner−Meerwein rearrangement prior to the carbonylation. The carbonylation of carbocations leads to the formation of acylium cations, which react with water to give tertiary carboxylic acids or with alcohols to give the corresponding esters.[15,20] Without the palladium(I) carbonyl catalyst, olefins and alcohols are converted to the carboxylic acids in yields as low as 10% and 15%, respectively, under atmospheric pressure of CO and at room temperature due to the oligomerization as a competing reaction. As shown in Table 1, addition of the palladium carbonyl catalyst drastically enhances the rate of carbonylation, which is completed in 1−2 h, and *tert*-carboxylic acids are formed in high yields. As proposed recently, an olefin−metal−carbonyl complex seems to act as an intermediate, which accounts for the high catalytic activity of the carbonylation of olefins in strong acid (vide infra).

Formation of New Palladium(I) Carbonyl Cation with Terminal CO Ligands and Its Role in Catalytic Carbonylation of Olefins and Alcohols. When an olefin or alcohol was added dropwise in a concd H_2SO_4 solution of complex **1** under atmospheric CO, tertiary carboxylic acids were obtained in high yields (Table 1), accompanied by the conversion of complex **1** to a new palladium carbonyl complex (**2**), which may be tentatively formulated as $[Pd_2(CO)_2]^{2+}$ (vide infra). For example, when 1-hexene was added to the concd H_2SO_4 solution of complex **1**, the IR absorption due to bridging CO (1972 cm^{-1}) decreased, and two new bands appeared at 2167 and 2144 cm^{-1} and grew concomitantly with the same intensity (Figure 1b).[29] The CO stretching frequencies, higher than 2143 cm^{-1} for free CO, indicate that complex **2** should be attributed to a cationic palladium carbonyl complex with terminal CO ligands, in which π-back-bonding is reduced.[7,13] At 1-hexene/Pd = 2 mmol/1 mmol, the IR absorption of bridging CO completely disappeared, and only the two bands of terminal CO ligands were observed (Figure 1c). Attempts to record a Raman spectrum were unsuccessful, quite possibly because of the limited concentration of the complexes in concd H_2SO_4. The two IR absorptions at 2167 and 2144 cm^{-1} survived after continuous evacuation for 1 h or after heating at 60 °C for 1 day, but they disappeared after continuous evacuation for over 1 day or on standing at 80 °C for 1 day. These facts indicate that the metal−CO bonds in complex **2** are relatively stable in comparison with those in the dicarbonyl cations of the metals in group 11, $[M(CO)_2]^+$ (M = Cu, Ag, and Au) in concd H_2SO_4, of which the CO ligands are reversibly absorbed and released. Similar results were obtained when use was made of the other substrates listed in Table 1. No change was observed when trimethylacetic acid (TMAA) was added in the concd H_2SO_4 solution of complex **1**, indicating that the conversion of complex **1** to complex **2** is not caused by tertiary carboxylic acids, the products of carbonylation of olefins and alcohols.

Table 2. IR and ^{13}C NMR Data of Carbonyl Derivatives of Palladium in Different Oxidation States

compd[a]	ν_{CO}(IR)/cm^{-1}	δ (^{13}C)/ppm	ref
$Pd(CO)^b$	2044		32
$Pd(CO)_2{}^b$	2040		32
$Pd(CO)_3{}^b$	2053		32
$Pd(CO)_4{}^b$	2066		32
$[c\text{-}Pd_2(\mu\text{-}CO)_2]^{2+}$ (**1**)[c]	1972	167	this work
$[c\text{-}Pd_2(\mu\text{-}CO)_2](SO_3F)_2$	1977	162	9c
$[c\text{-}Pd_2(\mu\text{-}CO)_2][Sb_2F_{11}]_2$	2006		9e
$[Pd_2(CO)_2(PPh_2py)_2Cl_2]^d$	2019, 1994		35
$[Pd_2(CO)_2]^{2+}$ (**2**)[c]	2167, 2144	177	this work
$Pd_2(CO)_2Cl_4{}^d$	2166		36
cis-$Pd(CO)_2(C_6Cl_5)_2{}^e$	2173, 2152		37
cis-$Pd(CO)_2(C_6F_5)_2{}^e$	2186, 2163		37
cis-$Pd(CO)_2(SO_3F)_2$	2227, 2208	145	9b,d
$[Pd(CO)_4][Sb_2F_{11}]_2$	2248	144	9a,e

[a] Unless otherwise stated, spectra are obtained on solid compounds. [b] In krypton matrix. [c] In concentrated H_2SO_4. [d] In dichloromethane solution. [e] Stable only below −30 °C under CO pressure.

The resonance at 167 ppm in the ^{13}C NMR spectrum of complex **1** disappeared and a new resonance at 177 ppm was observed when an olefin or alcohol was added into the concd H_2SO_4 solution of ^{13}C-labeled complex **1** under an atmosphere of ^{13}CO. Figure 2b shows the ^{13}C NMR spectrum of the solution in which *tert*-butyl alcohol was added.[30] At higher fields, only the resonances for the tertiary butyl groups were observed, ruling out that complex **2** is olefin-coordinated. The additional intense ^{13}C resonance at 199.1 ppm should be assigned to the −COOH group in TMAA, the products of carbonylation from *tert*-butyl alcohol, in the strongly acidic medium,[31] whereas a signal at 185.7 ppm is expected for the −COOH group in pure carboxylic acids.[20a] The signal at 199.1 ppm remained a singlet even at a temperature down to −10 °C, the freezing point of concd H_2SO_4, suggesting that only TMAA dissolved in concd H_2SO_4 existed, excluding the possibility that TMAA is involved in complex **2** as a ligand.

Table 2 shows a comparison of IR and ^{13}C NMR data for palladium carbonyl derivatives in different oxidation states. The CO stretching frequencies (ν_{CO}) for terminal CO ligands in Pd(0) carbonyl complexes in a noble gas matrix are much lower than that for free CO (2143 cm^{-1}), due to a large degree of metal-to-CO π-back-bonding.[32] In contrast to several dinuclear Pd(I) complexes with

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(28) (a) Tanaka, M.; Souma, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 1551. (b) Tanaka, M.; Iyoda, J.; Souma, Y. *J. Org. Chem.* **1992**, *57*, 2677. (c) Tanaka, M.; Souma, Y. *J. Org. Chem.* **1992**, *57*, 3738. (d) Tanaka, M.; Fujiwara, M.; Ando, H.; Souma, Y. *J. Org. Chem.* **1993**, *58*, 3213. (e) Tanaka, M.; Fujiwara, M.; Ando, H. *J. Org. Chem.* **1995**, *60*, 2106. (f) Tanaka, M.; Fujiwara, M.; Ando, H. *J. Org. Chem.* **1995**, *60*, 3846. (g) Tanaka, M.; Fujiwara, M.; Xu, Q.; Souma, Y.; Ando, H.; Laali, K. K. *J. Am. Chem. Soc.* **1997**, *119*, 5100. (h) Tanaka, M.; Fujiwara, M.; Xu, Q.; Ando, H.; Raeker, T. J. *J. Org. Chem.* **1998**, *63*, 4408.

(29) When an olefin or alcohol was added, a small amount of a purple colloidal substance, probably due to Pd(0) particles, was formed in the solution. By allowing the purple solution to stand for several days, the colloidal substance was precipitated and left a yellow clear solution of complex **2**, for which the IR absorption bands at 2167 and 2144 cm^{-1} remained unchanged.

(30) Carbonylation of *t*-BuOH produces 2,2-dimethylpropanoic acid (TMAA), of which the ^{13}C NMR spectrum for the −COOH group is the simplest of all of the tertiary carboxylic acids. The same ^{13}C resonance at 177 ppm was observed for the CO ligands when use was made of the other substrates listed in Table 1.

(31) Similar deshielding of the ^{13}C resonance (194 ppm) has been observed for the −COOH group of TMAA adsorbed in an H-type zeolite (H-ZSM-5), for which possible attributions have been proposed but not defined. (see: Stepanov, A. G.; Luzgin, M. V.; Romannikov, V. N.; Zamaraev, K. I. *J. Am. Chem. Soc.* **1995**, *117*, 3615.) By determining the H_2SO_4-concentration dependence of the ^{13}C chemical shift, $\delta(^{13}C)$, of the −COOH group of TMAA dissolved in H_2SO_4 solutions at room temperature, we conclude that the deshielding of $\delta(^{13}C)$ originates from the protonation of the −COOH group of TMAA in the strong acids. $\delta(^{13}C)$ of the −COOH group of TMAA dissolved in water (0% H_2SO_4) is 184.4 ppm (close to 185.7 ppm for pure TMAA), which shifts to 185.1, 191.2, and 199.1 ppm with increasing H_2SO_4 concentration to 50, 80, and 96%, respectively.

(32) (a) Darling, J. H.; Ogden, J. S. *Inorg. Chem.* **1972**, *11*, 666. (b) Darling, J. H.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1973**, 1079.

terminal ligands of isoelectronic isocyanides,[33] the carbonyl derivatives of monovalent palladium without bridging CO ligands reported so far are rare.[34] An example is $[Pd_2(CO)_2(2\text{-diphenylphosphinopyridine})_2Cl_2]$,[35] in which the coordination of the donor ligands, PPh_2py and Cl^{-1}, to Pd(I) gives rise to ν_{CO} well below 2143 cm^{-1}. Few mononuclear palladium(II) carbonyl derivatives have been reported so far.[34] The ν_{CO} for terminal CO ligands in Pd(II) carbonyl complexes without donor ligands are above 2200 cm^{-1}, rather higher than for free CO (2143 cm^{-1}), due to reduced π-back-bonding. The coordination of donor ligands lowers ν_{CO} as shown by $Pd_2(CO)_2Cl_4$,[36] *cis*-$Pd(CO)_2(C_6Cl_5)_2$, and *cis*-$Pd(CO)_2(C_6F_5)_2$.[37] The CO vibrational numbers (2167 and 2144 cm^{-1}) for complex **2** are considerably higher than those of the zerovalent palladium carbonyl complexes and significantly lower than those of the divalent palladium carbonyl cations without donor ligands.

The ^{13}C NMR resonance at 177 ppm remained a singlet even at a temperature down to the freezing point of concd H_2SO_4, excluding a CO exchange process between different species. Hence, only chemically equivalent CO ligands exist in complex **2**. So far, a trend has been well established for the ^{13}C chemical shift of the terminal CO groups in metal carbonyl complexes.[7b] The chemical shift of free ^{13}CO at $\delta = 184$ ppm relative to $(CH_3)_4Si$ (TMS) can be regarded as a limit for cationic metal carbonyl derivatives with smaller values, as well as typical metal carbonyls and highly reduced carbonylmetalates with higher resonance frequencies and correspondingly higher δ values. The ^{13}C chemical shift for complex **2** (177 ppm) is located in the range where those for the Pd(I) carbonyl cation (**1**) and the Cu(I), Ag(I), and Au(I) carbonyl cations[7,15] are located, in contrast with the chemical shifts upfield from 145 ppm for divalent palladium carbonyl cations (Table 2).

The above IR and ^{13}C NMR results suggest that complex **2** is a cationic carbonyl complex of monovalent palladium with chemically equivalent and terminal CO ligands. Complex **2** was found to be ESR silent and hence a diamagnetic dinuclear Pd(I) complex, in which the odd electrons on each palladium atom are spin-paired. Complex **2** can, therefore, be tentatively formulated to be $[Pd_2(CO)_2]^{2+}$, of which the isolation is expected. In well-characterized dinuclear Pd(I) complexes of isocyanides, such as $[(CH_3NC)_6Pd_2]^{2+}$, the two square planes with the Pd ions centered are nearly perpendicular.[33] The observation of the two IR absorptions at 2167 and 2144 cm^{-1} with the same intensity suggests that the two chemically equivalent CO ligands in complex **2** do not occupy the axial coordination sites, as in $Pd_2(CO)_2(PPh_2py)_2Cl_2$.[35]

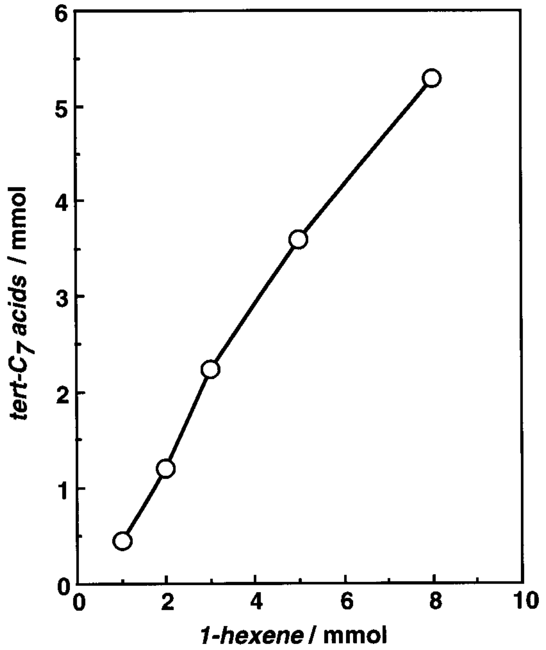

Figure 3. Plot of the yield of tertiary C_7 acids versus the amount of 1-hexene added in 10 mL of 96% H_2SO_4 solution of 0.1 M *cyclo*-bis(μ-carbonyl)dipalladium(I) cation at room temperature and atmospheric pressure of CO.

Figure 3 illustrates that the catalytic activity of the Pd(I) carbonyl catalyst does not decline even if more than 2 mol of 1-hexene per mole of Pd are added, where complex **1** has been completely converted to complex **2** as observed by IR (Figure 1c). This fact leads to the conclusion that complex **1** is a catalyst precursor and that complex **2** acts as the active species for the catalytic carbonylation of olefins and alcohols in concd H_2SO_4.

We can provide a qualitative discussion on the catalytic activity of the Pd(I) carbonyl catalyst and on the reaction mechanism of the metal carbonyl cation-catalyzed carbonylation of olefins and alcohols in strongly acidic solution by comparing the metal−CO bonds with those in the monovalent copper, silver, and gold carbonyl cations. Barnes et al. calculated (ab initio) $M^+{-}CO$ bond energies to be 29.0, 19.2, and 31.5 kcal/mol and $(CO)M^+{-}CO$ bond energies to be 30.8, 19.5, and 27.6 kcal/mol for M = Cu, Ag, and Pd, respectively.[38] Veldkamp and Frenking calculated (MP2 level of theory) $(CO)_xAg^+{-}CO$ bond energies to be 21, 27, and 12 kcal/mol and $(CO)_xAu^+{-}CO$ bond energies to be 45, 50, and 9 kcal/mol for $x = 0$, 1, and 2, respectively.[39] The calculations predicted the stability of the metal monocarbonyl cations to be in the order of Ag < Cu < Pd < Au and the stability of the metal dicarbonyl cations to be in the order of Ag < Pd < Cu < Au. The calculations, which neglected the effects from the counteranions and solvents, also predicted that the dicarbonyl cations are more stable than the corresponding monocarbonyl cations for Cu, Ag, and Au. It has, however, been found that in HSO_3F or concd H_2SO_4 solution the dicarbonyl cations of Cu(I), Ag(I), and Au(I) are so unstable that the reversible CO ligands are lost even after a brief evacuation for several seconds, while the corresponding monocarbonyl cations are so stable that they remain unchanged after continuous

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evacuation for 1 day.[15,21] The stabilization effects from the counteranions may account for the great stability of the monocarbonyl cations.

In contrast with the high catalytic activities of the dicarbonyl cations of the metals in group 11, the corresponding monocarbonyl cations were found to be catalytically inactive.[15] Originally, it was considered that the unstable metal polycarbonyl cations act as a *CO carrier* that transports CO from the gas phase to the H_2SO_4 solution,[16a,20a] resulting in high CO concentration in the solution and consequently accelerating the carbonylation of olefins and alcohols via the pathway of the original Koch reaction. However, complex **2**, from which an evacuation for 17 h is required to remove the CO ligands, is so stable that it cannot act as a mere CO carrier to transport CO from the gas phase and readily release the CO ligands to the H_2SO_4 solution. As shown in Table 1, the conversions of olefins and alcohols to tertiary carboxylic acids by the palladium carbonyl catalyst are comparable to those by Cu(I), Ag(I), and Au(I) carbonyl catalysts, despite the considerably high stability of the Pd−CO bonds in the Pd(I) carbonyl complex. The observations for the Pd(I) carbonyl catalyst conflict with the *CO carrier* model and support the recently proposed reaction mechanism involving an *olefin−metal−CO* intermediate for the carbonylation in strongly acidic media.[21] A recent theoretical study (B3LYP level of theory) on copper(I), silver(I), and gold(I) carbonyl cation-catalyzed carbonylation has indicated that the carbonylation of ethylene, propylene, and isobutene prefers to proceed via olefin−metal(I)−dicarbonyl intermediates.[40] The mechanism of the metal carbonyl cation-catalyzed carbonylation in strong acids is of interest and requires more investigation, such as kinetic studies (currently underway).

Conclusions

In summary, we have found a remarkably facile procedure to form the *cyclo*-bis(μ-carbonyl)dipalladium(I) cation (**1**), $[c\text{-Pd}_2(\mu\text{-CO})_2]^{2+}$, from palladium(II) sulfate, oxide, and acetate, respectively, in concd H_2SO_4 solution. A new palladium(I) carbonyl complex (**2**) with terminal CO ligands was formed by adding an olefin or alcohol to a concd H_2SO_4 solution of complex **1**. Complex **2** was suggested to be a carbonyl cation of monovalent palladium, which may be tentatively formulated to be $[\text{Pd}_2(\text{CO})_2]^{2+}$. In the concentrated H_2SO_4 solution of Pd(I) carbonyl cations, the olefin or alcohol reacted with CO to give *tert*-carboxylic acids in high yields at room temperature and atmospheric pressure. It was concluded that complex **1** is a catalyst precursor, whereas complex **2** functions as an active species for the carbonylation of olefins and alcohols. The catalytic behavior of the palladium carbonyl catalyst supported the recently proposed reaction mechanism involving an olefin−metal−CO intermediate for the catalytic carbonylation of olefins and alcohols in strong acids.

Experimental Section

Reagents. Commercial reagents $PdSO_4$ (Wako Pure Chemical), H_2SO_4 (96%, Kanto Chemical Co.), CO (Nippon Sanso), and ^{13}CO (^{13}C enrichment 99%, ICON) were used for the preparation and characterization of palladium(I) carbonyls.

Reagents (special grade, Wako Pure Chemical) 1-hexene, 1-octene, 1-decene, cyclohexene, *tert*-butyl alcohol, 1-hexanol, 1-octanol, 1-decanol, and cyclohexanol were used for the carbonylation without further purification.

Preparation of the palladium(I) carbonyl cations was carried out using a 200-mL three-necked flask connected to a CO gas buret, similar to the equipment used in the previous studies.[21] A mixture of 202.5 mg (1.0 mmol) of $PdSO_4$ and 10 mL of 96% H_2SO_4 in the three-necked flask was stirred and sonicated (40 kHz, 35 W) for 1 h. The three-necked flask was evacuated by a rotary pump to remove air, and then carbon monoxide was introduced into the gas buret. The mixture of $PdSO_4$ and H_2SO_4 was stirred vigorously to react with carbon monoxide for about 1 day, and *cyclo*-bis(μ-carbonyl)dipalladium(I) cation (**1**) was formed in an orange-red clear solution. Complex **2** was formed by adding dropwise an olefin or alcohol to the concd H_2SO_4 solution of complex **1**.

Carbonylation of olefins and alcohols was carried out by a method similar to that described in the previous papers.[21] Using a syringe, an olefin or alcohol was added dropwise to the concentrated H_2SO_4 solution of complex **1**. After the reaction was finished, the reaction mixture was poured over ice−water. The products were extracted with chloroform and analyzed by GC, NMR, and IR.

Identification of 2,2-dimethylpropanoic (TMAA), 2,2-dimethylpentanoic, 2-methyl-2-ethylbutanoic, 2,2-dimethylheptanoic, 2-methyl-2-ethylhexanoic, 2-methyl-2-propylpentanoic, 2,2-dimethylnonanoic, 2-methyl-2-ethyloctanoic, 2-methyl-2-propylheptanoic, 2-methyl-2-butylhexanoic, and 1-methylcyclopentanecarboxylic acids was carried out by comparison of retention times and "spiking" with authentic samples. The reagent 2,2-dimethylpropanoic acid from Nakarai Chemicals, Ltd., was used as one of the authentic samples. The other authentic samples were prepared by the carbonylation of olefins catalyzed by the Cu(I) carbonyl catalyst.

Characterization of the Palladium(I) Carbonyl Cations. Both complexes **1** and **2** were characterized by IR and NMR. The infrared spectra were obtained on thin films between two silicon disks on a JASCO FT/IR-230 spectrometer, and the background of concd H_2SO_4 was subtracted. ^{13}C NMR spectra were obtained on a JEOL JNM-AL400 spectrometer operating at 100.40 MHz. Liquid samples were contained in sample tubes of 5 mm o.d., in which coaxial inserts of $CDCl_3$ as an external reference and a lock were placed. ^{13}C enriched carbon monoxide was used for ^{13}C NMR measurements. Chemical shifts are given in δ unit (parts per million) downfield from tetramethylsilane.

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[40] Mogi, K.; Sonoda, T.; Sakai, Y.; Xu, Q.; Souma, Y. unpublished results.