ELSEVIER

Catalysis Today 36 (1997) 91–97

CATALYSIS TODAY

Synthesis of *tert.*-Alkanoic acid catalyzed by $Cu(CO)_n^+$ and $Ag(CO)_2^+$ under atmospheric pressure

Yoshie Souma [a], Hiroshi Kawasaki [b]

[a] *Osaka National Research Institute, AIST-MITI Midorigaoka-1, Ikeda, Osaka 563, Japan*
[b] *Idemitsu Petrochemical Co. Ltd., Chemical Research Laboratory, Shingucho 1, Tokuyama, Yamaguchi 745, Japan*

Abstract

Copper(I) and silver carbonyl catalysts were prepared in strong acids such as sulfuric acid, hydrogen fluoride, boron trifluoride-hydrate and fluoro sulfuric acid. Carboxylation of olefins, alcohols, dienes, diols, aldehydes and saturated hydrocarbons were carried out under atmospheric pressure and at room temperature by using copper(I) and silver carbonyl catalysts and *tert.*-alkanoic acids were obtained in high yields. If these catalysts were not used, carboxylation required high pressure and temperature.

Keywords: Copper carbonyl; Silver carbonyl; Carboxylation; *tert.*-Alkanoic acid

1. Introduction

It is known that copper(I) compounds absorb carbon monoxide under various conditions with a Cu:CO ratio of 1:1. The copper carbonyl complexes such as CuCO*X* (*X* = Cl, Br, I) [1], $CuCOCF_3COO$ [2] and CuCO-π-C_5H_5 [3] are unstable. The preparations of the stable copper(I) carbonyl complexes such as $HB(pz)_3CuCO$ (pz = pyrazolyl) and *t*-BuOCuCO were reported by Bruce [4–6] and Tsuda [7]. These copper monocarbonyl complexes do not have catalytic activity for the carboxylation of olefins and alcohols.

On the other hand, the formation of copper polycarbonyl cations such as $Cu(CO)_3^+$ or $Cu(CO)_4^+$ were found in acidic media [8,9]. These copper(I) polycarbonyl cations were used as catalysts for carboxylation reactions of olefins [10], alcohols [11] and saturated hydrocarbons [12] and enabled the synthesis of *tert.*-alkanoic acid under atmospheric pressure and room temperature. The existence of a silver carbonyl cation $Ag(CO)_2^+$ has also been reported [13,14]. The silver carbonyl cation has a similar catalytic activity to copper(I) carbonyl cations for the carboxylation reactions of olefins in acid solution [15].

The highly hindered alkanoic acid was prepared from isobutylene oligomer in copper carbonyl catalyst solution. The industrial process of highly hindered alkanoic acid was established by using sulfuric acid-phosphoric acid-water mixed solvent for the recycle use of catalyst [17–20]. The derivatives of highly hindered carboxylic acids are stable to hydrolysis and heat.

2. Experimental

In a 300-ml three-necked flask, equipped with a thermometer and carbon monoxide gas buret,

PII S0920-5861(96)00201-5

572 mg of Cu_2O and 20 ml of strong acid were placed. Carbon monoxide was introduced from the gas buret after the apparatus was evacuated. The mixture of Cu_2O and strong acid was then stirred vigorously. The amount of absorbed CO was measured by a gas buret. Olefin or alcohol (20 mmol) was added dropwise to the copper carbonyl catalyst solution. The reaction mixture was poured over ice water. The products were extracted by n-hexane, and analyzed by GC, IR, NMR and elemental analysis. In stead of Cu_2O, Ag_2O was used to prepare silver carbonyl catalyst, and carboxylation was carried out in the same way.

3. Results and discussion

3.1. The formation of $Cu(CO)_3^+$, $Cu(CO)_4^+$ and $Ag(CO)_2^+$

Under a CO atmosphere Cu_2O and Ag_2O absorbed CO to form colorless copper(I) carbonyl and silver(I) carbonyl cations in H_2SO_4, $BF_3 \cdot H_2O$, FSO_3H, CF_3SO_3H and HF. The amount of absorbed CO increased with decreasing temperature. The results were shown in Fig. 1 and Fig. 2. In dilute solutions of acids such as H_2SO_4, HCl, CH_3COOH, HCOOH, $HClO_4$ and H_3PO_4, $Cu(CO)^+$ is known to be comparatively stable. The formation of $Cu(CO)_3^+$ was known in 98% H_2SO_4 at 5 atm of CO [8]. The formation of $Cu(CO)_4^+$ was found in strong acids such as FSO_3H, CF_3SO_3H, $BF_3 \cdot H_2O$ and HF below −30°C. The amount of absorbed CO decreased when H_2SO_4 was added to the FSO_3H solution, and the number of coordinated CO groups decreased to 3, i.e., $Cu(CO)_3^+$ as shown in Fig. 1.

$$Cu^+ + nCO \rightarrow Cu(CO)_n^+ + Cu(CO)^+, \qquad (1)$$

$n = 3$ in H_2SO_4,

$n = 4$ in HF, $BF_3 \cdot H_2O$, FSO_3H, CF_3SO_3H,

$$Ag^+ + 2CO \rightleftharpoons Ag(CO)_2^+. \qquad (2)$$

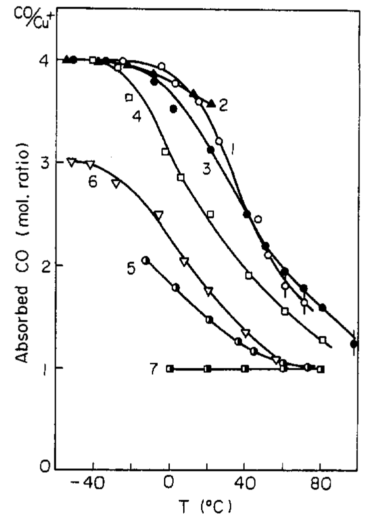


Fig. 1. Formation of $Cu(CO)_n^+$ in strong acids: (1) $BF_3 \cdot H_2O$; (2) HF; (3) FSO_3H; (4) CF_3SO_3H; (5) H_2SO_4 (98%); (6) 1.0:0.3 FSO_3H-H_2SO_4; (7) H_2SO_4 (80%), 36% HCl, 60% $HClO_4$, HCOOH, CH_3-COOH, H_3PO_4.

Among some acid solvents, the coordination number of CO to Cu^+ seems to decrease with the increase of solvation tendency of acid. On this assumption, the following order of solvation tendency can be given: $H_2SO_4 > CF_3SO_3H > FSO_3H > HF, BF_3 \cdot H_2O$. The same tendency was also observed with Ag^+. Both $Cu(CO)_3^+$ and $Cu(CO)_4^+$ are unstable and easily

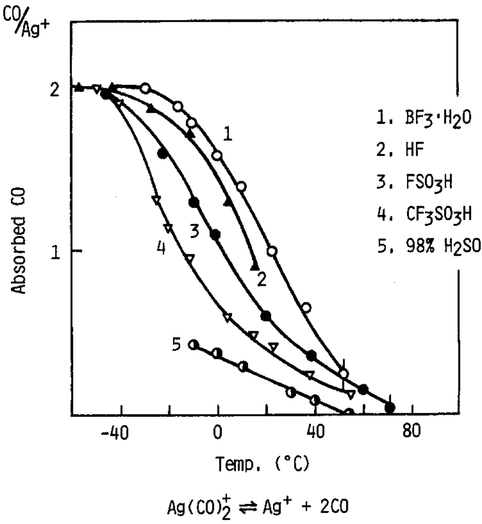


Fig. 2. Formation of $Ag(CO)_2^+$ in strong acids: (1) $BF_3 \cdot H_2O$; (2) HF; (3) FSO_3H; (4) CF_3SO_3H; (5) H_2SO_4 (98%).

release CO with the increase of temperature or decrease of acid concentration and exist in equilibrium with $Cu(CO)^+$, i.e.,

$$Cu(CO)_4^+ \rightleftharpoons Cu(CO)_3^+ + CO, \quad (3)$$

$$Cu(CO)_3^+ \rightleftharpoons Cu(CO)^+ + 2CO. \quad (4)$$

The formation of $Ag(CO)_2^+$ in H_2SO_4 at 20 atm of CO has been reported [14]. We have also observed the formation of $Ag(CO)_2^+$ in FSO_3H, CF_3SO_3H, $BF_3 \cdot H_2O$ and HF at $-30°C$ and even under atmospheric pressure of CO. $Ag(CO)_2^+$ is unstable and releases CO with increase in temperature, decomposing to Ag^+ and CO at 80°C.

In carboxylation reactions of olefin and alcohol, $Cu(CO)_3^+$, $Cu(CO)_4^+$ and $Ag(CO)_2^+$ are the active catalytic species, whereas $Cu(CO)^+$ exhibits no catalytic activity [10,11]. It seems that catalytic activity of the group IB metal carbonyl cations depends upon the ease of releasing CO.

The copper(I) carbonyl and silver carbonyl cations reported in this paper are too unstable to be isolated in the pure state. Therefore, infrared spectra and ^{13}C NMR chemical shifts were measured in acid solutions. The IR carbonyl stretching frequencies and ^{13}C NMR chemical shifts of $Cu(CO)_n^+$ and $Ag(CO)_2^+$ were shown in Table 1 comparing to those of transition metal carbonyls. The $\nu_{C=O}$ in IB metal carbonyl compounds was observed in higher wave number than in free CO or other metal carbonyl compounds. The ^{13}C-NMR chemical shifts of IB metal carbonyl compounds were observed at higher field than in other carbonyl compounds. This may be due to the shortening of C–O bond caused by the C → M dative bond. M–C bond seems to be formed mainly by σ dative bond of CO, and π-back donation is negligibly small. There is a report by Bodner that shielding of ^{13}C-NMR chemical shift is correlated with the decrease of π back-donation [16]. Among $Cu(CO)^+$, $Cu(CO)_3^+$ and $Cu(CO)_4^+$ $\nu_{C=O}$ became higher with increase in number of CO ligands.

Table 1
ν_{CO} and δ_{CO} of $Cu(CO)_n^+$ and $Ag(CO)_2^+$

M(CO)	ν_{CO} (cm^{-1})		δ_{CO} (ppm. TMS)	
	H_2SO_4	BF_3–H_2O	H_2SO_4	BF_3–H_2O
$Cu(CO)^+$	2140	2160	168.5	169.0
$Cu(CO)_3^+$	2175	-	169.2	-
$Cu(CO)_4^+$	-	2186	-	169.0
$Ag(CO)_2^+$	2186	2193	172.9	173.4
CO	2143		181.5	
$Ni(CO)_4$	2057		191.1	
$Co_2(CO)_8$	2070, 2043, 2025		203.8	

The measurements of the ^{13}C-NMR spectra of $Cu(CO)_3^+$ and $Cu(CO)_4^+$ were carried out at -30 to $-60°C$. The ^{13}C-NMR signals of $Cu(CO)_3^+$ and $Cu(CO)_4^+$ were broader than the signals of $Cu(CO)^+$ at 30°C [8]. The clear differences between the carbonyl chemical shifts for $Cu(CO)^+$, $Cu(CO)_3^+$ and $Cu(CO)_4^+$ were not found, although the high-field shifts were anticipated in $Cu(CO)_3^+$ and $Cu(CO)_4^+$ in parallel with the increase of $\nu_{C=O}$. It is assumed that the total electron density around the carbon atom does not change in these three species.

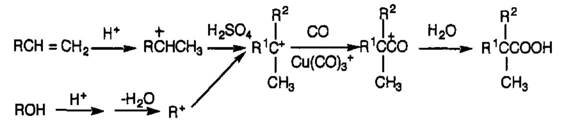
Recently Hurlburt and Strauss isolated $Ag(CO) \cdot B(OTeF_5)_4$ and $Ag(CO)_2 \cdot B(OTeF_5)_4$ by using weakly coordinating anion, and analyzed their structure by single-crystal X-ray diffraction [24–26]. According to their paper, ν_{CO} was 2189 to 2220 cm^{-1}, $\delta^{13}C$ was circa 171 ppm, and C–O bond distance (1.07–1.09 Å) of both Ag–carbonyls was shorter than gaseous CO (1.128 Å). From these results, Strauss suggested that there was little or no Ag → CO π-back bonding in these complexes, which makes them rare examples of σ-only metal carbonyls. Then, they proposed the name nonclassical metal carbonyls for these complexes. The formation of $Ag(CO)_3 \cdot Nb(OTeF_5)_6$ was also reported by Rack and Strauss [27]. The ν_{CO} of $Ag(CO)_3^+$ was 2192 cm^{-1} at 13 atm CO.

At the same time, Rack carried out precise study on CO absorption to $CuAsF_6$, and found the formation of colorless, glassy solid $Cu(CO)_2 \cdot AsF_6$ ($\nu_{CO} = 2164$), as well as $Cu(CO) \cdot AsF_6$ ($\nu_{CO} = 2170$) and $Cu(CO)_3 \cdot AsF_6$ ($\nu_{CO} = 2183$) [28].

On the other hand, Willner found Au(CO) · SO_3F ($\nu_{co} = 2196$) and $Au(CO)_2 \cdot Sb_2F_{11}$ ($\nu_{CO} = 2236$) in super acid [29,30]. These compounds were rather stable up to 130°C.

3.2. Carboxylation of olefins, alcohols, saturated hydrocarbons and aldehydes by Cu(I) and Ag carbonyl catalysts [10–12,20]

Olefins or alcohols were protonated in copper or silver carbonyl catalyst solution, and obtained alkyl carbocations rearranged to stable *tert.*-carbocations, which reacted with carbon monoxide to give *tert.*-alkanoic acids in high yield under atmospheric pressure and at room temperature. If these catalyst were not used, carboxylation required high pressure and temperature. The results are shown in Table 2.



The effect of $Cu(CO)_3^+$ in the carboxylation of 1-octene is shown in Fig. 3. Reaction rate increased about 30 times by the addition of $Cu(CO)_3^+$ catalyst.

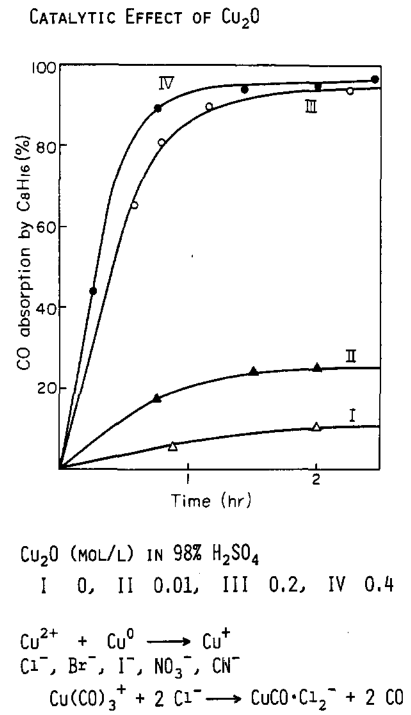


Fig. 3. Effect of Cu_2O compound. Amount of Cu_2O: (I) 0 mmol, (II) 1 mmol, (III) 2 mmol, (IV) 4 mmol 98% H_2SO_4 20 ml, 1-Octene 20 mmol, 35°C.

The effect of concentration of H_2SO_4 is shown in Table 3. With the decrease of H_2SO_4 concentration, the ratio of CO/Cu^+ decreased, and the yield of *tert.*-alkanoic acid decreased. It

Table 2
Carboxylation product of olefins and alcohols [a]

Substrate	Products	Yield (%)
1-Octene	2,2-Dimethylheptanoic acid	54
	2-Methyl-2-ethylhexanoic acid	27
	2-Methyl-2-propylpentanoic acid	13
1-Decene	2,2-Dimethylnonanoic acid	49
	2-Methyl-2-ethyloctanoic acid	24
	2-Methyl-2-peopylheptanoic acid	18
	2-Methyl-2-butylhexanoic acid	6
Cyclohexene	1-Methylcyclopentanecarboxylic acid	63
1-Pentanol	2,2-Dimethylbutanoic acid	62
1-Hexanol	2,2-Dimethylpentanoic acid	60
	2-Methyl-2-ethylbutanoic acid	25
	others	10
1-Octanol	2,2-Dimethylheptanoic acid	72
	2-Methyl-2-ethylhexanoic acid	15
	2-Methyl-2-propylpentanoic acid	5
2,5-Dimethylcyclo-hexanol	2,5-Dimethylcyclohexanecarboxylic acid	78

[a] Olefin or alcohol 5 mmol, 30°C, CO 1 atm., 98% H_2SO_4 10 ml, Cu_2O 0.286 g.

Table 3
Influence of H_2SO_4 concentration on the carboxylation of 1-octene

Concentration of H_2SO_4 (wt%)	CO/Cu^+	Yield of *tert.*-alkanoic acid (%)
100	1.45	95
95	1.33	88
90	1.20	75
85	1.07	16
80	1.00	1

is due to the decrease of active species of $Cu(CO)_3^+$ to inactive $Cu(CO)^+$ by the decrease of H_2SO_4 concentration as shown in Eq. (4).

Carboxylation proceeded in the higher concentration than 80% HF, and in the concentration of $1 < H_2O/BF_3 < 2$ in BF_3–H_2O. Products were obtained in higher yield with rapid rate with the increase of acid concentrations.

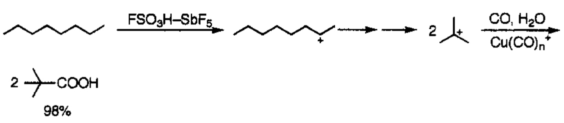
Dienes and diols also reacted with CO to give the mixture of dicarboxylic acids, monocarboxylic acids and lactones [21]. The reaction is depicted in Scheme 1. The results are shown in Table 4.

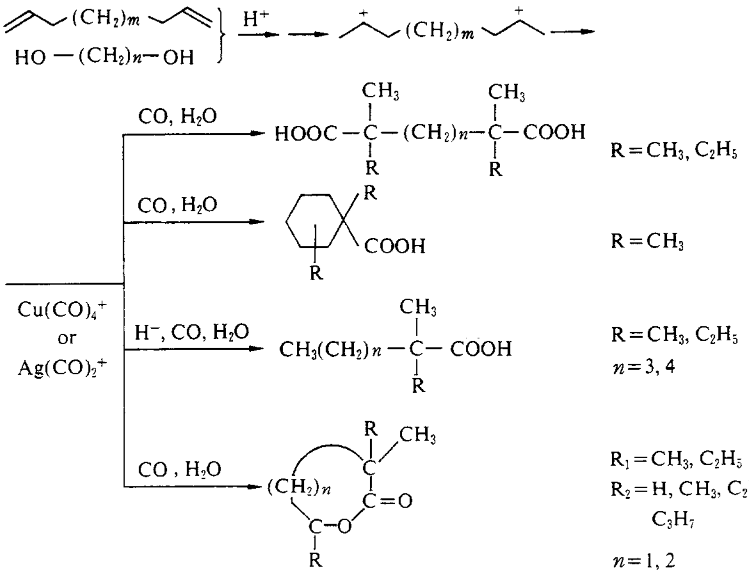
The composition of products was different by acid solvent or carbon number of substrate. Lactones (5 or 6 membered ring) were always obtained, and dicarboxylic acid was obtained from substrates having higher carbon number than 10. Carboxylation became easier by the addition of FSO_3H due to the easier protonation and dehydration of diol.

Glycolic acid was obtained by the carboxylation of formaldehyde in copper carbonyl catalyst solution under atmospheric pressure [22].

$$HCHO \xrightarrow{H^+} H_2\overset{+}{C} - OH \xrightarrow[Cu(CO)_n^+]{CO,ROH} \underset{99\%}{HOCH_2COOR}$$

Saturated hydrocarbons underwent hydride abstract in super strong acid such as FSO_3H–SbF_5 or HF–SbF_5 to give carbocation, and *tert.*-alkanoic acid was obtained by the existence of copper carbonyl catalyst [23]. The characteristics of the carboxylation in super strong acid is the cleavage of C–C bond.





Scheme 1. Reaction scheme.

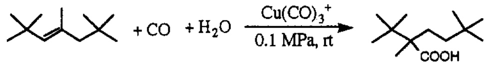
Table 4
Carboxylation of dienes and diols [a]

Substrate	Catalyst	Temp. (°C)	Product	Yield (%)
1,5-Hexadiene	Cu(CO)$_3^+$–H_2SO_4	0–5	2-Ethyl-4-pentanolide	46
1,8-Octanediol		20–30	2,2-Dimethyl-4-heptanolide	35
			2,2-Dimethyl-5-heptanolide	40
			2-Methyl-2-etyl-4-octanolide	20
1,9-Decadiene	Cu(CO)$_3^+$–H_2SO_4	5–10	2-Methyl-2-etyl-5-octanolide	15
			2,2,7,7-Tetramethyloctanedioic acid	45
			2-Ethyl-2,6,6-trimethylheptanedioic acid	10
			1,4-and 1,5-Lactone	50
1,12-Dodecanediol	Cu(CO)$_3^+$–H_2SO_4	20	2,2,9,9-Tetraethyldecanedioic acid	38
			2-Ethyl-2,8,8-trimethylnonanedioic acid	9

[a] 98% H_2SO_4 30 ml, Cu_2O 1.144 g, diene or diol 30 mmol.

3.3. Industrial application [17–19]

The synthesis of highly branched alkanoic acids was carried out by using butene dimers and butene trimers. The derivatives of highly branched alkanoic acids are strong for hydrolysis because of two big protecting alkyl group of α-position for carboxyl group.



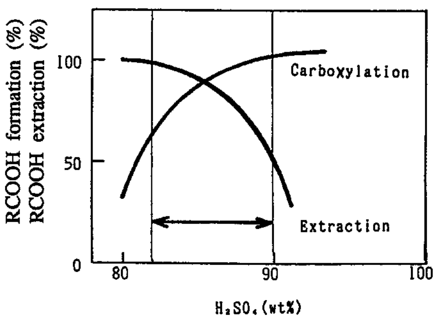


Fig. 4. Carboxylation and extraction on H_2SO_4 concentration. Starting material: triisobutylene.

With the increase of sulfuric acid, the yield of carboxylation increased and the yield of extraction decreased as shown in Fig. 4. Therefore, the concentration of sulfuric acid must be kept between 85–93 wt% to carry out recycle use of catalyst solution.

However, side products were accumulated and an activity of catalyst decreased during the recycle use of catalyst. The addition of phosphoric acid solved the deactivation of catalyst. The development of H_2SO_4 (65.1 wt%)–H_3PO_4 (28.4 wt%)–H_2O (6.5 wt%) made possible the recycle use of catalyst 100 times. More than 20 kg of *tert.*-tridecanoic acids were obtained from 1 kg of catalyst solution.

The usages of this hindered alkanoic acid are paint, microgel, surfactant, stabilizer, initiator of polymerization and agricultural chemicals.

Table 5
Production of *tert.*-Alkanoic Acids from Butene Trimers in Cu(CO)$_n^+$–H_2SO_4–H_3PO_4–H_2O system

Cat. recycle(runs)	1	10	20	30	40	50	60	70	80	90	100
RCOOH recovery (mol%)	88	113	118	105	103	104	87	100	97	91	89
Composition											
C_{13} acids (wt%)	90	82	81	81	80	80	70	81	81	82	78
C_{5-9} acids (wt%)	9	17	17	16	17	17	14	15	16	15	16
Sulfur in the product (ppm)	95	210	240	280	320	450	200	410	480	690	1000

CO 1.6 MPa, 15°C, Butene Trimers 77.2 g (each time), Cu_2O 13.2 g, H_2SO_4–H_3PO_4–H_2O 540 g, Product was extracted by 200 ml of n-hexane.

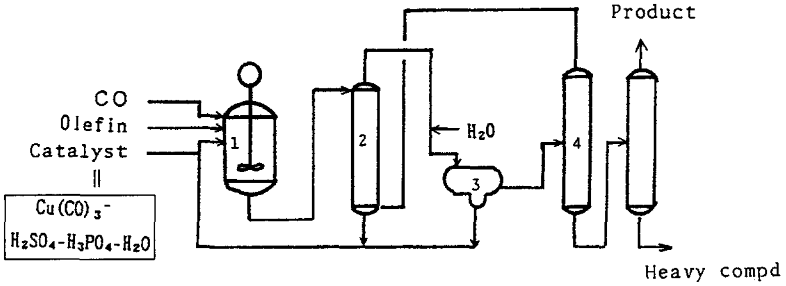


Fig. 5. Flow-sheet of *tert.*-alkanoic acid production. (1) Reactor; (2) Extractor; (3) Separator; (4) Distilling column. Reactants: Butene Trimers, CO 1.6 MPa, 15°C.

The composition of product in the recycle use of catalyst was shown in Table 5. The flow-sheet of *tert.*-alkanoic acids production is shown in Fig. 5.

References

[1] W. Manchot and J.N. Friend, Justus Liebigs Ann. Chem., 359 (1908) 100.
[2] A.F. Scott, L.L. Wilkening and B. Burin, Inorg. Chem., 8 (1969) 2533.
[3] F.A. Cotton and T.J. Marks, J. Am. Chem. Soc., 92 (1970) 5114.
[4] M.I. Bruce and A.P.P. Ostazewski, J. Chem. Soc., Chem. Commun., (1972) 1124.
[5] M.I. Bruce and A.P.P. Ostazewski, J. Chem. Soc., Dalton Trans., (1973) 2433.
[6] M.I. Bruce, J. Organomet. Chem., 44 (1972) 209.
[7] T. Tsuda, H. Habu, S. Horiguchi and T. Saegusa, J. Am. Chem. Soc., 96 (1974) 5930.
[8] Y. Souma and H. Sano, Nippon Kagaku Zasshi, 91 (1970) 625; Y. Souma, J. Iyoda and H. Sano, Inorg. Chem., 15 (1976) 968.
[9] Y. Matsushima, T. Kitamura and S. Wada, Chem. Lett., (1973) 433.
[10] Y. Souma and H. Sano, J. Org. Chem., 38 (1973) 2016.
[11] Y. Souma and H. Sano, Bull. Chem. Soc. Jpn., 46 (1973) 3237.
[12] Y. Souma and H. Sano, J. Org. Chem., 38 (1973) 3633.
[13] W. Manchot and J. Konig, Ber. Dtsch. Chem. Ges., 60 (1927) 2183.
[14] Y. Souma and H. Sano, Chem. Lett., (1973) 1059.
[15] Y. Souma and H. Sano, Bull. Chem. Soc. Jpn., 47 (1974) 1717.
[16] G.M. Bodner and L.J. Todd, Inorg. Chem., 13 (1974) 1335.
[17] H. Kawasaki, T. Kato, S. Imada, H. Miwa and T. Yamada, Sekiyu Gakkaishi, 37(3) (1994) 255.
[18] H. Kawasaki, T. Kato and T. Yamada, Sekiyu Gakkaishi, 37(4) (1994) 441.
[19] H. Kawasaki, T. Kato and T. Yamada, Sekiyu Gakkaishi, 37(3) (1994) 261.
[20] Y. Souma, H. Sano, H. Miwa, H. Kawasaki and O. Ichkawa, J. Syn. Org. Chem., 48 (1990) 92.
[21] Y. Souma, H. Sano and J. Iyoda, Bull. Chem. Soc. Jpn., 49 (1976) 3291.
[22] Y. Souma and H. Sano, Catalyst, 23 (1981) 48.
[23] Y. Souma, H. Sano and J. Iyoda, Bull. Chem. Soc. Jpn., 49 (1976) 3335.
[24] P.K. Hurlburt and S.H. Strauss, J. Am. Chem. Soc., 113 (1978) 6277.
[25] P.K. Hurlburt, J.J. Rack, Steven F. Dec, Orer P. Anderson and Steven H. Strauss, Inorg. Chem., 32 (1993) 373.
[26] P.K. Hurlburt, J.J. Rack, J.S. Luck, S.F. Dec, J.D. Webb, O.P. Anderson and S.H. Strauss, J. Am. Chem. Soc., 116 (1994) 10003.
[27] J.J. Rack, B. Moasser, J.D. Gargulak, W.L. Gladfelter, H.D. Hochheimer and S.H. Strauss, J. Chem. Soc., Chem. Commun., (1994) 685.
[28] J.J. Rack, J.D. Webb and S.H. Strauss, Inorg. Chem. 35 (1996) 277.
[29] H. Willner, J. Schaebs, G. Hwang, F. Mistry, R. Jones, J. Trotter and F. Aubke, J. Am. Chem. Soc., 114 (1992) 8972.
[30] H. Willner and F. Aubke, Inorg. Chem., 29 (1990) 2195.