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Metal carbonyl cations: generation, characterization and catalytic application

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Abstract

There has been a rapid development in the study of metal carbonyl cations, which exhibit distinguishing characteristics in comparison with typical metal carbonyl complexes. This review article gives an overview of the generation, spectroscopic characterization and catalytic application of this new class of metal carbonyls, including the metal carbonyl cluster cations. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Carbon monoxide is one of the most important and versatile ligands in transition metal chemistry [1]. Since the discovery of the first metal carbonyl complexes,

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$Pt(CO)_2Cl_2$, $Pt_2(CO)_4Cl_4$, and $Pt_2(CO)_3Cl_4$, by Schützenberger in 1868 [2–5], and the discovery of the first homoleptic metal carbonyl, $Ni(CO)_4$, by Mond in 1890 and its immediate industrial application for the preparation of ultrapure nickel [6–8], metal carbonyls have played a very important role in chemistry and the chemical industry [9,10]. Many industrial processes employ CO as a reagent and transition metal compounds as heterogeneous or homogeneous catalysts and involve the intermediates of metal carbonyls [11–15].

Carbon monoxide can bind in a terminal or multiply bridging fashion to a host of charged and uncharged metal atoms, clusters, organometallic fragments, and surfaces of metals or ionic crystals and give products ranging from diverse molecular complexes, through adsorbates, to matrix-isolated molecules. The metal–carbonyl bonding is suggested to involve a synergistic interaction between σ-donor bonding from the occupied 5σ molecular orbital of CO into an empty metal orbital with σ symmetry and π-backbonding from occupied metal orbitals into the π* molecular orbitals of CO [1].

Recently, there have been remarkable developments in the more than 100 years-old chemistry of metal carbonyls [16,17]. A number of highly-reduced metal carbonyl anions (carbonylmetalates) containing metals in negative formal oxidation states have been obtained through chemical reduction in basic solvents [18–20]. An increasing number of new homoleptic metal carbonyl cations and their derivatives, in which the CO ligand primarily functions as a σ donor, have been prepared in acidic or superacidic media or with weakly coordinating anions [21–28]. In addition, our knowledge of relatively stable neutral carbonyl complexes has also been remarkably enriched and the expectation of further developments in metal carbonyl chemistry have been made by the synthesis of the first metalloidal and alkaline earth metal carbonyls, $[Cp^*_2Si(CO)]$($Cp^* = C_5Me_5$) [29] and $[Cp^*_2Ca(CO)]$ [30], respectively, in solution and by the isolation and X-ray structural characterization of the first f-block metal carbonyl complex, $[(C_5Me_4H)_3U(CO)]$ [31,32], all of which include the important ligand pentamethylcyclopentadienyl or its derivatives [33,34].

In this review, we focus on the generation, spectroscopic characterization and catalytic application of the homoleptic carbonyl cations and cationic carbonyl derivatives of metals from Groups 6 through 12 in formal oxidation states ranging from +1 to +6, which are characterized by high CO stretching frequencies, ν(CO). Related cationic metal carbonyl species isolated in rare-gas matrices, CO adducts to metal oxides and halides and metal-exchanged zeolites will be described. Much attention will be paid to the new homoleptic metal carbonyl cluster cations, of which the number is still limited to three but expected to increase. The discussion will also include the metal hydridocarbonyl (cluster) cations formed by the protonation of neutral metal carbonyl (cluster) complexes with the metal atoms kept in the formal oxidation state 0, which exhibit properties related to the metal carbonyl (cluster) cations in which the metal atoms are in the formal oxidation states $\geq +1$.

2. Generation and characterization of metal carbonyl cations

2.1. Mononuclear metal carbonyl cations and related species

2.1.1. Historical perspective

It is indeed interesting that *cis*-$Pt(CO)_2Cl_2$, the first metal carbonyl discovered 130 years ago [2–5], is now, because of its high ν(CO) ($\nu(CO)_{av} = 2165$ cm^{-1}) [35–39], considered to be a member of the new class of metal carbonyls, in which the CO ligand functions primarily as a σ donor. This new class, i.e. the metal carbonyl cations and their cationic derivatives, remains a small group (~1%) in the metal carbonyl family, but is increasing in number and importance.

Historically, Manchot and co-workers are the first to systematically investigate the metal carbonyl compounds that were later shown to be primarily σ-bonded. During the beginning of the last century, they repeated the synthesis of the platinum carbonyl chlorides first described by Schützenberger [40]. In addition they discovered the first carbonyl derivative of palladium with the composition $Pd(CO)Cl_2$ [41], and the first carbonyl derivative of gold, Au(CO)Cl [42]. The first use was made by them of a strong protic acid (concentrated H_2SO_4) in the attempted preparation of silver carbonyl cations [43,44], which is the prototype for the recent syntheses of metal carbonyl cations. Most of the above noble metal carbonyl species are now considered to be primarily σ-bonded.

In the 1950–1960s, there appeared examples of cationic transition metal carbonyl species exhibiting ν(CO) values higher than 2143 cm^{-1}, the value for free CO. They involve, for example, $Cu(CF_3CO_2)(CO)$ (2155 cm^{-1}) [45], $[Pt(CO)Cl_2]_2$ (2152 cm^{-1}) [46,47], $[Fe(CO)_5Cl]BCl_4$ (2210 cm^{-1}) [48], $[Fe(CO)_5Br]BCl_4$ (2200 cm^{-1}) [48], $[Fe(CO)_5NO]Cl$ (2200 cm^{-1}) [48] and $[Fe(CO)_5H]PF_6$ (2196 cm^{-1}) [48]; the high ν(CO) values were suggested to arise from the reduced amount of π-backbonding [47,49]. High ν(CO) frequencies close to 2200 cm^{-1} were also observed for CO adsorbed on the surfaces of metal oxides such as NiO [50,51] or in a series of alkali, alkaline earth and transition metal-exchanged zeolites [52], for which the polarization of the carbon monoxide molecule in the electric field was suggested to be responsible.

The first thermally stable homoleptic carbonyl cations, octahedral $[M(CO)_6]^+$ (M = Mn, Tc, Re), were isolated by Fischer, Hieber and their co-workers in 1961 [53–57]. About 30 years then passed before the isolation of the next homoleptic metal carbonyl cation, $[Au(CO)_2]^+$; its discovery resulted as an accident from the attempts to prepare the $[HCO]^+$ ion by protonation of CO in the conjugated superacid $HSO_3F–Au(SO_3F)_3$ and its isolation required the development of a new carbonylation method in Lewis superacidic media such as SbF_5 [58,59]. In SbF_5, a number of thermally stable salts of metal carbonyl cations have subsequently been isolated and characterized spectroscopically and structurally [24,28]. Several homoleptic metal carbonyl cations have been isolated using weakly coordinating anions such as $[B(OTeF_5)_4]^-$ [60–62] and $[1\text{-Et-}CB_{11}F_{11}]^-$ [63,64] in organic solvents. In the meantime, a number of metal carbonyl cations have been generated in protic acids, which are used for spectroscopic characterization and applied as catalysts for the carbonylation of olefins and other organic compounds [25,65–71]. In addition, related cationic metal carbonyl species have been formed in zeolites and on the surfaces of metal oxides and halides [72], and a new laser-ablation technique has recently been successfully employed to isolate a series of metal carbonyl cations in rare-gas matrices which have been characterized in detail by FTIR [73].

2.1.2. *Isolable and soluble metal carbonyl cations and cationic carbonyl derivatives*

Most of the homoleptic neutral metal carbonyls reported so far are obtained from metal halogenides or oxides at high temperature and high CO pressure in the presence of reducing agents such as CO, H_2, and alkali metals [1]. Only $Ni(CO)_4$ and $Fe(CO)_5$ can be directly obtained from the metals [6,74,75]. The simplest and most straightforward approach to metal carbonyl anions (carbonylmetalates) is via the reduction of neutral metal carbonyls, usually with alkali metals, whereby a CO–ligand (two-electron donor) is formally replaced by two electrons or a metal–metal bond is reductively cleaved [19,20]. Another route to carbonylmetalates is the direct reduction of metal halogenides by alkali metals in basic solvents [19,20].

In contrast to the preparation methods for neutral and anionic metal carbonyl complexes, the metal carbonyl cations and the cationic derivatives, owing to their high electrophilicity, are usually synthesized in acidic or superacidic media. The pioneering synthesis of $[M(CO)_6]^+$ (M = Mn, Tc, Re) by Fischer, Hieber and their co-workers includes halide abstraction from $M(CO)_5X$ (X = Cl, Br) with Lewis acids like $M'X_3$ (M′ = Al, Fe; X = Cl, Br) at high temperature and CO pressure [53–57]. Using the same method, the compounds $[Ir(CO)_4][AlCl_4]$ [76] and $[Rh(CO)_4][Al_2Cl_7]$ [77,78] have recently been isolated from $Ir(CO)_3Cl$ and $[Rh(CO)_2Cl]_2$, respectively.

$$M(CO)_5X + AlCl_3 + CO \xrightarrow[200\ \text{atm}\ CO]{100\ ^\circ C} [M(CO)_6][AlCl_3X]$$

$$(M = Mn,\ Tc,\ Re)$$

$$Ir(CO)_3Cl + CO + AlCl_3 \xrightarrow{150\ ^\circ C} [Ir(CO)_4][AlCl_4]$$

Below are described the respective approaches to the metal carbonyl cations (Table 1). There are, interestingly, several examples of the same metal carbonyl cation being prepared in different ways.

2.1.2.1. *In Lewis superacid SbF_5*. Willner, Aubke and co-workers have isolated a series of metal carbonyl cations with the counteranion $[Sb_2F_{11}]^-$ in the Lewis superacid SbF_5 [24]. All of the thermally stable $[Sb_2F_{11}]^-$ salts of the metal carbonyl cations can be prepared by one of the following three synthetic methods: (a) solvolysis and carbonylation, (b) reductive carbonylation, and (c) oxidative carbonylation.

The synthetic method of solvolysis and carbonylation was first employed to isolate the linear $[Au(CO)_2]^+$ [59]. Attempts to isolate $[Au(CO)_2]^+$ by removing the solvent HSO_3F and the volatile reaction products in vacuo were unsuccessful, leading only to the carbonyl gold(I) sulfate, $Au(CO)SO_3F$, since SO_3F^- is sufficiently basic to compete with CO for a coordination site on gold [58]. The solvolysis of $Au(CO)SO_3F$ in SbF_5 in the presence of CO results in the formation of the thermally stable $[Au(CO)_2][Sb_2F_{11}]$ salt [59]. This method has been successfully employed for isolating the linear $[Hg(CO)_2]^{2+}$ from $Hg(SO_3F)_2$ [109,110], the octahedral $[M(CO)_6]^+$ (M = Mn, Re) from $M(CO)_5Cl$ [99], and the square-planar $[M(CO)_4]^{2+}$ (M = Pd, Pt) from MCl_2 [99]. During the solvolysis, the oxidation state of the metal in the starting compound remains unchanged.

$$Au(SO_3F)_3 + 3CO \xrightarrow[25\ ^\circ C]{HSO_3F} [Au(CO)_2]^+ + CO_2 + S_2O_5F_2 + SO_3F^-$$

$$[Au(CO)_2]^+ + SO_3F^- \xrightarrow[80\ ^\circ C]{HSO_3F} Au(CO)SO_3F + CO$$

$$Au(CO)SO_3F + CO + 4SbF_5 \xrightarrow{SbF_5} [Au(CO)_2][Sb_2F_{11}] + Sb_2F_9SO_3F$$

In reductive carbonylation, solvolysis is accompanied by reduction of the metal salt with CO acting as a reducing agent and ligand. Using this method, the square-planar $[Pt(CO)_4]^{2+}$ and $[Pd(CO)_4]^{2+}$ [77], the octahedral $[M(CO)_6]^{2+}$ (M = Ru, Os) [89] and the octahedral $[Ir(CO)_6]^{3+}$ [92], in which the +3 oxidation state of Ir is the highest of all the homoleptic metal carbonyl cations known, have been isolated from $Pt(SO_3F)_4$, $Pd(SO_3F)_3$, $M(SO_3F)_3$ (M = Ru, Os) and IrF_6, respectively, in SbF_5. The novel complex *trans*-

Table 1
Vibrational, ^{13}C-NMR and structural data of homoleptic metal carbonyl cations and related carbonyl derivatives

Compound	$\nu(CO)_{IR}$ (cm^{-1})	$\nu(CO)_{Raman}$ (cm^{-1})	$\delta(^{13}C)$ (ppm)	$d(MC)$ (Å)	$d(CO)$ (Å)	References
$[\{Mo(CO)_4\}_2(\textit{cis}\text{-}\mu\text{-}F_2SbF_4)_3]^+$ [a]	2156, 2105, 2092, 2086	2156, 2105, 2088, 2085		2.021–2.052	1.089–1.136	[79]
$[W(CO)_6(FSbF_5)]^+$ [a]	2205, 2170, 2147, 2088, 2075, 2064	2206, 2170, 2146, 2084, 2078, 2060		1.996–2.150	1.109–1.160	[80]
$[Mn(CO)_6]^+$ [a]	2100	2185, 2128	195			[24,81]
$[Re(CO)_6]^+$ [a]	2085	2197, 2122	171	1.89–2.07 [b]	1.12–1.19 [b]	[24,82–86]
$[Fe(CO)_6]^{2+}$ [a]	2204	2241, 2220	178	1.911	1.104	[87,88]
$[Ru(CO)_6]^{2+}$ [a]	2199	2254, 2222	166			[89]
trans-$[OsO_2(CO)_4]^{2+}$ [a]	2253	2280, 2269	134			[90]
$[Os(CO)_6]^{2+}$ [a]	2190	2259, 2218	147			[89]
$Co(CO)_4(L)^+$ [c]	2155, 2139, 2122	2195, 2156, 2141, 2128	186			[68]
$[Rh(CO)_5Cl]^{2+}$ [a]	2273, 2240	2272, 2240		1.999–2.032	1.087–1.107	[91]
$[Rh(CO)_4]^+$ [d]	2138	2215, 2176	172 [e]	1.947–1.958	1.109–1.124	[63,67,68,77]
$[Ir(CO)_6]^{3+}$ [a]	2254	2295, 2276	121			[92]
$[Ir(CO)_5Cl]^{2+}$ [a]	2279, 2227	2279, 2228		2.00–2.05	1.07–1.12	[91,92]
mer-$Ir(CO)_3(SO_3F)_3$	2249, 2208, 2198	2249, 2206, 2196		1.937–2.006	1.094–1.114	[93]
fac-$Ir(CO)_3F_3$ [f]	2213, 2165		131	2.03 [g]		[94,95]
$[Ir(CO)_4]^+$ [h]	2125	2216, 2170				[76]
$[Pd(CO)_4]^{2+}$ [a]	2249	2278, 2263	144	1.984–2.006	1.100–1.111	[77,96]
cis-$Pd(CO)_2(SO_3F)_2$	2228, 2208	2228, 2207	145	1.919, 1.945	1.102, 1.114	[24,97,98]
$[\textit{c}\text{-}Pd_2(\mu\text{-}CO)_2]^{2+}$ [a]	2006	2048				[99]
$[\textit{c}\text{-}Pd_2(\mu\text{-}CO)_2](SO_3F)_2$	1977	2027	162 [e]	1.966, 1.984	1.133	[24,100]
$[Pt(CO)_4]^{2+}$ [a]	2244	2289, 2267	137	1.979–1.987	1.086–1.118	[77,96,101]
cis-$Pt(CO)_2(SO_3F)_2$	2219, 2185	2218, 2181	131	1.868, 1.897	1.103, 1.130	[24,39,97]
$[(dfepe)Pt(CO)_2]^{2+}$ [e]	2235, 2222		153 [i]			[102]
cis-$Pt(CO)_2Cl_2$	2190, 2152	2189, 2146	152 [j]	1.893, 1.901	1.121, 1.110	[37–39]
$[\{Pt(CO)_3\}_2]^{2+}$ [k]	2218, 2187, 2174	2233, 2209, 2219, 2194, 2173	166, 159	1.960 [g]		[69,70]
$[Cu(CO)_4]^+$ [d]	2184	2181 [e]	171 [e]	1.961–1.968	1.109–1.114	[64,103,104]
$Cu(CO)_2(N(SO_2CF_3)_2)$	2184, 2158			1.895, 1.906	1.130, 1.115	[105]
$[Ag(CO)_2]^+$	2196 [l]	2220 [l]	172 [m]	2.06–2.20 [n]	1.07–1.09 [n]	[61,62]
$[Ag(CO)]^+$	2204 [l]	2206 [l]	171 [m]	2.10 [n]	1.077 [n]	[60,62]
$[Au(CO)_2]^{2+}$ [a]	2217	2254	174 [e]	1.962–1.982 [o]	1.107–1.153 [o]	[59,106]
$Au(CO)SO_3F$	2195	2198	162 [e]			[58,59]
$Au(CO)Cl$	2162 [j]	2183	172 [j]	1.93	1.11	[35,107,108]
$[Hg(CO)_2]^{2+}$ [a]	2278	2281	169	2.083	1.104	[109,110]
$[\{Hg(CO)_2\}_2]^{2+}$ [a]	2247	2248	189			[109,110]
$W(CO)_6$	1977	2115, 1998	192	2.058 [p]	1.148 [p]	[111–113]
CO [q]	2143		184		1.128	[59,108,114,115]
$CO^+(X^2\Sigma^+)$ [q]	2184				1.115	[115]
$[HCO]^+$ [q]	2184		140 [r]		1.107	[116–118]

[a] As salt of $[Sb_2F_{11}]^-$.
[b] As salt of $[Re_2F_{11}]^-$.
[c] In $HSO_3F \cdot SbF_5$ (1:1).
[d] As salt of $[1\text{-}Et\text{-}CB_{11}F_{11}]^-$.
[e] In HSO_3F.
[f] In HF solution.
[g] EXAFS data.
[h] As salt of $[AlCl_4]^-$.
[i] In SbF_5.
[j] In CH_2Cl_2.
[k] In concentrated H_2SO_4.
[l] As salt of $[Nb(OTeF_5)_6]^-$.
[m] As salt of $[Zn(OTeF_5)_4]^{2-}$.
[n] As salt of $[B(OTeF_5)_4]^-$.
[o] As salt of $[SbF_6]^- \cdot [Sb_2F_{11}]^-$.
[p] Electron diffraction data.
[q] Gas phase.
[r] In $HF \cdot SbF_5$ (1:1).

$[OsO_2(CO)_4]^{2+}$, in which the +6 oxidation state of Os is the highest in all the metal carbonyl cations known, is formed from OsO_4 in SbF_5 [90]. The alternative simplified synthetic route to $[Au(CO)_2][Sb_2F_{11}]$ is the direct reductive carbonylation of $Au(SO_3F)_3$ or $AuCl_3$ in SbF_5 [99].

$$2M(SO_3F)_3 + 16SbF_5 + 13CO \xrightarrow[1\ \text{atm CO},\ 60\text{–}90\ °C]{SbF_5} 2[M(CO)_6][Sb_2F_{11}]_2 + CO_2 + S_2O_5F_2 + 4Sb_2F_9(SO_3F)$$

(M = Ru or Os)

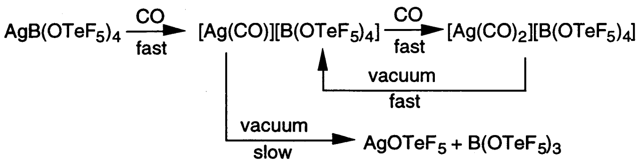
$$Au(SO_3F)_3 + 3CO + 4SbF_5 \xrightarrow[1\ \text{atm CO},\ 65\ °C]{SbF_5} [Au(CO)_2][Sb_2F_{11}] + CO_2 + S_2O_5F_2 + Sb_2F_9(SO_3F)$$

Two types of oxidative carbonylations have been reported for preparing metal carbonyl cations from neutral metal carbonyl derivatives. As the first type, the octahedral $[Fe(CO)_6]^{2+}$ has been isolated from SbF_5 with different external oxidizing agents of Cl_2, AsF_5, and XeF_2, respectively [87,88]. As the second type, SbF_5 serves simultaneously as an oxidizing agent and reaction medium in the transformation of $Mn_2(CO)_{10}$, $W(CO)_6$, $Mo(CO)_6$, $[Rh(CO)_2Cl]_2$ and $[Ir(CO)_3Cl]$ with CO into $[Mn(CO)_6][Sb_2F_{11}]$ [24], $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ [80], $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$ [79], $[Rh(CO)_5Cl][Sb_2F_{11}]_2$ [91] and $[Ir(CO)_5Cl][Sb_2F_{11}]_2$ [91], respectively.

$$Fe(CO)_5 + XeF_2 + CO + 4SbF_5 \xrightarrow[50\ °C,\ 1\ \text{atm CO}]{HF\text{–}SbF_5} [Fe(CO)_6][Sb_2F_{11}]_2 + Xe$$

$$6W(CO)_6 + 29SbF_5 \xrightarrow[40\ °C,\ 2\ \text{atm CO}]{HF\text{–}SbF_5} 6[W(CO)_6(FSbF_5)][Sb_2F_{11}] + 6SbF_3 \cdot 5SbF_5$$

2.1.2.2. CO addition to metal salts with weakly coordinating anions. Another route to metal carbonyl cations is the reversible CO addition to coordinatively unsaturated metal salts with bulky weakly coordinating anions [119] under a CO atmosphere. Strauss and co-workers have isolated the $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ cations by the direct but reversible CO addition to the silver(I) salts of $[B(OTeF_5)_4]^-$, $[Zn(OTeF_5)_4]^{2-}$, $[Nb(OTeF_5)_6]^-$, and $[Ti(OTeF_5)_6]^{2-}$ under different CO pressures; single-crystals of $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$ were obtained from the very weakly coordinating solvent 1,1,2-$C_2Cl_3F_3$, and their low temperature X-ray diffraction studies revealed nearly linear Ag–C–O arrays in both of the salts and a linear structure for $[Ag(CO)_2][B(OTeF_5)_4]$ [60–62]. The direct but reversible CO addition to metal salts with weakly coordinating anions results in the formation of $[Cu(CO)_n][AsF_6]$ (n = 1, 2, 3) [120], $[Ag(CO)_3][Nb(OTeF_5)_6]$ [121] and $[Ag(CO)_n][B(CF_3)_4]$ (n = 1–4) [122]. The exposure of $[Au(CO)_2][Sb_2F_{11}]$ to CO at a pressure as high as 100 atm leads to the reversible formation of $[Au(CO)_3][Sb_2F_{11}]$ [123].



Another weakly coordinating anion $[1\text{-Et-CB}_{11}F_{11}]^-$ has been used to prepare the tetrahedral $[Cu(CO)_4]^+$ [64] and square-planar $[Rh(CO)_4]^+$ [63] cations; the synthesis involves the metathesis reaction of $Ag[1\text{-Et-CB}_{11}F_{11}]$ with CuCl or $[Rh(CO)_2Cl]_2$ and subsequent CO addition under a CO atmosphere. Furthermore, $Cu(CO)_2(N(SO_2CF_3)_2)$ is formed by treating a CH_2Cl_2 solution of mesitylcopper(I) and $HN(SO_2CF_3)_2$ with 1.3 atm of CO at 0 °C; placing this complex under vacuum or at high pressure results in the formation of $Cu(CO)(N(SO_2CF_3)_2)$ or $Cu(CO)_3(N(SO_2CF_3)_2)$ [105]. As a related example, the metathesis followed by CO addition with the appropriate metal complexes has been used to prepare the $[HB(3,5\text{-}(CF_3)_2Pz)_3]M(CO)$ (M = Cu, Ag, Au) complexes [124–126].

$$[Rh(CO)_2Cl]_2 + 2Ag[1\text{-Et-CB}_{11}F_{11}] + 4CO \xrightarrow[-2AgCl]{CH_2Cl_2} 2[Rh(CO)_4][1\text{-Et-CB}_{11}F_{11}]$$

2.1.2.3. In protic acids. Protic acids have been used to generate a number of metal carbonyl cations and cationic carbonyl derivatives as well as molecular adducts of CO to metal cations, as first done by Manchot and co-workers in 1920s [43,44]. The reactions can also be divided to three types: (a) solvolysis and carbonylation, (b) reductive carbonylation, and (c) oxidative carbonylation. The two protic superacids HSO_3F and anhydrous hydrogen fluoride HF are very suited for the preparation of metal carbonyl fluorosulfates and fluorides, which include $Au(CO)SO_3F$ [58], $cis\text{-}Pd(CO)_2(SO_3F)_2$ [97,98], $cis\text{-}Pt(CO)_2(SO_3F)_2$ [39,97], $mer\text{-}Ir(CO)_3(SO_3F)_3$ [93], $[cyclo\text{-}Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ [100] and $fac\text{-}Ir(CO)_3F_3$ [94,95]. In particular, a number of solvated cationic metal carbonyl complexes (for sake of brevity, solvated cations that should exist in the form of $[M(CO)_n(L)_m]^{a+}$ (L denotes the weakly coordinating ligand probably being the conjugate base of the solvent acid or a closely related species) will be simply formulated as $M(CO)_n^{a+}$), including $Cu(CO)_n^+$ (n = 1–4) [103,127], $Ag(CO)_n^+$ (n = 1–3) [103,127], $Au(CO)_n^+$ (n = 1, 2) [58,65], $Co(CO)_4^+$ [68], $[Rh(CO)_4]^+$ [67,68], $[Pt(CO)_4]^{2+}$ [101], $[cyclo\text{-}Pd_2(\mu\text{-}CO)_2]^{2+}$ [66] and $[\{Pt(CO)_3\}_2]^{2+}$ [69–71], are formed in protic acids, most of which exhibit catalytic activities for the carbonylation of organic compounds (vide infra). $[Pt(dfepe)(CO)(SO_3F)]^+$ (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$), $[Pt(dfepe)(CO)(CF_3SO_3)]^+$, $[Pt(dfepe)(CO)(CH_3)]^+$ and $[Pt(dfepe)(CO)_2]^{2+}$ are observed in FSO_3H and CF_3SO_3H solutions, respectively [102].

It was known that a number of copper(I) compounds absorb carbon monoxide with the CO/Cu stoichiometric ratio ≤ 1.0 to form Cu(CO)X under various conditions [128–134]. Souma et al. previously reported the formation of $Cu(CO)_4^+$, $Cu(CO)_3^+$ and $Cu(CO)^+$ from Cu_2O, which are in equilibrium in strong acids such as H_2SO_4, CF_3SO_3H, HSO_3F, HF and $BF_3 \cdot H_2O$, while $Cu(CO)_2^+$ was not considered [103]. Recent re-examination [127] of this system shows that Cu_2O or Cu reacts with CO in the above protic acids to form the solvated cations of $Cu(CO)_n^+$ ($n = 1$–4), which are in equilibrium in the strong acids. The IR and Raman spectra show that $Cu(CO)_2^+$ is bent (C_{2v}) and $Cu(CO)_3^+$ is non-planar (C_{3v}), and therefore, Cu^+ seems to assume a tetrahedral coordination geometry, in which the coordination sites unoccupied by CO ligands are occupied by the solvent molecules, in contrast to the formation of the two-coordinate, linear structure ($D_{\infty h}$) for $[Cu(CO)_2]^+$ and the three-coordinate, trigonal-planar structure (D_{3h}) for $[Cu(CO)_3]^+$ in solid $[Cu(CO)_n][AsF_6]$ ($n = 2$, 3) [120] and in the rare-gas matrices [135]. The monocarbonyl $Cu(CO)^+$ is more stable than $Cu(CO)_2^+$ and $Cu(CO)_3^+$ in concentrated H_2SO_4 solution; the unstable polycarbonyls readily release CO ligands to form $Cu(CO)^+$ upon brief evacuation, but $Cu(CO)^+$ survives even after a continuous evacuation over 24 h. It seems that the stability of the Cu(I) carbonyls increases with increasing acidity of the solvent acid. Note that the lower stability was observed in solid than in solution as the solid $[Cu(CO)][AsF_6]$ releases CO to form $CuAsF_6$ at 0 Torr CO [120], while $[AsF_6]^-$ is less nucleophilic than the above acid solutions.

$$Cu_2O \rightarrow Cu^+ \xrightarrow{+CO} Cu(CO)^+ \underset{-CO}{\overset{+CO}{\rightleftarrows}} Cu(CO)_2^+ \underset{-CO}{\overset{+CO}{\rightleftarrows}} Cu(CO)_3^+ \underset{-CO}{\overset{+CO}{\rightleftarrows}} [Cu(CO)_4]^+$$

Manchot et al. first reported that Ag_2SO_4 reversibly absorbed CO in concentrated H_2SO_4 [43,44]. A CO/Ag stoichiometric ratio of 0.5 was achieved at 0 °C and 1 atm of CO. Souma et al. reported that Ag_2O in neat HSO_3F, $BF_3 \cdot H_2O$, and other strong acids absorbed up to 2 equivalents CO per equivalent Ag, the exact stoichiometry being dependent on temperature and pressure; only the dicarbonyl $Ag(CO)_2^+$ was considered in the strong acids [103]. Recent re-examination [127] shows that in concentrated H_2SO_4 only solvated $Ag(CO)^+$ is formed, which is, similarly to $Ag(CO)^+$ in solid salts with weakly coordinating anions [60–62], unstable with the loss of CO ligands under vacuum in contrast with the high stability of $Cu(CO)^+$ in the strong acids. In HSO_3F, only $Ag(CO)^+$ is formed at room temperature, but at low temperatures, further absorption of CO leads to the formation of $Ag(CO)_2^+$, which is in equilibrium with $Ag(CO)^+$. At temperatures down to −80 °C, a small amount of $Ag(CO)_3^+$ is formed. A small amount of $Ag(CO)_3^+$ is formed in magic acid, $HSO_3F \cdot SbF_5$, even at room temperature and atmospheric CO pressure, which is in equilibrium with $Ag(CO)_2^+$. The IR and Raman data indicate a linear structure ($D_{\infty h}$) for $Ag(CO)_2^+$, as observed for solid $[Ag(CO)_2][B(OTeF_5)_4]$ [62].

$$Ag_2O \rightarrow Ag^+ \underset{-CO}{\overset{+CO}{\rightleftarrows}} Ag(CO)^+ \underset{-CO}{\overset{+CO}{\rightleftarrows}} Ag(CO)_2^+ \underset{-CO}{\overset{+CO}{\rightleftarrows}} Ag(CO)_3^+$$

In addition to the formation of $Au(CO)_2^+$ in HSO_3F [58], we recently reported a facile synthetic method of gold(I) carbonyls suitable for the catalytic carbonylation of olefins and alcohols; the direct reductive carbonylation of gold(III) oxide, Au_2O_3, with CO leads to the formation of $Au(CO)_n^+$ ($n = 1$, 2), which are in equilibrium in concentrated H_2SO_4 solution [65]. Raman and IR studies have shown a linear coordination ($D_{\infty h}$) for $Au(CO)_2^+$, as observed for $[Au(CO)_2][Sb_2F_{11}]$ [59]. $Au(CO)^+$ is more stable than $Au(CO)_2^+$; the unstable $Au(CO)_2^+$ readily releases one CO ligand to form $Au(CO)^+$ upon brief evacuation, while $Au(CO)^+$ remains unchanged even after a continuous evacuation over 24 h. Alternative routes to the formation of the gold(I) carbonyl cations in H_2SO_4 are the oxidation carbonylation of metallic Au with SO_3 as an oxidizing agent and the solvolysis and carbonylation of AuOH [65].

$$Au_2O_3 \xrightarrow{+CO} Au^+ \xrightarrow{+CO} Au(CO)^+ \underset{-CO}{\overset{+CO}{\rightleftarrows}} Au(CO)_2^+$$

A new type of oxidative carbonylation of neutral metal carbonyl derivatives has been developed in protic acids where H^+ of the reaction medium serves simultaneously as an oxidizing agent [68]. We have reported that the dissolution of $Rh_4(CO)_{12}$ in concentrated H_2SO_4, HSO_3F or magic acid ($HSO_3F \cdot SbF_5$) under a CO atmosphere leads to the formation of the square-planar Rh(I) tetracarbonyl cation, $[Rh(CO)_4]^+$, and H_2; it is an unusual example for the oxidation of Rh(0) to Rh(I) by H^+ [67,68]. The dissolution of the neutral Co carbonyl cluster, $Co_2(CO)_8$ or $Co_4(CO)_{12}$, in HSO_3F or magic acid ($HSO_3F \cdot SbF_5$) under a CO atmosphere results in the formation of the Co(I) tetracarbonyl cation, $Co(CO)_4(L)^+$, with the evolution of H_2, which has a trigonal bipyramidal structure including two axial CO ligands and two equatorial CO ligands with another coordination site in the equatorial plane occupied by a solvent ligand (L) [68]. $Co(CO)_4^+$ is stable under a CO atmosphere but extremely unstable in the absence of gaseous CO in magic acid; upon brief evacuation, it releases CO to give the Co^{2+} solution. By lowering the acidity of the solution, the stability of $Co(CO)_4^+$ is reduced; it decomposes within several hours to give the Co^{2+} solution in HSO_3F under a CO atmosphere and cannot be formed in 96% H_2SO_4.

$$Rh_4(CO)_{12} + 4CO + 4H^+ \rightarrow 4[Rh(CO)_4]^+ + 2H_2$$

$$Co_2(CO)_8 + 2H^+ \rightarrow 2Co(CO)_4^+ + H_2$$

2.1.2.4. Characteristics of the cationic metal carbonyl complexes. In general, the metal carbonyl cations and the cationic carbonyl derivatives display the following distinguishing features (see Table 1) in comparison with the typical metal carbonyls:

1) The metal carbonyl cations and the cationic carbonyl derivatives have a high electrophilicity so that they must be generated and stabilized in acidic (superacidic) media or with weakly coordinating anions as described above, or in an unusual environment such as rare-gas matrices, metal cation-exchanged zeolites and surfaces of metal oxides and halides as described below, where no strongly nucleophilic ligands compete with the CO ligands in the coordination to metal.
2) The unprecedented coordination geometries in metal carbonyl chemistry are observed for the metal carbonyl cations with the electron configurations d^8 and d^{10} with coordination numbers 4 (square-planar coordination) and 2 (linear coordination), respectively, for which the number of valence electrons (16 or 14) violates the noble gas rule, although such geometries have been exhibited by analogous complexes of ligands such as CN^- and PPh_3 [1]. However, the typical metal carbonyls almost always observe strictly the 18-electron rule (an exception is the 17e molecule $V(CO)_6$) [1].
3) As shown in Table 1, the cationic metal carbonyl complexes have M–C bond lengths d(MC) longer than those of the corresponding typical metal carbonyls and short C–O bond lengths d(CO) (usually shorter than 1.128 Å, the value for free CO [115]) with C–O stretching vibrational frequencies ν(CO) (up to 2300 cm^{-1}; for most of them higher than 2143 cm^{-1}, the value for free CO [114]) much higher than the values for the corresponding typical metal carbonyls. CO is largely σ-bonded to the metal and the metal-to-CO π-backbonding is highly reduced, whereas the π-backbonding serves to stabilize the M–CO bond for the typical metal carbonyls, especially in the presence of a low formal charge [1].
4) As shown in Table 1, the cationic complexes show ^{13}C-NMR chemical shifts (up to $\delta(^{13}C) = 121$ ppm; with only few exceptions) high field-shifted from 184 ppm, the value for free CO [59,108,136], whereas a low-field shift from 184 ppm is usually observed for typical metal carbonyls [24].
5) The cationic complexes exhibit high catalytic activity even at r.t. and atmospheric pressure as will be described later. However, reactions (for example, Roelen [137] and Reppe [138] reactions) catalyzed by the typical metal carbonyls such as $Co_2(CO)_8$ or $Ni(CO)_4$ require severe conditions of high temperature and high CO pressure [9,10].

Emphasis should be put on point (3) regarding the high ν(CO), short d(CO) and long d(MC) for the metal carbonyl cations and cationic carbonyl derivatives. As mentioned above, in the 1950–1960s, there already appeared reports of cationic transition- metal carbonyl species, and their high ν(CO) values were suggested to arise from the reduced amount of π-backbonding [45,49]. The high ν(CO) frequencies close to 2200 cm^{-1} were also observed for CO adsorbed on metal oxides or in a series of alkali, alkaline earth and transition metal-exchanged zeolites, for which the polarization of the carbon monoxide molecule in the electric field was suggested to be responsible [50–52].

When the silver(I) carbonyl cations with high ν(CO), short d(CO) and long d(MC) were discovered in the early 1990s, the name nonclassical metal carbonyl [62] was proposed by Strauss et al. for metal carbonyls with $\nu(CO) > 2143$ cm^{-1}, which were considered to contain only carbon-to-metal σ-bonding, and the metal ions cannot, for whatever reason, participate in the metal-to-carbon π-back-donation based on the existence of simple Lewis acid/base adducts such as HCO^+ (2184 cm^{-1}) [139,140], CH_3CO^+ (2295 cm^{-1}) [141], and BH_3CO (2165 cm^{-1}) [142,143]. Indeed, there have been reports on high ν(CO) shown by s-block metal–CO species such as $[Cp^*_2Ca(CO)]$ (2158 cm^{-1}) [30] in addition to the above-mentioned CO adducts to metal oxides and alkali and alkaline earth metal-exchanged zeolites [52], and by p-block metal and metalloid carbonyl species such as $AlMe_3(CO)$ (CO matrix, 2185 cm^{-1}) [144], $SiO_2(CO)$ (surface, 2158 cm^{-1}) [145], $Sn(CO)Cl_2$ (Ar matrix, 2176 cm^{-1}) [146] and $Pb(CO)Cl_2$ (Ar matrix, 2175 cm^{-1}) [146] and non-metal–CO species such as $[N(CO)_2][Sb_3F_{16}]$ (Raman: 2359, 2320 cm^{-1}) [147] and $[Cl(CO)][Sb_nF_{5n+1}]$ ($n > 2$) (2256 cm^{-1}) [148–150].

The well-known explanation for the increase in ν(CO) where σ-bonding is the dominant factor was first given by Fenske et al.; the Mulliken population analysis of approximate molecular orbitals showed that the HOMO of CO is antibonding in the interatomic region [151].

However, recent calculations by Goldmann and Krogh-Jespersen showed that the electrostatic effect upon CO is the main reason for the bond shortening and the increase in the force constant F(CO) [152]. Their ab initio electronic structure calculations on CO in the presence of a positive point charge (located on the carbon side of the bond axis) revealed that a simple Coulombic field increases the C–O stretching force constant F(CO) and decreases the bond length; electron donation from the 5σ orbital has no intrinsic positive effect on the magnitude of F(CO). Calculations conducted on several symmetrical, neutral and cationic transition metal complexes indicated that F(CO) can be quantitatively interpreted using a model which invokes only the effects of M–CO π-backbonding and an electrostatic parameter and there is no correlation between the extent of σ-bonding (as measured by the depopulation of the CO σ orbitals) and F(CO). Calculations on trigonal bipyramidal d^8 metal pentacarbonyls permitted a comparison between inequivalent ligands (axial and equatorial) which, being coordinated to the same metal center, must experience approximately the same electrostatic field. In the case of $Ru(CO)_5$, π-backbonding to the axial and equatorial carbonyls is of virtually equal magnitude, while σ-donation is much greater from the axial ligands than from the equatorial ligands. Nevertheless, the F(CO) and d(CO) values of the two ligand sets are essentially equal, confirming that the magnitude of σ-donation does not affect these parameters [152].

A modification has been made for the definition of classical and nonclassical metal carbonyls [23,26]. In the new definition, the separation of classical and nonclassical metal carbonyls is based on their position relative to the ν(CO) versus M–C curve maximum: classical, $\partial(\nu(\mathrm{CO}))/\partial(d(\mathrm{MC})) > 0$; nonclassical, $\partial(\nu(\mathrm{CO}))/\partial(d(\mathrm{MC})) < 0$. That is, by increasing the M–C distance, ν(CO) increases for classical metal carbonyls but decreases for nonclassical metal carbonyls [23]. It was pointed out that there is an indirect experimental approach to determine the position of a polycarbonyl complex relative to the curve maximum ($LM(CO)_n \rightarrow LM(CO)_{n-1}$ criterion). Thus removing a CO ligand from a classical complex should increase the π-backbonding to the remaining CO ligands which results in a decrease in ν(CO), and the reverse for a nonclassical complex. Three pairs of $[Au(CO)_3]^+/[Au(CO)_2]^+$ (2212/2217 cm^{-1}) [123], $[Ag(CO)_3]^+/[Ag(CO)_2]^+$ (2192/2198 cm^{-1}) [62,121] and $[Cu(CO)_3]^+/[Cu(CO)_2]^+$ (2183/2164 cm^{-1}) [120] were analyzed and accordingly the gold(I) and silver(I) tricarbonyl cations were regarded as nonclassical carbonyls but the copper(I) tricarbonyl cation as a classical one although its ν(CO) value is higher than 2143 cm^{-1} [23]. Theoretical studies have also been performed to demonstrate the difference between the two categories of classical and nonclassical metal carbonyls [153–156]. One approach was to monitor the effect of the two F^- ions placed 3 Å away from the metal centers of the linear dicarbonyl complexes of Rh^-, Pd^0, Cu^+, Ag^+, Au^+, Zn^{2+}, Cd^{2+}, Hg^{2+}. The C–O bond length increased in all the cases when the F^- ions were added to the metal dicarbonyl complexes; however, the same ligand-field perturbation led to a decrease in the M–C bond length (indicative of significant π-backbonding) for $[Rh(CO)_2]^-$, $[Pd(CO)_2]$, $[Cu(CO)_2]^+$ and $[Au(CO)_2]^+$, which were regarded as classical carbonyls, but to an increase in the M–C bond length for $[Ag(CO)_2]^+$, $[Zn(CO)_2]^{2+}$, $[Cd(CO)_2]^{2+}$ and $[Hg(CO)_2]^{2+}$, which were regarded as nonclassical ones [155].

There is an argument regarding the classification of classical and non-classical metal carbonyls [92]. The metal–CO bond in all metal carbonyl complexes was described by Willner and Aubke using a modified synergistic bonding model, which indicated the qualitative contributions of the σ- and π-bonding along with the oxidation states (n) of the metal atoms and the approximate wavenumber regions of the CO vibrations (ν(CO)), respectively, for (a) predominantly π-bonded, highly reduced carbonylmetalates ($n = -2, -3, -4$; $\nu(\mathrm{CO}) < 2080\ \mathrm{cm}^{-1}$), (b) typical metal carbonyls ($n = -1, 0, +1$; $2080\ \mathrm{cm}^{-1} < \nu(\mathrm{CO}) < 2180\ \mathrm{cm}^{-1}$), and (c) largely σ-bonded metal carbonyl cations ($n = +1, +2, +3$; $\nu(\mathrm{CO}) > 2180\ \mathrm{cm}^{-1}$) [24,28]. Apart from the covalent (σ- and π-) bonding contributions which were regarded as complementary, the electrostatic effects, which significantly influence the CO bond as pointed out recently by Goldmann and Krogh-Jespersen [152], were considered to cause the charges on the CO ligands. It was pointed out that interionic contacts are directed toward the O atom in carbonylmetalates and toward the C atom in carbonyl cations. C···F interionic interactions of variable strength have been reported for most of the thermally stable superelectrophilic metal carbonyl salts with $[Sb_2F_{11}]^-$ and $[SbF_6]^-$ as anions and the observed preference of the C···F over M···F interactions for fluoroantimonate(V) salts in the solid state has been supported by calculated partial atomic charges from the natural population analysis [28]. It is noted, however, that preferred M···F contacts have been reported for the metal carbonyl cations such as $[Ag(CO)_2][B(OTeF_5)_4]$ [62] and $[Rh(CO)_4][1\text{-}Et\text{-}CB_{11}F_{11}]$ [63] and have been used in the computational model for the linear metal dicarbonyls having a pair of F^- ions placed 3 Å away from the metal centers [155].

Undoubtedly, the understanding of the M–CO bonding in metal carbonyls has been significantly enriched in the past decade and is expected to be further deepened by both experimental and theoretical studies.

2.1.3. Metal carbonyl cations and metal carbonyl oxides and halides isolated in rare-gas matrices

Rare-gas matrix isolation is another efficient method for investigating metal carbonyl cations. As early matrix-isolation spectroscopic studies employed thermal evaporation techniques to produce neutral species [157–160], recent development of the laser-ablation technique has extended the rare-gas matrix-isolation infrared spectroscopy to the study of metal carbonyl cations [73]. The addition of CCl_4 as an electron trap has significant enhanced the yield, and therefore, facilitated the identification of the cations in the matrix. A recent review by Zhou et al. can be found for a comprehensive treatment of the laser-ablation rare-gas matrix-isolation FTIR studies of the homoleptic metal carbonyl cations along with the neutrals and anions [73].

So far, FTIR studies on rare-gas matrix-isolated homoleptic carbonyl cations have been reported for the early transition metals of Sc, Ti, V, Cr, Mo, Mn and Re and all the members from Groups 8 through 11 (Table 2) [135,161–174]. As seen for the first-row transition-metal monocarbonyls (see Fig. 1), the C–O stretching frequencies for the transition-metal carbonyls follow the order of cations > neutrals > anions with large separations. ν(CO) is usually lower for the early transition-metal carbonyl cations and normally higher for the late transition-metal carbonyl cations than 2143 cm^{-1}. In general, there is an increase in ν(CO) with increasing metal atomic number, which demonstrates the expected decrease in the metal-to-CO π-backbonding with the increasing second ionization potential. A 'double humped' plot of ν(CO) versus the metal atomic number was observed for the cations as observed for the neutrals [159]; some of the structure arises from the extra stability of the filled and half-filled d shell and from the electron pairing that occurs at the middle of the transition metal row. The C–O stretching frequency ν(CO) of $ScCO^+$, 1962.4 cm^{-1} in neon and 1923.5 cm^{-1} in argon [161], is the lowest for a monovalent, homoleptic terminal transition-metal carbonyl cation known so far and the ν(CO) value at 2236.8 cm^{-1} for $Au(CO)^+$ in solid neon [170] is the highest for a matrix-isolated homoleptic metal carbonyl cation.

Table 2
Infrared C–O stretching frequencies ν(CO) for homoleptic metal carbonyl cations and related species in rare-gas matrices

Cation [a]	ν(CO) [b] (cm^{-1})	References
$ScCO^+$	1962.4 (1949.9)	[161]
$Sc(CO)_2^+$	1926.0 (1922.6)	[161]
$Sc(CO)_3^+$	1974.20	[161]
$TiCO^+$	2041.3	[162]
VCO^+ [c]	2116.3	[162]
$CrCO^+$	2200.8	[73]
$MoCO^+$	2189.1	[73]
$MnCO^+$	2089.5	[163]
$ReCO^+$	2102.1	[163]
$FeCO^+$	2123.0	[164,165]
$Fe(CO)_2^+$	2134.0	[164,165]
$RuCO^+$	2134.9	[166]
$OsCO^+$	2106.0	[166]
$CoCO^+$	2165.5	[167]
$Co(CO)_2^+$	2168.9	[167]
$RhCO^+$	2174.1	[167,168]
$Rh(CO)_2^+$	2184.7	[167,168]
$Rh(CO)_3^+$	2167.8	[167,168]
$Rh(CO)_4^+$	2161.5	[167]
$IrCO^+$	2156.5	[167]
$Ir(CO)_2^+$	2153.8	[167]
$NiCO^+$	2206.5	[169]
$Ni(CO)_2^+$	2205.3 (2209.2)	[169]
$Ni(CO)_3^+$	2192.4, 2186.2	[169]
$Ni(CO)_4^+$	2176.2	[169]
$PdCO^+$	2206.4	[169]
$Pd(CO)_2^+$	2210.5	[169]
$PtCO^+$	2204.7	[169]
$Pt(CO)_2^+$	2210.3	[169]
$Pt(CO)_3^+$	2207.9	[169]
$CuCO^+$	2234.4	[135]
$CuCO^+$ [c]	2174.4	[135]
$Cu(CO)_2^+$	2230.4 (2233.1)	[135]
$Cu(CO)_3^+$	2211.3	[135]
$Cu(CO)_4^+$	2202.1	[135]
$AgCO^+$	2233.1	[170]
$Ag(CO)_2^+$	2234.6	[170]
$Ag(CO)_3^+$	2216.0	[170]
$Ag(CO)_4^+$	2205.7	[170]
$AuCO^+$	2236.8 (2238.9)	[170]
$Au(CO)_2^+$	2233.4	[170]
$Au(CO)_3^+$	2203.5	[170]
$Au(CO)_4^+$	2193.5	[170]
$Sc(CO)O^+$ [c]	2221.8 (2207.2)	[171]
$Y(CO)O^+$ [c]	2206.0 (2203.3)	[171]
$U(CO)O^+$	2073.0	[172]
$Th(CO)O^+$	2009.9	[172]
$Ti(CO)O^+$ [c]	2188.0 (2185.5)	[173]
$V(CO)O^+$ [c]	2205.4 (2203.3)	[173]
$Cr(CO)O^+$ [c]	2175.5	[174]
$Mn(CO)O^+$ [c]	2173.0 (2177.7)	[174]
CO^+	2194.3	[135]
$(CO)_2^+$	2056.3	[135]
CO	2140.8	[135]
CO [c]	2138.2	[135]

[a] In a neon matrix unless otherwise noted.
[b] Value in parenthesis for the species at a different site.
[c] In an argon matrix.

From the matrix-isolation FTIR studies also recognized is the importance of the vibrational perturbations from the medium. The ν(CO) values are 2140.8 and 2138.2 cm^{-1} for the CO molecules in solid neon and argon, respectively [135]. The ν(CO) values are 2194.3 and 2056.3 cm^{-1} for CO^+ and $(CO)_2^+$, respectively, in solid neon, whereas the CO^+ and $(CO)_2^+$ cations are not observed in solid argon as the first ionization energy of CO (14.014 eV) is close to the ionization energy of argon (15.76 eV) (for comparison, 21.56 eV for neon) [135]. For matrix-isolated species, the ν(CO) in solid argon matrices is always lower than that in solid neon. The $CuCO^+$ cation in argon red-shifts by 60 cm^{-1} relative

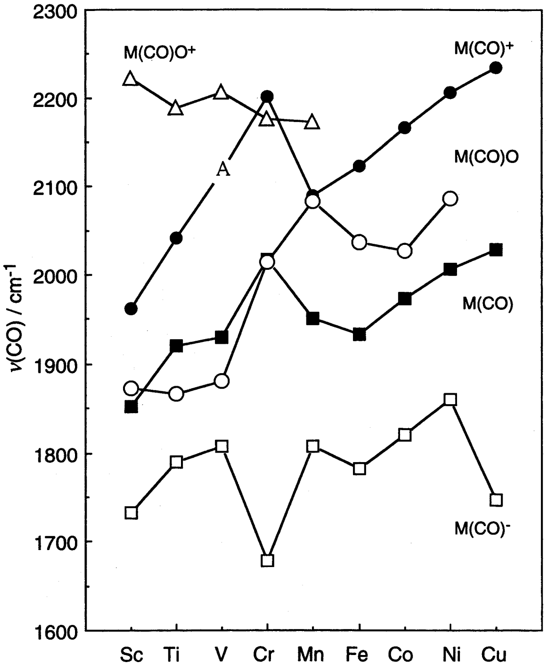


Fig. 1. Infrared C–O stretching frequencies ν(CO) for M(CO)$^+$, M(CO)O$^+$, M(CO)O, M(CO) and M(CO)$^-$ of the first-row transition metals in solid neon matrices (A denotes the argon matrix value) (Ref. [73]).

to the neon value, which suggests that CuCO$^+$ is strongly solvated in the more polarized solid argon [135]. In fact, the Ar matrix value at 2174.4 cm^{-1} for CuCO$^+$ is even a few wavenumbers lower than 2178 cm^{-1} for solid [Cu(CO)][AsF$_6$] [120]. The metal carbonyl cation is usually less perturbed by the neon matrix than by the counteranions in a solid or the counteranions and solvent molecules in solution; the neon matrix ν(CO) values for the metal carbonyl cations may be the closest to the yet-to-be-measured gas phase frequencies. As metal carbonyl cations in a solid or in solution are usually stabilized by coordination or interionic contacts with counteranions or solvent molecules, the C–O stretching frequencies, depending on the counteranions or solvent, are usually tens wavenumbers lower than the neon matrix-isolated counterparts. For example, [Rh(CO)$_4$]$^+$ with the weakly coordinating anion [1-Et-CB$_{11}$F$_{11}$]$^-$ [63] or in strong acids [68] exhibits ν(CO) at 2138–2143 cm^{-1}, in contrast to the value at 2162 cm^{-1} for the neon matrix-isolated [Rh(CO)$_4$]$^+$ cation [167]. The same applies to Cu(CO)$_n^+$ ($n = 1$–4) [120,135], Ag(CO)$_n^+$ ($n = 1$–3) [62,121,170] and Au(CO)$_n^+$ ($n = 1$, 2) [59,170] with the exception for Au(CO)$_3^+$ (2203.5 cm^{-1} in solid neon [170] vs. 2212 cm^{-1} in [Au(CO)$_3$][Sb$_2$F$_{11}$] [123]). For M(CO)$_n^+$ (M = Cu, Ag, Au) in matrices, the symmetries are $C_{\infty v}$, $D_{\infty h}$ (linear), D_{3h} (trigonal-planar) and T_d (tetrahedral) for $n = 1$, 2, 3 and 4, respectively [135,170]. There is the general tendency of a decrease in ν(CO) with increasing CO coordination number for Cu(I), Ag(I) and Au(I) carbonyl cations in solid neon matrices, which is consistent with the prediction by DFT calculations [135,170]. The silver(I) [62,121] and gold(I) [59,123] carbonyl cations with weakly coordinating anions behave similarly but the copper(I) carbonyl cations in the salt of [AsF$_6$]$^-$ (2164 and 2183 cm^{-1} for [Cu(CO)$_2$]$^+$ and [Cu(CO)$_3$]$^+$, respectively [120]) behave contrary to the corresponding cations in rare-gas matrices. Note the different trends between the copper(I) polycarbonyl cations in the different media and the difficulties in applying the LM(CO)$_n$ → LM(CO)$_{n-1}$ criterion [23,26] to real polycarbonyls.

In addition to the rare-gas matrix-isolated homoleptic metal carbonyl cations, laser-ablated early transition-metal atoms of Sc, Y, Ti, V, Cr and Mn and f-block metal atoms of U and Th react with CO$_2$ to give primarily the insertion product M(CO)O and their photoionization leads to the formation of the M(CO)O$^+$ type cations with high ν(CO) values in solid argon (Table 2) [171–174]. A theoretical study on the M$^+$–CO$_2$ and M(CO)O$^+$ systems of the first-row transition metals showed that the M$^+$OCO structure is the most favorable coordination for CO$_2$, but for early transition metals, the inserted M(CO)O$^+$ structure is more stable than the M$^+$OCO isomer due to the strong terminal MO$^+$ bond that is formed [175].

Apart from the homoleptic metal carbonyl cation M(CO)$_n^+$ and metal carbonyl oxide cations M(CO)O$^+$, related carbonyl species of metal oxides and halides have been isolated in rare-gas matrices (Table 3). A series of the carbonyl species of metal halides [39,146,176–179] in the matrices exhibit ν(CO) values much higher than 2143 cm^{-1}, reflecting the positive charge on the metal centers. On the other hand, the matrix carbonyl species of metal oxides [171–174] except for Be(CO)O (2189.5 cm^{-1}) [180] show ν(CO) values much lower than 2143 cm^{-1}; they (e.g. Ni(CO)O, 2086.6; Mn(CO)O, 2082.5; Cr(CO)O, 2014.4 cm^{-1} [174]) are much lower than those of the corresponding halides (e.g. Ni(CO)F$_2$, 2200.4; Mn(CO)F$_2$, 2183.2; Cr(CO)F$_2$, 2188.4 cm^{-1} [178]), reflecting that the effective local charge on the metal centers of the oxides is less positive than that of the halides as the halogen atoms have a higher electron affinity. It seems that the net charge on the metal center of the M(CO)O molecules is close to +1 for Mn, between 0 and +1 for Sc, Fe, Co and Ni, nearly 0 for Cr and less than 0 for Ti and V (Fig. 1). Note that the metal carbonyl oxides such as Ni(CO)O (2086.6 cm^{-1}) and Co(CO)O (2026.6 cm^{-1}) in matrices [174] show ν(CO) values lower than those of the corresponding surface species on metal oxides such as NiO (2152 cm^{-1}) [181] and CoO (2179 cm^{-1}) [182].

Table 3
Selected infrared C–O stretching frequencies ν(CO) for CO species of metal halides and oxides in argon matrices

Species	ν(CO) [a] (cm^{-1})	References
Li(CO)F	2185.1	[176]
Na(CO)F	2172.4	[176]
$Mg(CO)F_2$	2205	[176]
$Ca(CO)F_2$	2187.3, 2180.4	[176]
$Sr(CO)F_2$	2181.2, 2173.8, 2166.4	[176]
$Ba(CO)F_2$	2172.8, 2163.5, 2159.6	[176]
$Sc(CO)F_3$	2212.4, 2208.3	[176]
$Y(CO)F_3$	2197.5	[176]
$La(CO)F_3$	2185.2	[176]
$Nd(CO)F_3$	2187.4	[176]
$Gd(CO)F_3$	2194.4	[176]
$Ho(CO)F_3$	2198.2	[176]
$Lu(CO)F_3$	2204.8	[176]
$U(CO)F_4$	2181.8	[177]
$Cr(CO)F_2$	2188.4	[178]
$Mn(CO)F_2$	2183.2	[178]
$Ni(CO)F_2$	2200.4	[178]
$Ni(CO)Cl_2$	2189.2	[178]
cis-$Pt(CO)_2Cl_2$	2171.1, 2126.9	[39]
$Cu(CO)F_2$	2210.4	[178]
Cu(CO)Cl	2156.5	[179]
$Zn(CO)F_2$	2185.9	[178]
$Sn(CO)Cl_2$	2175.5	[146]
$Pb(CO)F_2$	2176.4	[146]
$Pb(CO)Cl_2$	2174.5	[146]
$Pb(CO)Br_2$	2161.2	[146]
$Pb(CO)I_2$	2149	[146]
Be(CO)O	2189.5	[180]
Sc(CO)O	1873.4	[171]
Y(CO)O	1861.5	[171]
$U(CO)O_2$ [b]	2021.6	[172]
U(CO)O [b]	1806.9	[172]
Th(CO)O [b]	1778.4, (1762.8) (1756.8)	[172]
Ti(CO)O	1866.8 (1864.4)	[173]
$Ti(CO)_2O$	2027.3, 1833.2	[173]
$V(CO)_2O_2$	2150.6, 2115.4 (2121.9) (2111.9)	[173]
V(CO)O	1881.1 (1874.3)	[173]
$V(CO)_2O$	1851.6	[173]
Cr(CO)O	2014.4	[174]
$Mn(CO)O_2$	2097.3	[174]
$Mn(CO)_2O_2$	2126.0, 2056.0	[174]
Mn(CO)O	2082.5	[163,174]
$Fe(CO)O_2$	2108.2	[174]
Fe(CO)O	2037.1	[174]
Co(CO)O	2026.6 (2018.8) (2015.3)	[174]
Ni(CO)O	2086.6 (2072.7)	[174]

[a] Value in parenthesis for the species at a different site.
[b] In a neon matrix.

Table 4
Selected infrared C–O stretching frequencies ν(CO) of M–CO species adsorbed on surfaces of metal oxides and halides

Surface	Conditions	ν(CO) (cm^{-1})	References
LiF	77 K; 100 face, low coverage	2155	[181]
NaCl	77 K; 100 face, low coverage	2159	[181]
NaI	77 K; 100 face, low coverage	2160	[181]
KCl	77 K; 100 face, low coverage	2153	[181]
CuF		2146	[182]
BeO	77 K; low coverage	2207, 2200, 2188	[145]
MgO	77K; 001 face, low coverage	2203, 2170, 2157	[183]
MgO	77 K; 100 face, low coverage	2170, 2151	[181]
CaO/Al_2O_3	300 K; 3% CaO	2182	[184]
La_2O_3	77 K	2175	[185,186]
CeO_2		~2170	[187]
TiO_2 (rutile)		2182	[187]
TiO_2 (anatase)	77 K; low coverage	2212, 2195, 2180	[145]
TiO_2/SiO_2	80 K; 7% TiO_2	2183–2178	[188]
ZrO_2		~2190	[189]
SO_4/ZrO_2		2220–2170	[189]
ZrO_2 [a]	273 K	2216	[127]
α-Cr_2O_3	77–298 K	2200–2162	[187,190]
Fe_2O_3	77 K	2165	[183]
CoO		2179	[182]
NiO	77K; 100 face, low coverage	2152	[181]
CuO/SiO_2	298 K	2136	[191]
ZnO	298 K	2212, 2200, 2187	[191]
ZnO	77 K; low coverage	2192, 2189	[145]
α-Al_2O_3	77 K; low coverage	2165, 2153	[192]
δ-Al_2O_3	77 K	2230–2184	[193]
η-Al_2O_3	77 K; low coverage	2235, 2202	[145]
SiO_2	77 K; low coverage	2158	[145]

[a] Surface of the zirconia ATR sensor of ReactIR spectrometer (ASi), washed with magic acid.

2.1.4. M–CO species adsorbed on metal oxide and halide surfaces and in metal-exchanged zeolites

There have been a large number of reports on the use of CO as a probe for investigating the structures of adsorption sites of metal oxides and halides and metal-exchanged zeolites, which are widely used as catalysts [72].

As shown in Table 4, most of the surface M–CO species exhibit ν(CO) higher than 2143 cm^{-1}. The vibrational perturbation depends on the charge at the cationic metal center and at the anions in the nearest neighbor positions and upon the electronic structure of the cation (with or without d-electrons). A vibrational spectroscopic method with CO as a probe molecule, combined with the change in adsorption coverage, has been used for investigating the structure of the adsorption sites and surface morphology of the metal oxide and halides [72]. The probe molecule adsorbed on highly coordinatively unsaturated defects (e.g. corners and edges) are usually more strongly perturbed than those adsorbed on flat faces; for example, the three ν(CO) bands for CO adsorbed on the 001 face of MgO were attributed to the corner O_3Mg-sites (2203 cm^{-1}), edge or step O_4Mg-sites (2170 cm^{-1}) and face O_5Mg-sites (2157 cm^{-1}) [183]. It is noted that M–CO surface species on metal oxides like NiO (2152 cm^{-1}) [181] and CoO (2179 cm^{-1}) [182], due to the more positive charge at the adsorption sites on the surfaces, show ν(CO) much higher than the corresponding rare-gas matrix species like Ni(CO)O (2086.6 cm^{-1}) [174] and Co(CO)O (2026.6 cm^{-1}) [174]. Another example of the CO stretching frequency as a probe for the local charge at the metal center is demonstrated by the shift to higher ν(CO) with increasing Lewis acidity of the adsorption sites by loading sulfate to ZrO_2 [189].

FTIR studies of the interaction of CO with the extraframework cations in the alkali metal-exchanged zeolites have been known for a long time and the C–O stretching frequencies have been used to evaluate the local electric-field strength with CO as the probe molecule [52,194,195]. It has been found that CO interacts with the extraframework alkali cations (M^+) of zeolites to form both M^+–CO and M^+–OC species, which are in a temperature-dependent equilibrium [196–199]. ν(CO) for the C-bonded species (e.g. in ZSM-5, H^+, 2172; Li^+, 2188; Na^+, 2178; K^+, 2166; Rb^+, 2162; Cs^+, 2157 cm^{-1}) are usually higher than 2143 cm^{-1}, whereas ν(CO) for the O-bonded species (e.g. in ZSM-5, H^+, 2115; Li^+, 2108; Na^+, 2112; K^+, 2117; Rb^+, 2119; Cs^+, 2122 cm^{-1}) are usually lower than 2143 cm^{-1} [198]. For M^+–CO species in mordenite and ZSM-5 zeolites, ν(CO) decreases continuously from Li^+ to Cs^+ samples as the ionic radius of the alkali metal increases in the order of $Li < Na < K < Rb < Cs$ [194–196,199,200]. The electrostatic field at the cation sites evaluated from the observed frequency shifts can be reproduced by the sum of the positive contribution of the cation itself, and two negative contributions, the first from the negatively charged oxygen atoms surrounding the cation and the second from the polarized zeolite framework; the last contribution increases, and therefore, ν(CO) decreases with the decreasing Si/Al ratio [194]. A similar tendency of the decrease in ν(CO) for the divalent alkaline earth metal-exchanged zeolites has also been found from Mg^{2+} to Ba^{2+} (e.g. in Y-zeolites at 77 K, Mg^{2+}, 2213; Ca^{2+}, 2197; Sr^{2+}, 2186; Ba^{2+}, 2178 cm^{-1}) [52].

High ν(CO) values have been reported for a long time for CO adsorbed in zeolites exchanged by transition metals such as Mn, Fe, Co and Ni and by post-transition metals such as Zn and Cd (e.g. in Y-zeolites, Mn^{2+}, 2208; Fe^{2+}, 2198; Co^{2+}, 2208; Ni^{2+}, 2217; Zn^{2+}, 2214; Cd^{2+}, 2209 cm^{-1}. In X-zeolites, Mn^{2+}, 2203; Co^{2+}, 2204; Ni^{2+}, 2211 cm^{-1}) [52,201]. Note that the ν(CO) values are higher than those for the corresponding metal oxides and halides in rare-gas matrices. In dealuminated Y-zeolites, a $Rh(CO)_2^+$ species with C_{2v} symmetry and an angle of ca. 106° between the two CO groups shows two IR absorptions at 2118 and 2053 cm^{-1} [202]. At low temperatures, a $Rh(CO)_3^+$ species with C_{3v} symmetry [203], showing two bands at 2119 and 2083 cm^{-1}, and a $Rh(CO)_4^+$ species with C_{2v} symmetry [203] as in *cis*-$X_2M(CO)_4$ compounds [204], showing four bands at 2151, 2135, 2124 and 2111 cm^{-1}, are formed in the presence of CO. It was reported that two reversible Rh(III)–CO species were observed in Rh-exchanged Y (2172, 2138 cm^{-1}), mordenite (2175, 2140 cm^{-1}), ZSM-34 (2188, 2140 cm^{-1}) and ZSM-11 (2184, 2150 cm^{-1}) zeolites [205]. CO adsorbed in copper-exchanged zeolites have been mostly extensively investigated by IR spectroscopy [206–211]. $Cu(CO)^+$ (2157 cm^{-1}), $Cu(CO)_2^+$ (2178, 2151 cm^{-1}) and $Cu(CO)_3^+$ (2192, 2167, 2138 cm^{-1}) have been observed in the copper(I)-exchanged ZSM-5 zeolite (also in mordenite and the Y, L and MFI zeolites) [206–211]. Note that the Cu(I) dicarbonyl and tricarbonyl are bent (C_{2v}) and non-planar (C_{3v}), respectively, in zeolites [209] as observed in the protic acids mentioned above [127], while they are linear ($D_{\infty h}$) and trigonal-planar (D_{3h}), respectively, in the solid salts of $[AsF_6]^-$ [120] and in rare-gas matrices [135]. An IR band at 2175 cm^{-1} was assigned to CO weakly interacting with Cu(II) cations in ZSM-5 [210]. Also, well-investigated is the IR spectroscopy of CO adsorbed in silver-exchanged zeolites [212–217]. $Ag(CO)^+$ is formed in the ZSM-5, Y-, and A-zeolites. In the ZSM-5 zeolite, the $Ag(CO)^+$ species, highly resistant toward evacuation even at ambient temperature, shows an IR band at 2192 cm^{-1}, higher than 2169 cm^{-1}, the value for Ag^+/SiO_2 [216]. The $Ag(CO)_2^+$ species is formed at low temperature in the presence of gaseous CO, for which one research group reported two IR bands at 2190 and 2184 cm^{-1} [217], while the two reports by another research group seem confusing, one giving two bands at 2195 and 2189 cm^{-1} [215], the other one giving a single band at 2186 cm^{-1} [216]. Further investigation is required to clarify the structure of $Ag(CO)_2^+$ in zeolites.

2.2. *Metal carbonyl cluster cations*

Most of the homoleptic metal carbonyl cations known are mononuclear except for the three dinuclear complexes, [*cyclo*-$Pd_2(\mu\text{-}CO)_2]^{2+}$ [99,100], $[\{Hg(CO)\}_2]^{2+}$ [109,110], and $[\{Pt(CO)_3\}_2]^{2+}$ [69,70], which are described below.

2.2.1. *The dinuclear palladium(I) carbonyl cation, [cyclo-$Pd_2(\mu\text{-}CO)_2]^{2+}$*

An isomeric mixture of $Pd(CO)_2(SO_3F)_2$ has been prepared by the reductive carbonylation of $Pd[Pd(SO_3F)_6]$ in HSO_3F [97], which is suitable for obtaining *cis*-$Pd(CO)_2(SO_3F)_2$ [98], $[Pd(CO)_4][Sb_2F_{11}]_2$ [96], and [*cyclo*-$Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ [100]. Yellow single crystals of *cis*-$Pd(CO)_2(SO_3F)_2$ are obtained by recrystallizing the isomeric mixture of $Pd(CO)_2(SO_3F)_2$ from HSO_3F with short, intermittent heating of the solution to 60 °C [98]. The molecular structure reveals the square-planar coordination of palladium with terminal CO groups and monodentate fluorosulfates in a cis-geometry.

$$\mathrm{Pd^{II}Pd^{IV}(SO_3F)_6 + 5CO \xrightarrow[\sim 0.5\ \text{atm},\ 25\ ^\circ\text{C}]{HSO_3F} 2Pd(CO)_2(SO_3F)_2 + CO_2 + S_2O_5F_2}$$

Homoleptic palladium carbonyls were rather rare, including the CO adsorbates on palladium surfaces of the compositions PdCO and $Pd_2(CO)$ [218,219] and matrix-isolated molecules of the types $Pd(CO)_n$ with $n = 1$–4 [169,220–222]. The first isolable homoleptic palladium carbonyl, $[Pd(CO)_4]^{2+}$, was formed by the solvolysis of $Pd(CO)_2(SO_3F)_2$ in liquid SbF_5 in the presence of CO and stabilized by the very weakly nucleophilic anion $[Sb_2F_{11}]^-$ [96]. The crystalline $[Pd(CO)_4][Sb_2F_{11}]_2$ has been alternatively obtained by the direct reductive carbonylation of $Pd[Pd(SO_3F)_6]$ in HF–SbF_5 [77]. This cation is square planar with only slight angular and out-of-plane deviations from D_{4h} symmetry [77].

$$\mathrm{Pd(CO)_2(SO_3F)_2 + 8SbF_5 + 2CO \xrightarrow[\sim 0.5\ \text{atm CO},\ 60\text{–}80\ ^\circ\text{C}]{SbF_5} [Pd(CO)_4][Sb_2F_{11}]_2 + 2Sb_2F_9SO_3F}$$

The dinuclear metal carbonyl cation [*cyclo*-$Pd_2(\mu\text{-}CO)_2]^{2+}$ is obtained under the conditions close to that for obtaining *cis*-$Pd(CO)_2(SO_3F)_2$ [100]. When $Pd(CO)_2(SO_3F)_2$ is recrystallized from HSO_3F, a needle-like orange–red crystalline [*cyclo*-$Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ is formed from solution over the long period of about 3 weeks. It has been considered that the reductive elimination of SO_3F radicals, their dimerization to $S_2O_6F_2$, and the simultaneous loss of 1 mol of CO have occurred. The structure reveals planar [*cyclo*-$Pd_2(\mu\text{-}CO)_2]^{2+}$ cations formed with two symmetrically CO-bridged palladium atoms (Fig. 2), linked by bidentate-bridging fluorosulfate anions into a polymeric sheet. The cyclic [*cyclo*-$Pd_2(\mu\text{-}CO)_2]^{2+}$ cation is stabilized both by weak coordination to the fluorosulfate anions and by O···Pd and Pd···Pd interlayer contacts of 2.653 and 3.478 Å, respectively. The cross-ring Pd–Pd bond length of 2.694 Å corresponds to a single bond. The C–O distance (1.133 Å) is slightly longer than in free CO. The IR and Raman spectra indicate a D_{2h} symmetry for the molecular cation [*cyclo*-$Pd_2(\mu\text{-}CO)_2]^{2+}$ [100].

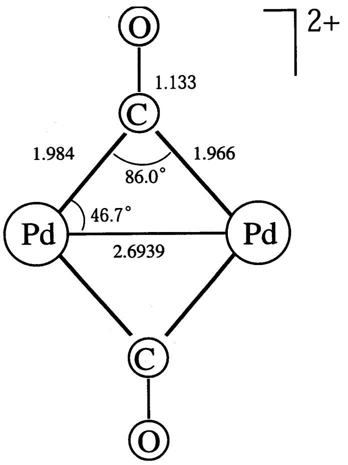


Fig. 2. Molecular structure of the [*cyclo*-$Pd_2(\mu\text{-}CO)_2]^{2+}$ cation (Ref. [100]). The bond lengths are in Å.

$$\mathrm{2Pd(CO)_2(SO_3F)_2 \xrightarrow{HSO_3F} [\mathit{cyclo}\text{-}Pd_2(\mu\text{-}CO)_2](SO_3F)_2 + 2CO + S_2O_6F_2}$$

The solvolysis of [*cyclo*-$Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ in SbF_5 results in the formation of [*cyclo*-$Pd_2(\mu\text{-}CO)_2][Sb_2F_{11}]_2$, of which the C–O stretching frequencies (IR, 2006 cm^{-1}; Raman, 2048 cm^{-1}), much higher than those of the fluorosulfate (IR, 1977 cm^{-1}; Raman, 2027 cm^{-1}), are the highest for a bidentate-bridging CO ligand in metal–carbonyl chemistry [99].

$$\mathrm{[\mathit{cyclo}\text{-}Pd_2(\mu\text{-}CO)_2](SO_3F)_2 + 8SbF_5 \xrightarrow[25\ ^\circ\text{C},\ 6\ \text{months}]{SbF_5} [\mathit{cyclo}\text{-}Pd_2(\mu\text{-}CO)_2][Sb_2F_{11}]_2 + 2Sb_2F_9SO_3F}$$

There is a precedent for the presence of the [*cyclo*-$Pd_2(\mu\text{-}CO)_2]^{2+}$ group in the acetate derivative $[Pd_4(\mu\text{-}CO)_4(\mu\text{-}O_2CCH_3)_4] \cdot 2CH_3COOH$ [223,224]. The cluster consists of two [*cyclo*-$Pd_2(\mu\text{-}CO)_2]^{2+}$ groups with symmetrically bridging CO groups and bond distances and angles very similar to those of the fluorosulfate. Some carbonyl derivatives of palladium(I), such as the $[Pd_2(\mu\text{-}CO)_2Cl_4]^{2-}$ anion, the polymeric $[Pd(CO)Cl]_n$ and $Pd_2(\mu\text{-}CO)Cl_2(Ph_2AsCH_2AsPh_2)_2$, are known [225–230]. It has been pointed out that in all of the structurally characterized palladium(I) carbonyl derivatives, only bridging CO groups are encountered [100], whereas several dinuclear Pd(I) complexes with terminal ligands of isoelectronic isocyanides have been reported [231–237]. It is interesting to note that a homoleptic, dinuclear platinum(I) carbonyl cation is formed with only terminal CO ligands in contrast (vide infra).

In concentrated H_2SO_4, the reductive carbonylation of $PdSO_4$ with CO readily leads to the formation of [*cyclo*-$Pd_2(\mu\text{-}CO)_2]^{2+}$ (IR, 1972 cm^{-1}; Raman, 2025 cm^{-1}) [66]. $[Pd(CO)_4][Sb_2F_{11}]_2$ is immediately converted into [*cyclo*-$Pd_2(\mu\text{-}CO)_2]^{2+}$ when dissolved in concentrated H_2SO_4 [66]. It is reasonable that a metal carbonyl complex in a lower oxidation state tends to be formed in a medium which is less acidic. In concentrated H_2SO_4 and in the presence of either olefins or alcohols, [*cyclo*-$Pd_2(\mu\text{-}CO)_2]^{2+}$ is converted to a Pd(I) dimer tentatively formulated as $Pd_2(CO)_2^{2+}{}_{(solv)}$, in which the palladium atoms may possess other ligands in addition to the terminal CO ligands [66]. It exhibits IR $\nu(CO)$ values of 2167 and 2144 cm^{-1}, ruling out a linear OC–Pd–Pd–CO framework. In addition to $[Pd_2(CO)_2$(2-diphenylphosphinopyridine)$_2$Cl$_2$] [238], this complex is the second exception that a Pd(I) carbonyl derivative possesses no bridging CO ligands. This is the active species for the catalytic carbonylation of olefins or alcohols to produce tertiary carboxylic acids [66].

$$\mathrm{PdSO_4 + CO} \xrightarrow{\mathrm{H_2SO_4}} [cyclo\text{-}\mathrm{Pd_2(\mu\text{-}CO)_2}]^{2+}_{(\mathrm{solv})} \xrightarrow{\text{olefin or alcohol}} \mathrm{Pd_2(CO)_2^{2+}}_{(\mathrm{solv})}$$

2.2.2. The dinuclear mercury(I) carbonyl cation, $[\{Hg(CO)\}_2]^{2+}$

The ability to form thermally stable metal carbonyl species is not limited to d-block elements (Groups 4–11); the first thermally stable carbonyl derivatives of a post-transition metal, $[Hg(CO)_2][Sb_2F_{11}]_2$ and $[\{Hg(CO)\}_2][Sb_2F_{11}]_2$, have recently been reported by Willner et al. [109,110].

$[Hg(CO)_2][Sb_2F_{11}]_2$ is prepared by the solvolysis of $Hg(SO_3F)_2$ in a large excess of liquid SbF_5 at 100 °C under a CO atmosphere [109,110]. $[Hg(CO)_2]^{2+}$ lies on a crystallographic inversion center, with a linear C–Hg–C array and a Hg–C–O angle of 177.7(7)°. This white solid exhibits unprecedented high C–O stretching frequencies (IR, 2278 cm^{-1}; Raman, 2281 cm^{-1}) and a stretching force constant ($F(\mathrm{CO}) = 21.0 \times 10^2$ N m^{-1}). Equally unprecedented is the coupling constant $^1J(^{13}\mathrm{C}-^{199}\mathrm{Hg})$ of 5219 Hz observed in the ^{13}C MAS-NMR spectrum of the ^{13}C labeled isotopomers ($\delta = 168.8$ ppm), which is much higher than 3142.5 Hz for $Hg(CN)_2$ in methanol solution, the highest previously reported value [239].

$$\mathrm{Hg(SO_3F)_2 + 8SbF_5 + 2CO} \xrightarrow[100\ ^\circ\mathrm{C},\ 1\ \mathrm{h}]{\mathrm{SbF_5}} \mathrm{[Hg(CO)_2][Sb_2F_{11}]_2 + 2Sb_2F_9SO_3F}$$

The dinuclear mercury(I) carbonyl compound $[\{Hg(CO)\}_2][Sb_2F_{11}]_2$ is obtained by the solvolysis of Hg_2F_2 (treated with HSO3F at 80 °C) in liquid SbF_5 at 60 °C in an atmosphere of CO [109,110]. This compound shows lower thermal stability than $[Hg(CO)_2]$-$[Sb_2F_{11}]_2$; the decomposition point in a sealed tube is 140 versus 160 °C for the $[Hg(CO)_2]^{2+}$ salt and the decomposition CO pressure is 8 Torr at 20 °C. The thermal decomposition of $[\{Hg(CO)\}_2][Sb_2F_{11}]_2$ at 50 °C in vacuo results in the loss of all CO and the quantitative formation of $Hg_2[Sb_2F_{11}]_2$. The mercury(I) complex is sensitive toward oxidation to $[Hg(CO)_2]$-$[Sb_2F_{11}]_2$ during the synthesis. For the mercury(I) carbonyl cation $[\{Hg(CO)\}_2]^{2+}$, slightly lower ν(CO) values for the symmetric and asymmetric stretches (2248 and 2247 cm^{-1}) and F(CO) (20.4×10^2 N m^{-1}) are obtained, compared with the corresponding data for $[Hg(CO)_2][Sb_2F_{11}]_2$. The separation between both bands is very small. Both $[\{Hg(CO)\}_2][Sb_2F_{11}]_2$ and its decomposition product, $Hg_2[Sb_2F_{11}]_2$, show single intense Raman lines attributed to Hg–Hg stretchings at 169 and 190 cm^{-1}, respectively, which are compared with those of related metal carbonyl cluster compounds (Table 5) [240–249]. In addition, evidence for the linearity of the $[\{Hg(CO)\}_2]^{2+}$ cation rests with the observation that ν(Hg–Hg) is only Raman-active [109,110].

2.2.3. The dinuclear platinum(I) carbonyl cation, $[\{Pt(CO)_3\}_2]^{2+}$

As the first metal carbonyl complexes discovered by Schützenberger are of platinum [2–5], the carbonyl derivatives of platinum continue to have the richest chemistry.

Although $Ni(CO)_4$, the first homoleptic metal carbonyl [6–8], comes from the same Group 10, compounds of platinum(0) containing only carbon monoxide, such as $Pt(CO)_n$ ($n = 1$–4), remain accessible only by matrix-isolation methods [169,250,251]. In the 1970s, Chini and co-workers reported homoleptic, anionic platinum carbonyl clusters, e.g. $[Pt_3(CO)_6]_n^{2-}$ ($n = \sim 10$, 6, 5, 4, 3, 2, 1) and $[Pt_{19}(CO)_{12}(\mu_2\text{-}CO)_{10}]^{4-}$, in which the Pt atoms are bridged by CO ligands (Fig. 3a and b) [252–257]. They are usually prepared by the reductive carbonylation of platinum halides in basic media.

The first homoleptic Pt(II) carbonyl complex, $[Pt(CO)_4][Pt(SO_3F)_6]$, was isolated by Willner and co-

Table 5
Metal–metal Raman frequencies ν(M–M) of seletced metal carbonyl clusters

Compound	ν(M–M) (cm^{-1})	References
$[\{Hg(CO)\}_2][Sb_2F_{11}]_2$ [a]	169	[109,110]
$[\{Pt(CO)_3\}_2]^{2+}$ [b]	165	[69,70]
$(n\text{-}Pr_4N)_2[\{PtCl_2(CO)\}_2]$ [a]	170	[240]
$(n\text{-}Pr_4N)_2[\{PtBr_2(CO)\}_2]$ [a]	135	[240]
$[Ir_4(CO)_{12}H_2]^{2+}$ [b]	199, 163	[68]
$Ir_4(CO)_{12}$ [a]	207, 161, 131	[241]
$Os_3(CO)_{12}$ [a]	158, 117	[242]
$Ru_3(CO)_{12}$ [a]	185, 149	[242]
$Fe_2(CO)_9$ [a]	225	[243]
$Fe_3(CO)_{12}$ [a]	219	[243]
$(t\text{-}BuC_2\text{-}t\text{-}Bu)_2[\{Fe(CO)_2\}_2]$ [c]	284	[244]
$Re_2(CO)_{10}$ [a]	122	[245–248]
$Tc_2(CO)_{10}$ [d]	148	[245,246]
$Mn_2(CO)_{10}$ [a]	160	[245–247]
$(Et_4N)_2[\{W(CO)_5\}_2]$ [a]	111	[249]
$(Et_4N)_2[\{Mo(CO)_5\}_2]$ [a]	138	[249]
$[\{Cr(CO)_5\}_2]^{4+}$ [e]	334	[127]
$(Et_4N)_2[\{Cr(CO)_5\}_2]$ [a]	160	[249]

[a] In solid state.

[b] In concentrated H_2SO_4.

[c] In CS_2 solution.

[d] In cyclohexane.

[e] Tentative formulation for the species formed in magic acid, $HSO_3F \cdot SbF_5$ (1:1).

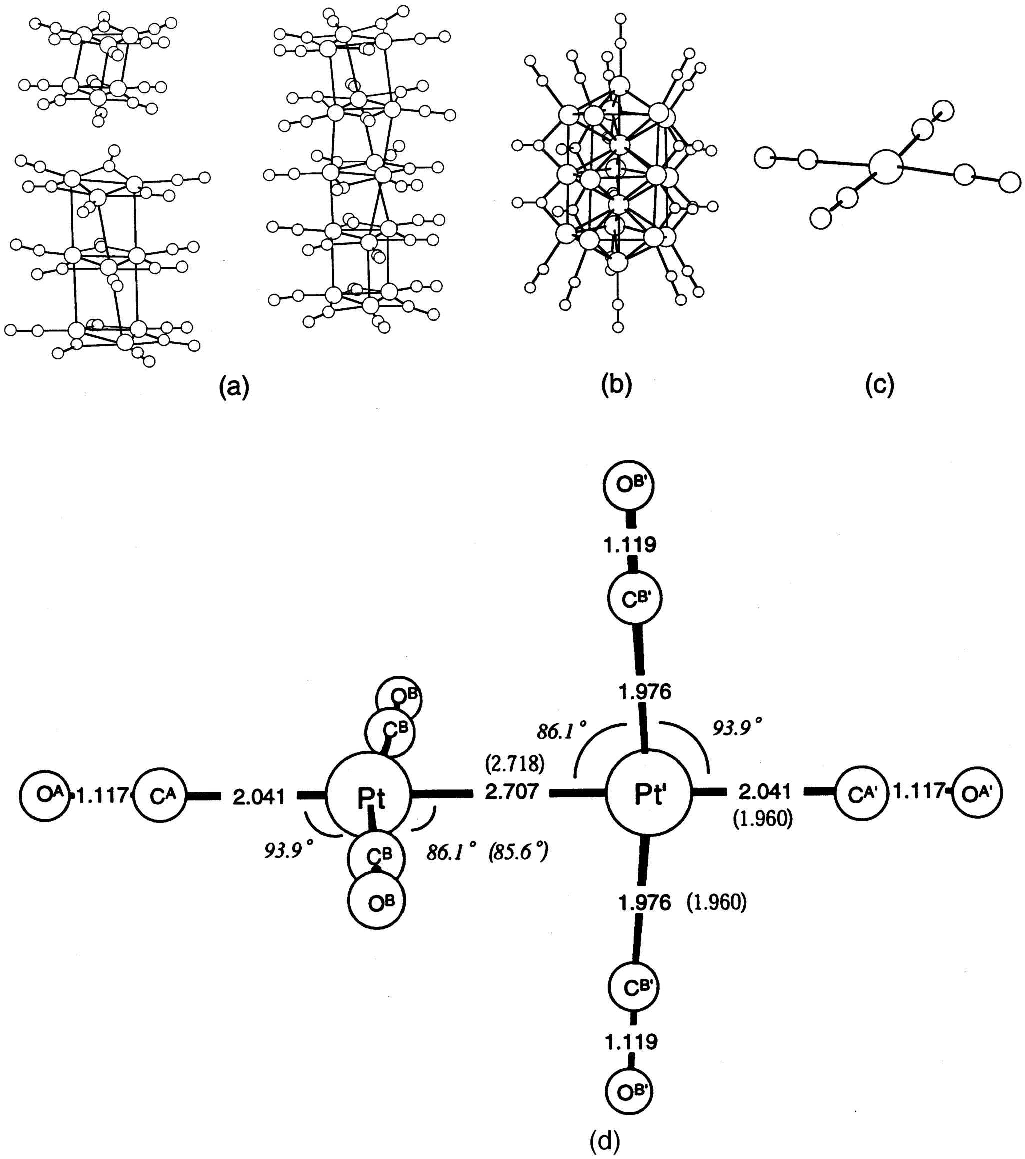


Fig. 3. The homoleptic platinum carbonyl complexes of (a) $[Pt_3(CO)_6]_n^{2-}$ ($n = 2$, 3, 5) (Ref. [253]), (b) $[Pt_{19}(CO)_{12}(\mu_2\text{-}CO)_{10}]^{4-}$ (Ref. [255]), (c) $[Pt(CO)_4]^{2+}$ (Ref. [77]) and (d) $[\{Pt(CO)_3\}_2]^{2+}$ (Ref. [70]). In the salt $[Pt(CO)_4][Sb_2F_{11}]_2$, there exist interionic interactions almost exclusively of the C--F type, which contribute to tight packing of the $[Pt(CO)_4]^{2+}$ cations and $[Sb_2F_{11}]^-$ anions as well as to the formation of extended structures (see Ref. [77]). For $[\{Pt(CO)_3\}_2]^{2+}$, the geometry optimization using B3LYP/cc-pVTZ predicts that the dihedral angle between the two coordination planes of the T-shaped $Pt(CO)_3$- groups is exactly 90.0° and the overall symmetry is D_{2d} (Ref. [70]). The platinum L_{III}-edge EXAFS data are shown in parentheses. The bond lengths are in Å.

workers via the reductive carbonylation of $Pt(SO_3F)_4$ in HSO_3F with CO [101].

$$2Pt(SO_3F)_4 + 5CO \xrightarrow[\sim 2\ \text{atm},\ 25\ ^\circ C]{HSO_3F} [Pt(CO)_4][Pt(SO_3F)_6] + CO_2 + S_2O_5F_2$$

This reaction represents the partial reduction of Pt(IV) by CO. Increasing the reaction temperature from 25 to 80 °C results in further reduction to $Pt(CO)_2(SO_3F)_2$, via the yellow intermediate, $[Pt(CO)_4][Pt(SO_3F)_6]$ [97].

$$Pt(SO_3F)_4 + 3CO \xrightarrow[80\ ^\circ C]{HSO_3F} Pt(CO)_2(SO_3F)_2 + CO_2 + S_2O_5F_2$$

In SbF_5, the creamy white complex, $Pt(CO)_2(SO_3F)_2$, can be readily converted to $[Pt(CO)_4][Sb_2F_{11}]_2$ in the presence of CO [96]. The thermally stable, white salt $[Pt(CO)_4][Sb_2F_{11}]_2$ is alternatively isolated by direct reductive carbonylation of PtF_6 in liquid SbF_5, in which the $[Pt(CO)_4]^{2+}$ cation is square planar with slight angular and out-of-plane deviations from D_{4h} symmetry (Fig. 3c) [77]. The average interatomic distances ($d(MC)_{av} = 1.982$, $d(CO)_{av} = 1.110$ Å), bond angles and average ν(CO) value (2261 cm^{-1}) for $[Pt(CO)_4]^{2+}$ are essentially identical to the Pd(II) analogue.

$$Pt(CO)_2(SO_3F)_2 + 8SbF_5 + 2CO \xrightarrow[\sim 0.6\ \text{atm}\ \ CO,\ \ 60-80\ ^\circ C]{SbF_5} [Pt(CO)_4][Sb_2F_{11}]_2 + 2Sb_2F_9SO_3F$$

Recently, $[\{Pt(CO)_3\}_2]^{2+}$, the first homoleptic, dinuclear platinum(I) carbonyl cation, has been prepared in concenreated H_2SO_4 [69,70].

$$2Pt^{IV}O_2 + 9CO + 2H^+ \xrightarrow[\text{r.t.,}\ \ 1\ \ \text{atm}]{\text{concentrated}\ \ H_2SO_4} [\{Pt^I(CO)_3\}_2]^{2+} + 3CO_2 + H_2O$$

This involves a greater degree of reduction of Pt(IV) than has been observed in superacids and must result from the use of a less acidic medium; it implies that homoleptic carbonyl cations of the transition metals in low oxidation states can be formed in media which are less acidic than the superacids that have been previously used. Prolonged evacuation of the colorless solution of $[\{Pt(CO)_3\}_2]^{2+}$ in concentrated H_2SO_4 results in disproportionation and the exclusive formation of the nearly colorless complex, *cis*-$Pt(CO)_2(L)_2^{2+}{}_{(solv)}$[69,70].

$$[\{Pt^I(CO)_3\}_2]^{2+} \underset{+4CO/\text{concentrated}\ \ H_2SO_4}{\overset{-4CO/\text{concentrated}\ \ H_2SO_4}{\rightleftharpoons}} cis\text{-}Pt^{II}(CO)_2(L)_2^{2+}{}_{(solv)} + Pt^0$$

The hexacarbonyldiplatinum(I) cation, $[\{Pt(CO)_3\}_2]^{2+}$, is the first well-characterized stable, homoleptic metal carbonyl cation containing a metal–metal bond unsupported by bridging ligands (Fig. 3d). Its formulation containing two T-shaped $Pt(CO)_3$-groups is based on both ^{13}C and ^{195}Pt-NMR studies at natural ^{13}C-abundance and 99% ^{13}CO-enrichment. At room temperature, its structure is rigid on the NMR time scale in contrast with the nonrigidity of the related Pd(I) isocyanide analogue, $[\{Pd(CNCH_3)_3\}_2]^{2+}$ [235]. The value of $^1J(Pt–Pt')$ for $[\{Pt(CO)_3\}_2]^{2+}$ is 550.9 Hz, almost the same as that for $[\{Pt(CNCH_3)_3\}_2]^{2+}$ (507 Hz) [258]. A strongly polarized, sharp Raman band due to the symmetric Pt–Pt stretch has been observed at 165 cm^{-1} ($\rho = \sim 0.25$), indicating the presence of a direct Pt–Pt bond. The ν(Pt–Pt) value is compared with those of the M–M bonds in related metal carbonyl clusters (see Table 5). The IR and Raman spectra in the CO stretching region are entirely consistent with the presence of only terminal CO's on a non-bridged Pt–Pt bond with a D_{2d} symmetry. The average CO stretching frequency, $\nu(CO)_{av}$, is 2199 cm^{-1}, higher than 2143 cm^{-1}, the value for free CO, but well below 2261 cm^{-1}, the value for the homoleptic divalent platinum carbonyl cation, $[Pt(CO)_4]^{2+}$ [77,96].

The complex, $[\{Pt(CO)_3\}_2]^{2+}$, represents one of the few simple M_2L_6 systems known where M is a transition element [231–237,259–271]. Its geometric optimization at the B3LYP level predicts that a direct Pt–Pt bond of 2.707 Å joins the two Pt atoms and each Pt atom possesses an essentially square-planar coordination geometry; the dihedral angle between the two coordination planes is 90° and the overall complex symmetry is D_{2d} (see Fig. 3d) [70,272]. The *cis* C–Pt–Pt bond angle is 86.1°, indicating displacement of the equatorial CO ligands towards the neighboring Pt atom. This structure is related to that of the nickel(I) cyanide system $[\{Ni(CN)_3\}_2]^{4-}$ [269–271], the isocyanide analogues of Pd(I) and Pt(I), $[\{M(CNCH_3)_3\}_2]^{2+}$ (M = Pd, Pt) [231–237], and the well-known $M_2(CO)_{10}$ (M = Re, Mn) neutrals [273,274]. $[\{Pt(CO)_3\}_2]^{2+}$ is the first metal carbonyl complex with the $[\{Ni(CN)_3\}_2]^{4-}$-like structure. The metal-metal bond in $[\{Pt(CO)_3\}_2]^{2+}$ shows a large trans influence and thus the 'equatorial' Pt–C bonds are significantly shorter than the 'axial' Pt–C bonds (1.976 vs. 2.041 Å), as observed for its isocyanide analogue of Pd(I), $[\{Pd(CNCH_3)_3\}_2]^{2+}$ (1.963 vs. 2.049 Å) [231,233]. The Pt–Pt bonding is characterized as a single bond. The bond parameters for $[\{Pt(CO)_3\}_2]^{2+}$ obtained by EXAFS measurements are in satisfactory agreement with the theoretical results (Fig. 3d) [70]. With respect to the Pt(I)–Pt(I) bond, theoretical studies have been performed on $[Pt_2Cl_2(CO)_4]$ and $[Pt_2Cl_4(CO)_2]^{2-}$ [275]. Experimental data can also been found for the halide-substituted derivatives of $[\{Pt(CO)_3\}_2]^{2+}$ [240,276,277].

It is interesting to note that under the same conditions, Pd(I) and Pt(I) form remarkably different types of dinuclear carbonyl cations, the former with two bridging CO ligands [66] but the latter with six terminal CO's. Theoretical studies have been carried on the structures of the dinuclear $[M_2(CO)_6]^{2+}$ and $[M_2(CO)_2]^{2+}$ (M = Ni, Pd, Pt) cations [272] and the related dinuclear $Fe_2(CO)_x$ ($x = 9, 8, 7, 6$) [278] and $Ni_2(CO)_x$ ($x = 5, 6, 7$) [279] neutrals.

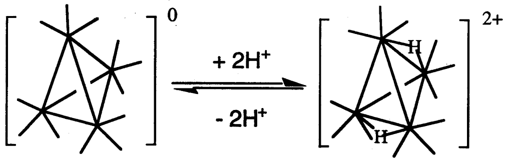
Besides the dinuclear Pd(I), Hg(I) and Pt(I) carbonyl cations described above, a new Cr metal carbonyl cation has been recently found to be formed in magic acid, $HSO_3F \cdot SbF_5$, which may be tentatively formulated as $[\{Cr(CO)_5\}_2]^{4+}$ ($\nu(CO)_{av} = 2121$ cm^{-1}) [127]. A polarized, sharp Raman band, probably due to the stretch of a quadruple Cr–Cr bond, appears at 334 cm^{-1}, which is higher than ν(Cr–Cr) at 160 cm^{-1} for the single Cr–Cr bond in $(Et_4N)_2[\{Cr(CO)_5\}_2]$ [249], and close to ν(Cr–Cr) at 340 cm^{-1} for the quadruple Cr–Cr bond in $Cr_2(mhp)_4$ (mhp = deprotonated 6-methyl-2-hydroxypyridine) [280].

2.3. *Protonation of metal carbonyl complexes*

Described above are the metal carbonyl (cluster) cations in which the formal oxidation state of the central metal is $\geq +1$. A brief survey of protonated metal carbonyl (cluster) cations in which the formal oxidation state of central metal atoms remains 0 is now presented.

In the 1960s, Wilkinson and co-workers investigated the interaction of a variety of transition-metal carbonyls and substituted carbonyls with sulfuric, trifluoroacetic and other strong acids and first found that the central metal atoms of complexes are protonated to form complexes such as $[Fe(CO)_5H]^+$, $[Fe(CO)_3(PPh_3)_2H]^+$, $[\{\pi\text{-}C_5H_5Mo(CO)_3\}_2H]^+$, and $[C_6H_5MeCr(CO)_3H]^+$ [281]. A few salts, e.g. $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2H]PF_6$, were isolated. The presence of M–H bonds was revealed by the infrared spectra of the solids and high-field lines in the ^{1}H-NMR spectra in solution (Table 6) [281–287]. The $[Fe(CO)_5H]^+$ cation is unstable at room temperature, and violently decomposes within 1–2 min in concentrated H_2SO_4, but can be isolated as the $[PF_6]^-$ salt at low temperature. The dinuclear carbonyl-π-cyclopentadienyl-molybdenum and -tungsten compounds provided unusual examples of the H bridging in protonated species [281].

The protonation of polynuclear metal carbonyl complexes in strong acids has been investigated in a variety of strong acids. Knight and Mays revealed the first polynuclear hydridocarbonyl cations, $[M_3(CO)_{12}H]^+$ (M = Ru, Os), in strong acids or as $[PF_6]^-$ salts [283,284]. The ^{13}C-NMR spectra demonstrated that intramolecular rearrangement occurs via an internuclear mechanism in $[Os_3(CO)_{12}H]^+$ [287]. The formation of $[Ir_4(CO)_{12}H_2]^{2+}$ by the addition of two protons to the neutral iridium carbonyl cluster, $Ir_4(CO)_{12}$, has been reported in a variety of strong acids [68,284,285]. The protonation to these clusters is reversible; by lowering the concentration of the acids, the neutral metal carbonyl clusters are recovered. For these metal hydridocarbonyl cations, high-field shifts of ^{1}H-NMR are observed, as noted for the neutral and anionic metal carbonyl hydrides [1]. Interestingly, the metal hydridocarbonyl (cluster) cations exhibit $\delta(^{13}C)$ high field-shifted from 184 ppm, the value for free CO, as observed for the metal carbonyl (cluster) cations [24]. They also show average $\nu(CO)_{IR}$ values higher than their neutral counterparts (Table 6); the average $\nu(CO)_{IR}$ values for $Fe(CO)_5$, $Ru(CO)_5$, $Os(CO)_5$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ are 2011, 2017, 2012, 2033, 2030 and 2053 cm^{-1}, respectively [127,288]. This observation implies reduced metal-to-CO π-backbonding, probably owing to a positive charge to certain extent at the central metal atoms although the formal oxidation state of the central metal atoms is 0 in the metal hydridocarbonyl cations. Nevertheless, the CO ligands are tightly bound to the metal clusters; the CO ligands are not removed upon evacuation.



$Ir_4(CO)_{12}$ $[Ir_4(CO)_{12}H_2]^{2+}$

In contrast with $Ir_4(CO)_{12}$, which dissolves in strong acids with retention of the cluster skeleton to give a protonated species, $[Ir_4(CO)_{12}H_2]^{2+}$, the dissolution of $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ or $Co_4(CO)_{12}$ in strong acids under a CO atmosphere results in the breaking of the metal–metal bonds to form $[Rh(CO)_4]^+$ and $Co(CO)_4^+$, respectively, along with evolution of H_2 [68]. This is an unusual example of the oxidation of Rh(0) to Rh(I) by H^+. These reactions can probably be considered to proceed via an intermediate like $[M_4(CO)_{12}H_x]^{x+}$ (M = Rh, Co), in which the charge at the central metal atoms may be somewhat positive. One may expect the species of $[M_4(CO)_{12}H_x]^{x+}$ (M = Rh, Co) to be isolated by using adequate counteranions and controlling the reaction conditions such as acidity and temperature. The different behaviors shown by the neutral Co, Rh and Ir carbonyl clusters in strong acids reflect the fact that the

Table 6
Spectroscopic data of metal hydridocarbonyl cations

Complex [a]	$\nu(CO)_{av}$ [b] (cm^{-1})	$\delta(^1H)$ (ppm)	$\delta(^{13}C)$ (ppm)	References
$[Fe(CO)_5H]^+$ [c]	2137 [d]	−8.1 [e]		[48,281]
$[Ru(CO)_5H]^+$		−7.2	180.5, 178.2	[282]
$[Ru_3(CO)_{12}H]^+$	2106 [f]	−19.4	201.8, 194.5, 184.9, 184.1, 179.1 [g]	[283–285]
$[Os(CO)_5H]^+$	2080	−8.2	159.0 [g]	[285,286]
$[Os_3(CO)_{12}H]^+$	2085	−19.9	177.6, 171.1, 166.7, 161.4, 160.8	[283–287]
$[Ir_4(CO)_{12}H_2]^{2+}$	2138	−19.6	144.2, 142.0	[68,285]

[a] In concentrated H_2SO_4 unless otherwise stated.

[b] Average of $\nu(CO)_{IR}$.

[c] Decomposes rapidly in concentrated H_2SO_4.

[d] As $[PF_6]^-$ salt.

[e] In $BF_3 \cdot H_2O\text{–}CF_3COOH$.

[f] In CF_3COOH.

[g] In HF solution.

Table 7
Metal carbonyl cation-catalyzed carbonylation of olefins and alcohols in concentrated H_2SO_4 at 1 atm of CO

Substrate	Carbonyl catalyst	Tertiary carboxylic acid	Yield [a] (%)	References
1-Pentene	Pt(I) [b]	2,2-Dimethylbutanoic	70	[71]
		Others	1	
1-Hexene	Pd(I) [c]	2,2-Dimethylpentanoic	48	[66]
		2-Methyl-2-ethylbutanoic	23	
		Others	1	
1-Octene	Rh(I) [d]	2,2-Dimethylheptanoic	41	[67]
		2-Methyl-2-ethylhexanoic	22	
		2-Methyl-2-propylpentanoic	10	
		Others	3	
1-Decene	Au(I) [e]	2,2-Dimethylnonanoic	33	[65]
		2-Methyl-2-ethyloctanoic	16	
		2-Methyl-2-propylheptanoic	12	
		2-Methyl-2-butylhexanoic	5	
		Others	4	
Cyclohexene	Cu(I) [f]	1-Methylcyclopentanecarboxylic	63	[294]
t-Butanol	Pd(I) [c]	2,2-Dimethylpropanoic	70	[66]
		Others	2	
1-Hexanol	Ag(I) [g]	2,2-Dimethylpentanoic	79	[296]
		2-Methy-2-ethylbutanoic	19	
1-Octanol	Cu(I) [h]	2,2-Dimethylheptanoic	72	[297]
		2-Methyl-2-ethylhexanoic	15	
		2-Methyl-2-propylpentanoic	5	
Cyclohexanol	Ag(I) [g]	1-Methylcyclopentanecarboxylic	81	[296]

[a] Based on substrate.
[b] PtO_2/substrate = 2.0 mmol/5.0 mmol, 96% H_2SO_4 10 ml, 25 °C.
[c] $PdSO_4$/substrate = 1.0 mmol/5.0 mmol, 96% H_2SO_4 10 ml, 25 °C.
[d] $Rh_4(CO)_{12}$/substrate = 0.17 mmol/2.5 mmol, 96% H_2SO_4 5 ml, 25 °C.
[e] Au_2O_3/substrate = 0.5 mmol/5.0 mmol, 96% H_2SO_4 10 ml, 25 °C.
[f] Cu_2O/substrate = 20 mmol/200 mmol, 98% H_2SO_4 105 ml, 30 °C.
[g] Ag_2O/substrate = 8.0 mmol/20 mmol, 98% H_2SO_4 40 ml, 30 °C.
[h] Cu_2O/substrate = 4.0 mmol/20 mmol, 98% H_2SO_4 21 ml, 30 °C.

M–M bond may be strengthened by changing the transition metal from the first row to the third row.

$$M_4^0(CO)_{12} + xH^+ \longrightarrow [M_4^0(CO)_{12}H_x]^{x+}$$
$$\xrightarrow[+(4-x)H^+]{+4CO} 4M^I(CO)_4^+ + 2H_2 \quad (M = Co,\ Rh)$$

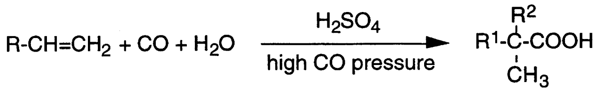
3. Application of metal carbonyl cations to catalytic reactions

3.1. Carbonylation of olefins, alcohols and other organic compounds

3.1.1. Carbonylation of olefins and alcohols

The Koch reaction has been well known for the synthesis of tertiary carboxylic acids from olefins and water, or alcohols, with carbon monoxide in strong acids [10,289]. The reaction occurs at temperatures between −20 and 80 °C and pressures up to 100 atm. Generally H_2SO_4, H_3PO_4, HF and $BF_3 \cdot H_2O$ are employed as catalysts and solvents. The Koch process was operated in commercial plants by Esso and Shell [10].

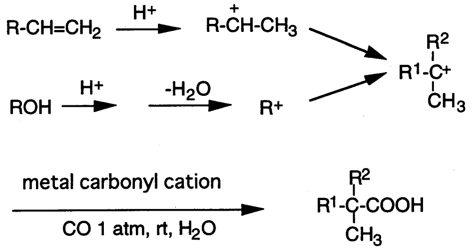
In concentrated H_2SO_4, for example, the olefin is protonated, or the alcohol is protonated and dehydrated, to form a carbenium ion intermediate, which isomerizes to tertiary carbenium ions via the Wagner–Meerwein rearrangement prior to the carbonylation [290,291]. The carbonylation of the carbenium ions leads to the formation of acylium cations, which react with water to give tertiary carboxylic acids or with alcohols to give the corresponding esters. However, olefins are converted to carboxylic acids in a yield lower than 10% under atmospheric CO pressure owing to the presence of olefin oligomerization as a competitive reaction. For achieving a high conversion to the corresponding carboxylic acids, a high CO pressure is needed. Haaf developed an alternative pressure-free variant with formic acid as the CO source [292,293]. However, this method has been restricted to the laboratory due to the high cost of formic acid.



$$R\text{-}CH{=}CH_2 + CO + H_2O \xrightarrow[\text{high CO pressure}]{H_2SO_4} R^1\text{-}\underset{CH_3}{\overset{R^2}{C}}\text{-}COOH$$

The previous work by Souma et al. showed that copper(I) and silver(I) carbonyls in strong acids catalyze the carbonylation of olefins and alcohols to give tertiary carboxylic acids in high yields at r.t. and atmospheric pressure (Table 7) [294–297].

Very recently, the gold(I) carbonyl cations have been reported to work as an excellent catalyst, with which olefins readily react with CO to produce tertiary carboxylic acids in high yields at ambient pressure and temperature (Table 7) [65]. It is the first application of gold(I) carbonyls to organic syntheses, while very few gold catalysts have been reported so far [298–305].



The influence of the H_2SO_4 concentration on the formation of Au(I) carbonyls and on the carbonylation of 1-hexene is shown in Table 8 [65]. The dependence of the carbonylation on the H_2SO_4 concentration parallel to that of the formation of the unstable Au(I) dicarbonyl cation $Au(CO)_2^+$ leads to the conclusion that the gold dicarbonyl but not the monocarbonyl is the active species for the carbonylation. Similar behavior was observed for the Cu(I) catalyst, indicating that both $Cu(CO)_2^+$ and $Cu(CO)_3^+$ are the active species, but $Cu(CO)^+$ is inactive [306].

Furthermore, the Pd(I), Rh(I) and Pt(I) carbonyl cations have been found to be excellent catalysts for the carbonylation of olefins and alcohols (Table 7) [66–71]. In the presence of an olefin or alcohol, the precursor, [*cyclo*-$Pd_2(\mu\text{-}CO)_2]^{2+}$ is converted to a Pd(I) dimer tentatively formulated as $Pd_2(CO)_2^{2+}{}_{(solv)}$, which is considered to be the active species for the Pd(I) carbonyl cation-catalyzed carbonylation of olefins or alcohols [66]. For the platinum carbonyl cation-catalyzed carbonylation, $[\{Pt(CO)_3\}_2]^{2+}$ is the active species, whereas *cis*-$Pt(CO)_2(L)_2^{2+}{}_{(solv)}$ has a very low catalytic activity [71]. The Rh(I) tetracarbonyl, $[Rh(CO)_4]^+$, is the active species for the Rh(I) carbonyl cation-catalyzed carbonylation [67]. The high catalytic activities of the metal carbonyl cations for the carbonylation of olefins under mild conditions, in comparison to the typical metal carbonyl-catalyzed carbonylation such as the Roelen and Reppe reactions [137,138], may be related to the active CO ligands. On the other hand, in contrast with $Cu(CO)_n^+$ ($n = 2$, 3), $Ag(CO)^+$, $Au(CO)_2^+$ and $[Rh(CO)_4]^+$, which require only a brief evacuation (several seconds) to remove the reversible CO ligands [65,67,127], $Pd_2(CO)_2^{2+}{}_{(solv)}$ and $[\{Pt(CO)_3\}_2]^{2+}$, from which a prolonged evacuation (ca. 1 day) is required to remove the CO ligands [66,69–71], are so stable that they 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. However, the conversions of olefins and alcohols to tertiary carboxylic acids by the Pt(I) and Pd(I) carbonyl catalysts are comparable to those by the Cu(I), Ag(I), Au(I), and Rh(I) carbonyl catalysts. In addition, it has recently been found that $[Ir_4(CO)_{12}H_2]^{2+}$ holding tightly bound CO ligands also exhibits catalytic activity for the carbonylation of olefins in strong acids at room temperature and atmospheric CO pressure [127]. These observations conflict with the CO carrier model, in which the unstable metal polycarbonyl cations were considered to act merely as a CO carrier which transports CO from the gas phase to the H_2SO_4 solution, resulting in a high CO concentration in the solution and consequently accelerating the carbonylation of olefins and alcohols via the pathway of the original Koch reaction [10,294].

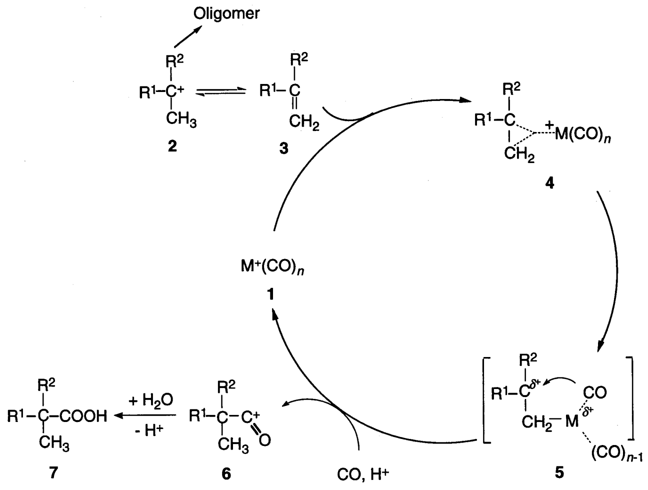
Table 8
Dependence on H_2SO_4 concentration of the ratio of CO/Au^+ and the yield of tertiary carboxylic acids from 1-hexene [a]

Concentration of H_2SO_4 (wt.%)	CO/ Au^+	Yield of tertiary C_7 acids [b] (%)
75	1.00	0
80	1.05	20
85	1.10	32
90	1.36	58
93	1.58	79
96	1.65	80

[a] Au_2O_3/(1-hexene) = 0.5 mmol/5.0 mmol, H_2SO_4 10 ml, CO 1 atm, r.t. (Ref. [65]).

[b] Based on 1-hexene.

A reaction mechanism involving an olefin–gold–carbonyl intermediate has recently been proposed for the gold(I) carbonyl cation-catalyzed carbonylation of an olefin in strongly acidic media [25,65], which can be modified as shown in Scheme 1. When the olefin is added to the strong acid H_2SO_4, it forms a carbenium ion, which isomerizes to the carbenium ion **2**. An equilibrium process exists between the carbenium ion **2** and the isomerized olefin **3** [307], a part of which oligomerize to give higher weight molecules in a competitive reaction. Complex **3** coordinates to M to form the π complex **4**. In the complex **4**, since the tertiary and primary carbons are unsymmetrically bridged, the relatively positive charge should be located at the tertiary carbon. CO migrates to the partially positively charged tertiary carbon via the intermediate **5**, which transforms into the acylium cation **6**. The acylium cation **6** consequently reacts with water to give the carboxylic acid **7**. Such an olefin-metal-carbonyl intermediate has not been directly observed but similar organometallic ions like ethylene-, norbornylene- and cyclohexene-mercurium ions, which were prepared from



Scheme 1.

Hg^{2+}, the isoelectronic ion of Au^{+}, have been observed by Olah et al. in superacidic media [308–311]. Theoretical studies (B3LYP level of theory) have supported the reaction mechanism involving the olefin–metal–carbonyl intermediate [312].

3.1.2. Carbonylation of dienes, diols, aldehydes and saturated hydrocarbons

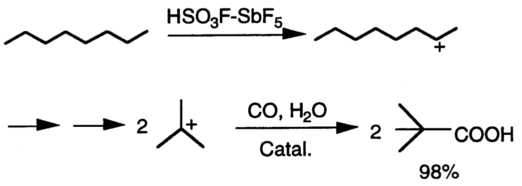
Dienes and diols also react with CO to give a mixture of dicarboxylic acids, monocarboxylic acids and lactones [313,314]. These reactions are depicted in Scheme 2 and selected results are shown in Table 9.

The composition of products depends on the acid solvent and the number of carbons in the substrate [313]. Lactones (five or six-membered ring) are always obtained, while dicarboxylic acids are produced from the substrate having more than ten carbon atoms. Larger amounts of the lactones are obtained from the diols than from the dienes. The appropriate reaction temperatures of the dienes and diols were found to be 0–10 and 20–30 °C, respectively. Cyclic monocarboxylic and saturated monocarboxylic acids are obtained by the carbonylation of 1,7-octadiene. During the formation of the cyclic monocarboxylic acid, the carbenium cation formed by the protonation of one of the two double bonds undergoes a ring-closure reaction via the intramolecular attack on the second double bond. To form the saturated tertiary monocarboxylic acid, the carbenium cations are saturated by hydride abstraction from other molecules. It appears that the secondary carbenium ions are more susceptible to saturation than the tertiary carbenium ions.

Glycolic acid and the corresponding esters can be obtained by the carbonylation of formaldehyde in metal carbonyl catalyst solution under atmospheric CO pressure (Table 9) [315].

$$\mathrm{HCHO} \xrightarrow{\mathrm{H^+}} \mathrm{H_2C^+{-}OH} \xrightarrow[\text{Catalyst}]{\text{CO, ROH}} \mathrm{HOCH_2COOR}\ (99\%)$$

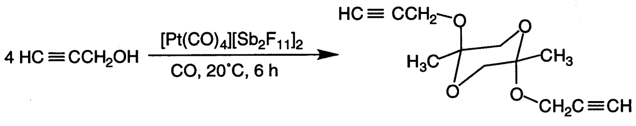
Saturated hydrocarbons react with carbon monoxide in the presence of metal carbonyl catalysts in superacids such as $HSO_3F \cdot SbF_5$ or $HF \cdot SbF_5$ to give tertiary and secondary carboxylic acids (Table 9) [316]. The cleavage of the C–C bond of the intermediate carbenium cations formed via hydride abstraction of the saturated hydrocarbons in the superacids was recognized.



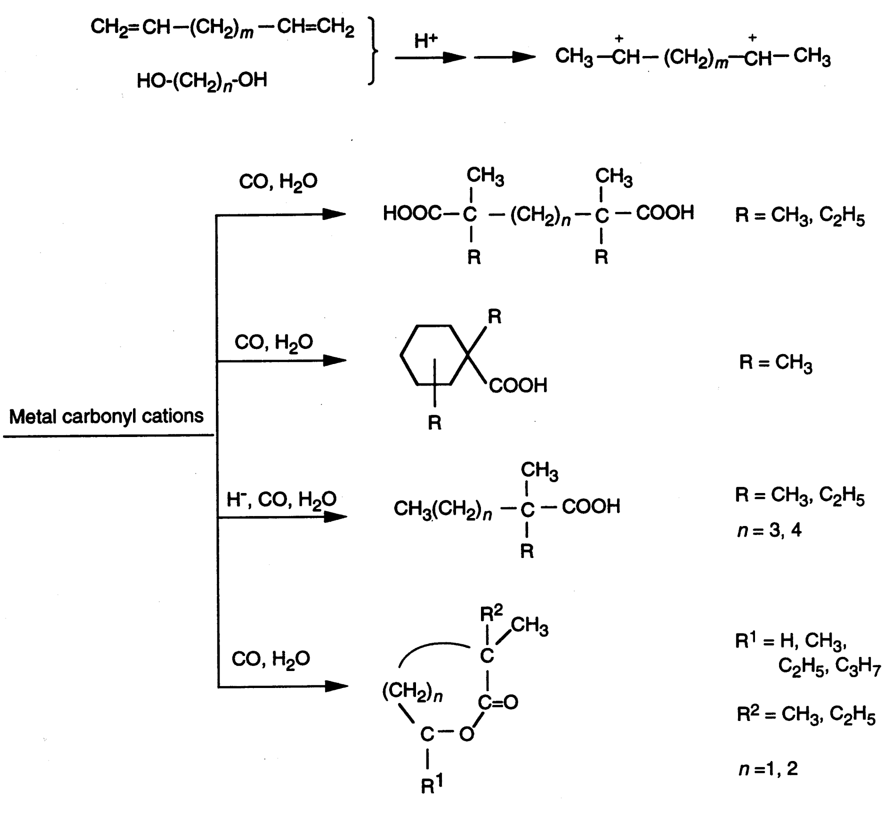
3.2. Tetramerization and polymerization of alkynes

Apart from the carbonylation of olefins, alcohols and other organic compounds, another example of the catalytic application of the metal carbonyl cations is the stereospecific tetramerization of 2-propynol and the polymerization of arylacetylenes by the homoleptic Pt(II) carbonyl, $[Pt(CO)_4][Sb_2F_{11}]_2$ [317].

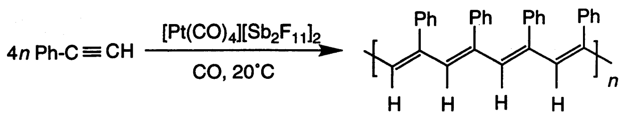
In an atmosphere of CO, 2-propyn-1-ol is tetramerized to 2,5-dimethyl-2,5-bis(2-propynoxy)-1,4-dioxane in high yield in the presence of a small amount (7×10^{-3} mol%) of $[Pt(CO)_4][Sb_2F_{11}]_2$ at 20 °C. A positive CO pressure is crucial for this reaction although no carbonylation products are formed. An η^2-alkyne-Pt(II)-carbonyl complex and subsequently an η^2-alkene-Pt(II)-carbonyl complex formed by the nucleophilic addition of propynol to the activated C≡C triple bond have been proposed to be the reaction intermediates [317].



Selected arylacetylenes are polymerized by $[Pt(CO)_4][Sb_2F_{11}]_2$ under a CO atmosphere to afford poly(arylacetylenes) with an all-trans transoidal microstructure. With 2.1×10^{-2} up to 2.7×10^{-2} mol% of catalyst, average weights (M_w) between 3000 and 4300 are obtained. A complex such as $[(CO)_2Pt(C{\equiv}CPh)_2]$ was proposed to be the reactive molecule, where the polymerization proceeds via the insertion of arylacetylene into the Pt–C bonds [317].



Scheme 2.



4. Conclusions and future prospects

There has recently been a rapid development in the synthesis, characterization and catalytic application of homoleptic metal carbonyl cations and their derivatives

Table 9
Copper(I) carbonyl-catalyzed carbonylation of dienes, diols, aldehydes and saturated hydrocarbons in strong acids at 1 atm of CO

Substrate	Temperature (°C)	Product	Yield[a] %	References
1,5-Hexadiene [b]	0–5	2-Ethyl-4-pentanolide	46	[313]
1,7-Octadiene [b]	3–8	2,2-Dimethyl-4-heptanolide	15	[313]
		2,2-Dimethyl-5-heptanolide	8	
		2,2-Dimethylheptanoic acid	14	
		2-Methyl-2-ethylhexanoic acid	6	
		1,4-Dimethylcyclohexanecarboxylic acid	35	
1,9-Decadiene [b,c]	5–10	2-Methyl-2-ethyl-4-octanolide	20	[313]
		2-Methyl-2-ethyl-5-octanolide	15	
		2,2,7,7-Tetramethyloctanedioic acid	45	
		2-Ethyl-2,6,6-trimethylheptanedioic acid	10	
1,8-Octanediol [b]	20–25	2,2-Dimethyl-4-heptanolide	35	[313]
		2,2-Dimethyl-5-heptanolide	40	
1,12-Dodecanediol [b]	20	1,4- and 1,5-Lactone	50	[313]
		2,2,9,9-Tetramethyldecanedioic acid	38	
		2-Ethyl-2,8,8-trimethylnonanedioic acid	9	
Formaldehyde [d]	20	Glycolic acid	96	[315]
Octane [e]	−2 to 2	2,2-Dimethylpropanoic acid	195	[316]

[a] Based on substrate.

[b] Cu_2O/substrate = 8.0 mmol/30 mmol, 98% H_2SO_4 30 ml.

[c] 10 ml of HSO_3F added.

[d] Cu_2O/HCHO = 1.0 g/2.5 g, 98% H_2SO_4 20 ml.

[e] Cu_2O/octane = 6.0 mmol/30 mmol, HSO_3F 20 ml, SbF_5 10 ml.

from Groups 6 through 12. Especially, the Lewis superacid, SbF_5, has allowed preparation of highly reactive naked metal cations that are carbonylated under very mild conditions and can be isolated in the form of the thermally stable salts of metal cations with $[Sb_2F_{11}]^-$ as the counteranion; indeed, most of the recent thermally stable metal carbonyl cations have been prepared with SbF_5 [24]. On the other hand, the discovery of $[\{Pt(CO)_3\}_2]^{2+}$ points to the possibility that the homoleptic carbonyl cations of metals in low oxidation states may be prepared in media which are less acidic than the superacids that have been previously used [69,70]. Another strategy for preparing carbonyl cations of metals in low oxidation states is the use of anions that are weakly coordinating but not strongly oxidizing, of which the development is expected. The synthesis of (especially, high-nuclearity) metal carbonyl cluster cations is, in particular, challenging.

Both experimental and theoretical studies of the metal carbonyl cations have significantly enriched the understanding of metal–CO bonding. It has turned out that metal carbonyl cations have characteristics distinct from the typical metal carbonyl complexes. The properties of metal–CO bonding will still be the focus of much attention in future experimental and theoretical studies.

Metal hydridocarbonyl cations have characteristics related to those of the homoleptic metal carbonyl cations and their derivatives. Further studies on their bonding properties and the finding and, especially, the isolation of new homonuclear and heteronuclear metal hydridocarbonyl cluster cations are expected.

The metal carbonyl cations exhibit high catalytic activities under mild conditions in comparison with the typical metal carbonyl complexes. They have been employed for the carbonylation of olefins, alcohols, dienes, diols, aldehydes and saturated hydrocarbons, as well as the tetramerization and polymerization of alkynes. A goal in future studies is to extend their application to new catalytic reactions.

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