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Carbon monoxide as a σ-donor ligand in coordination chemistry

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CONTENTS

ABSTRACT

In addition to the numerous and varied examples of organometallic and coordination compounds where carbon monoxide functions as a π-acceptor ligand, there is a small but select group of derivatives

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where the CO–metal bonding relies predominantly on σ-bonding only. The metal derivatives, which include $Pt(CO)_2Cl_2$, known since 1868, are formed by electron-rich metals (Pd, Pt, Ag and Au), in oxidation states +1 and +2, are cationic in nature, and are for the most part thermally stable. Their generation in strong protonic and Lewis acids (HSO_3F, HSO_3F–SbF_5 and liquid SbF_5) allows convenient synthesis. The predominance of σ-bonding results in unusual spectroscopic properties, such as $\bar{\nu}$CO stretching vibrations as high as 2280 cm^{-1}, relative to 2143 cm^{-1} in free CO, and ^{13}C chemical shifts which are 180–130 ppm rather than 190–220 ppm for classical transition-metal carbonyls. Consequently two basic principles, the synergic bonding model and the rule of 18, fail for these complexes. Recent structural studies point to the importance of secondary OC···OS or OC···FSb contacts, which in place of π-back-donation provide for a measure of charge compensation both in solution or in the solid state. This review concentrates on very recent (since 1990) developments in this field, which is expanding rapidly beyond the transition metals.

1. INTRODUCTION

1.1. Carbon monoxide

Carbon monoxide is an important and versatile reagent in inorganic and organic chemistry. On both laboratory and industrial scales, numerous reactions and processes with CO as a reactant are presently in use. Many of the reactions and industrial processes involving carbon monoxide are catalytic in nature (homogeneous as well as heterogeneous catalyses are encountered), which implies coordination, adsorption or chemisorption of CO to a metal surface, a metal atom or ion, a proton, or a molecular Lewis acid, to form reactive intermediates. There are also isolable CO complexes, where the bonding of CO to a substrate can be studied by structural and spectroscopic methods. Depending on the nature and electronic structure of the substrate, two principal coordination and bonding modes of CO may be discerned. (a) Towards electron-rich transition metals with the metal in a low oxidation state, synergic or synergetic bonding is encountered, which consists of CO-to-metal σ-donation and metal-to-CO π-back-donation. The latter process results in strengthening of the metal–carbon bond and appears to be responsible for the thermal stability of many classical transition-metal CO complexes. The emphasis on the π-acceptor ability of CO has led to the interesting suggestion by Pearson [1] that in these complexes CO acts predominantly as a *Lewis acid.* (b) Towards strong Lewis acids with little or no propensity towards π-back-donation, CO will be expected to act as a *Lewis base.* Since carbon monoxide is a very weak Lewis base, examples in this group will be limited in number and possibly of rather low thermal stability. Where metal ions are involved as acceptors, the complexes may be termed *non-classical metal carbonyls.*

It is the purpose of this review to summarize the known examples of complexes where CO acts as Lewis base, either solely or predominantly. Topics for discussion include the following: (i) conditions under which coordination complexes, with CO acting as a Lewis base, may be thermodynamically stable; (ii) synthetic routes to these unusual compounds; (iii) criteria and structural spectroscopic features of the complexes; (iv) an answer to the question why π-back-donation, which is an important and crucial feature of classical transition-metal carbonyls, may be absent or strongly reduced in non-classical carbonyl derivatives.

To this end we summarize briefly in Table 1 relevant physical, structural, spectroscopic, and bonding features of carbon monoxide. This is followed by a brief summary of the experimental evidence for synergic metal–CO bonding. Finally, the so-far known non-classical carbonyl derivatives are discussed in some detail, and an attempt is made to describe the main bonding features of these derivatives.

As is seen in the subsequent sections, a very intriguing dichotomy emerges: the first non-classical metal carbonyls, three platinum(II) carbonyl chlorides, among them $Pt(CO)_2Cl_2$, were reported by Schützenberger [2] as early as 1868. Their discovery predates the synthesis of $Ni(CO)_4$ by about 22 years, making these the first metal-carbonyl compounds to be discovered. However, recent developments in this field, which contribute the bulk of the material presented here, started in 1990 when the first non-classical carbonyl cation, $[Au(CO)_2]^+$(solv), was reported. At present the field is expanding rapidly as more examples become available and are characterized structurally. Hence a review is appropriate at this time.

The main thrust of this review is towards isolable, thermally stable complexes

TABLE 1

Selected physical, structural and spectroscopic properties of carbon monoxide

Physical properties
m.p. (°C) −199, b.p. (°C) at 1 atm. −191.5
Dipole moment μ (D) 0.112

Structural properties
Internuclear distance (Å) CO(g) 1.12819, CO^+(g) 1.11506
van der Waals radii according to Bondi (Å)
Cl 1.75, C 1.72, O 1.52, Sum of C+O 3.24
Covalent single bond radii (Å) C 0.77, O 0.66

Vibrational data ^{13}C-NMR chemical shift 184 ppm
Stretching frequency (cm^{-1})

$\bar{\nu}$	$^{12}C^{16}O$	2143.16	$^{13}C^{16}O$	2096.07
ω	$^{12}C^{16}O$	2170.21	$^{13}C^{16}O$	2121.41
$\bar{\nu}$	$[^{12}C^{16}O]^+$	2184		
ω	$[^{12}C^{16}O]^+$	2214.24		

Point group $C_{\infty v}$

Electronic structure electronic groundstate $'\Sigma_g^+$
Electronic configuration $(1\sigma)^2\ (2\sigma)^2\ (3\sigma)^2\ (4\sigma)^2\ (1\pi)^4\ (5\sigma)^2$
First ionization energy (eV) 14.014
Electron affinity (eV) −1.8

and derivatives of CO, which will also permit spectroscopic and structural investigations. Systems where CO is chemisorbed on metallic or ionic surfaces, and CO adducts obtained by matrix isolation and similar techniques, are only introduced by using selected examples that either support or contradict our conclusions.

The name *non-classical carbonyl derivatives* refers to the way CO is bonded to Lewis acids. The majority of these complexes are cations or cationic, where the term "cationic" implies a carbonyl-containing metal moiety that is bonded to an anionic, weak nucleophile through a weak and polar covalent bond. A further subdivision into thermally stable or *persistent* and *transient* derivatives refers to the ability of the carbonyl complexes to survive at ambient temperature and atmospheric pressure for some time (persistent) or to decompose under these conditions with CO release (transient).

This review is written from the vantage point of a physical inorganic chemist with emphasis on synthesis as well as on the study of spectroscopic properties and structural details. Views on bonding will be on a basic, "user-friendly" level, and reference is made to more advanced theoretical treatments where appropriate.

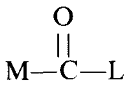
1.2. Comments on carbon monoxide as a potential ligand

The data summarized in Table 1 are taken from standard references such as *Gmelin's Handbuch der Anorganischen Chemie,* 8th edn., Springer-Verlag, Berlin, *Carbon and its Compounds,* 1970, pp. 115–125, and G. Herzberg, *Spectra of Diatomic Molecules,* 1950, pp. 520–522, 2nd edn, Van Nostrand, Toronto, 1966. More detailed referencing is found in the appropriate sections of this review.

Carbon monoxide, as the physical properties indicate, is a gas at ambient temperature. Reactions with CO are hence largely heterogeneous reactions that will frequently require high pressures and temperatures. The in situ generation methods of CO from formic or oxalic acid [3] are attractive alternatives and methods to obtain very pure or isotopically labelled CO in small quantities.

The dipole moment of CO is rather small as a consequence of the electronic structure (vide infra). The polarity $C^{\delta+}$–$O^{\delta-}$ suggested by the respective electronegativities of carbon and oxygen is most probably not correct and should, based on the MO picture, rather be $C^{\delta+}$–$O^{\delta-}$. Formation of a coordinate bond using only σ donation from the lone pair on carbon would result in a polarization of the carbonyl ligand in the sense $M^+ \leftarrow C^{\delta+}$–$O^{\delta-}$. It would also lead, in cases where the acceptor is positively charged, e.g. a metal cation, to a juxtaposition of two positively charged atoms. This situation is avoided in classical metal carbonyls by involving zero- or low-valent metals and by π-back-donation, which provides for intramolecular charge compensation.

Where this charge compensation does not occur, two possible reaction pathways may be considered: (i) nucleophilic attack on M^{n+} and a displacement of CO by a more basic ligand, and (ii) nucleophilic attack on C and the formation of derivatives of the type



$$\mathrm{M{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}L}$$

The latter reaction pathway is an important step in many carbonylation processes that are catalysed homogeneously by metal complexes. Examples of both reaction types are discussed in this review. Judging by the short C–O distance of 1.12819 Å, the CO bond is best viewed as a triple bond and the canonical resonance form $|C^{-1}\equiv O^{+1}|$ makes a major contribution to the bonding in free carbon monoxide. A molecular orbital approach suggests a bond order of three. The HOMO orbital of CO is the 5σ MO, a carbon-based orbital that is predominantly non-bonding and only very weakly antibonding. The antibonding nature of the 5σ orbital is apparent from the decrease in the internuclear distance, the increase in the stretching frequency when going from CO to CO^+, and the vibrational fine-structure of the first ionization peak at 14.014 eV in the U-PES spectrum.

The decrease in C–O bond length on coordination is very slight, while the increase in either $\bar{\nu}$ or ω is larger and readily measurable with a conventional vibrational spectrometer. It hence becomes apparent that in areas of high C–O bond order (approximately 3), vibrational spectroscopy will provide a clearer picture of any small changes in the CO bond order than does X-ray crystallography, where in addition to limits in accuracy, expressed in terms of estimated standard deviations (ESDs), thermal motion and weak secondary contacts in the solid state tend to obscure the situation. Additionally, in most CO derivatives the CO stretching vibrations fall into an uncluttered spectral region, where band overlap with most bands except for $C\equiv N$ or $C\equiv C$ vibrations is unlikely. However, vibrational mixing and Fermi resonance can still present problems that can be overcome by a complete vibrational assignment, a normal coordinate analysis, force-constant calculations, and a comparison of observed and calculated frequencies. Isotopic substitution of ^{13}C vs. ^{12}C and ^{18}O vs. ^{16}O is of enormous use in a careful vibrational analysis, as are ^{13}C-NMR measurements on isotopically enriched samples. In general for terminal CO groups in transition-metal carbonyls, the C–O bond distances are approximately 1.15 Å, with little variation, while $\bar{\nu}$CO ranges from 2125 to 1850 cm^{-1}.

Finally, consistent with the overall view of CO as a very poor Lewis base, the first ionization energy of CO is, with 14.014 eV, very high, much higher than found for many molecular N- and O-donor systems that will, where present, compete with CO for coordination sites.

In summary, the review of physical spectroscopic and structural parameters of CO allows the conclusion that chances for the use of CO as Lewis base on a synthetic scale and at ambient temperatures are seemingly not promising, unless special conditions can be found. There is, however, some hope in the fact that the first metal-carbonyl derivatives synthesized [2], three Pt(II) carbonyl chlorides, are examples of thermally stable, non-classical carbonyls. The question that needs to be answered is why are they thermally stable, against all the odds summarized in this chapter?

2. DISCUSSION

2.1. *Synergic bonding of carbon monoxide as π-acceptor ligand: experimental criteria*

Carbon monoxide, CO, is the single most important, and most extensively studied ligand in transition-metal chemistry, and carbonyl derivatives of one type or another are known for all transition metals [4–6]. This may seem surprising, because CO is a very poor Lewis base or σ-electron pair donor. However, the ability of carbon monoxide to function as a π-acceptor or π-acid ligand results in synergic bonding, where π-back-donation from filled d-orbitals of the metal to the π^*-molecular orbitals of CO increases its basicity and the ability to function as σ-donor towards the metal. As a consequence of synergic bonding the metal–carbon bond is strengthened, while the carbon–oxygen bond is weakened. The weakening of the CO bond is most readily detected by vibrational spectroscopy [7,8], where $\bar{\nu}$CO, the stretching frequency, is found to be very sensitive to changes in the CO-bond order caused by π-back-donation. Shifts to lower wavenumbers from the value of $\bar{\nu}$CO(g) at 2143 cm^{-1} [9] are not only used to detect and estimate the extent of synergic bonding, but also to assign coordination modes to the carbonyl ligand: terminal, monodentate CO groups are usually found to absorb between 2125 and 1850 cm^{-1}, while bridging bidentate groups have $\bar{\nu}$CO values between 1860 and 1700 cm^{-1} [4,7,8] (see Table 2).

Metal–carbon vibrations are less easily detected and their shifts are not readily analysed because they are usually found in a more "cluttered" region of the vibrational spectrum and the bands are occasionally of low intensity, but some attempts have been made [10]. However, ^{13}C-NMR has become a valuable diagnostic tool [11], where chemical shifts are observed between 190 and 215 ppm, compared with δ for CO at 184 ppm. Some limited use has been made of X-ray photoelectron spectroscopy (X-PES) where C1s and O1s binding energies shift to lower energies relative to CO. These shifts in binding energy are correlated with the extent of metal-to-CO π-back-donation [12,13].

In addition to these experimental criteria, which are summarized in Table 2, the conditions for the formation of synergic metal–CO bonds have become well established and are summarized briefly here.

(i) The metal should have electrons in orbitals of suitable symmetry available for π-back-donation, should be found in the middle section of the three d-series, and should be in a low oxidation state, preferably 0 ± 1. As a consequence there are very

TABLE 2

Spectroscopic criteria for synergic metal–CO bonding

CO		
Vibrational spectroscopy		
(i) Terminal CO	$\tilde{\nu}$C–O $\tilde{\nu}$ (cm^{-1})	f_r 10^2 (N m^{-1})
	2125–1850	18.8–14.5
	$\tilde{\nu}$M–C (cm^{-1})	
	360–560	
(ii) Bridging bidentate CO	$\tilde{\nu}$C–O $\tilde{\nu}$ (cm^{-1})	f_r 10^2 (N m^{-1})
	1860–1700	14.6–13.0
^{13}C-NMR δ (ppm)		
(i) Terminal CO	185–200	
(ii) Bidentate bridging CO	239–275	
He and X-PES First ionization energy (eV)	14.013(3)	
Binding energies (eV)		
(i) C1s	295–300	
(ii) O1s	541–538	
Metal radii (Å)		
Metallic radii for cubic close packing and CN 12		
Cu 1.77, Ag 1.44, Au 1.44, Pd 1.37, Pt 1.38		
Shannon ionic radii for CN 2 (Cu, Ag) and 4 (Pd, Pt)		
Cu 0.60, Ag 0.81, Pd 0.78, Pt 0.74		
van der Waals radii		
Cu 1.40, Ag 1.72, Au 1.66, Pd 1.63, Pt 1.75		

few cationic carbonyl complexes known [14], with the vast majority of the carbonyl derivatives neutral or anionic.

(ii) The ready formation of supported and unsupported metal–metal bonds will widen the scope from mononuclear to polynuclear complexes with the metal again in a low overall oxidation state.

(iii) Of the additional ligands, better π-acceptor ligands will labilize the metal–CO bond and will often replace CO in substitution reactions. Among the halides, a very common substituent in metal-carbonyl derivatives, strongly electron-withdrawing halides decrease the ability of the metal centre to engage in π-back-donation, while good π-donors will enhance the scope of derivatives and their thermal stability. For metal-carbonyl halides the general order of stability is found to be $I > Br > Cl$, with metal-carbonyl fluorides rather uncommon [4,5].

(iv) The effective atomic number rule (i.e. the tendency of the metal to achieve the next nearest noble gas configuration) is generally obeyed. This rule is used to judge chemical reactivity (e.g. oxidizing or reducing ability) and thermal stability of transition-metal carbonyls. It also permits one to deduce the presence or absence of metal–metal bonds in polynuclear complexes, where molecular structures are either not available or are difficult to interpret owing to bridging ligands.

The essential features of synergic metal—CO bonding appear also to apply to three additional, interrelated areas: (i) CO adsorbates on transition-metal surfaces [15,16]; (ii) the products of the reaction of metal atoms with carbon monoxide, studied by matrix-isolation techniques [17] in cases where no thermally stable metal carbonyls are known; (iii) highly reduced carbonylate anions such as $[M(CO)_5]^{3-}$, M = Nb or Ta [18], or $[Ti(CO)_6]^{2-}$ [19].

For metal—CO absorbates, $\bar{\nu}$CO for monodentate terminal groups are found between 2130 and 2000 cm^{-1} [15,16], with lower $\bar{\nu}$CO values attributed to various bridging configurations [15].

Of the thermally unstable binary carbonyls studied by matrix isolation, three examples of particular relevance to this account may be mentioned: tetrahedral $Pd(CO)_4$ [20], $Pt(CO)_4$ [21], and linear $Au(CO)_2$ [22]. The tetracarbonyls of palladium and platinum extend the series in group 10 from $Ni(CO)_4$, the first binary carbonyl to be reported [23], downwards. All of these molecules are observed together with smaller fragments of the type $M(CO)_n$, M = Pd or Pt and $n = 1$, 2 or 3, and evidence for bonding of gold to CO over oxygen is also obtained from vibrational spectra. In all instances of matrix-isolated metal carbonyls the CO stretching frequencies are observed well below 2143 cm^{-1} [9], $\bar{\nu}$CO found for gaseous CO. Alkali metal reduction in liquid ammonia produces isolable thermally stable, but occasionally shock-sensitive, sodium salts with carbonylate anions with the metal in very high negative formal oxidation states such as −3 or −2 [18,19,24,25], termed highly reduced metal carbonylates. In all instances the effective atomic number rule is obeyed. High formal negative charges on the metal are very favourable for π-back-donation and $\bar{\nu}$CO may be found as low as approximately 1800–1500 cm^{-1} [18]. Conventional geometries (trigonal bypyramidal or octahedral) appear to be present.

Of the three groups, the highly reduced carbonyls are useful reagents in organometallic chemistry, while the metal CO adsorbates on metallic surfaces play an important role both in surface chemistry and in the elucidation of heterogeneously catalysed carbonylation processes [15,16]. The matrix-isolated binary metal carbonyls, owing to their low thermal stabilities, have not progressed markedly beyond mere laboratory curiosities. The extensive studies [17] have so far not revealed new bonding modes or unexpected coordination geometries, and the molecular fragments that have been identified in these studies show no similarities to the thermally stable binary carbonyl cations of gold, platinum and palladium that are discussed in this review.

In summary, metal-to-carbon π-back-donation plays an essential role in numerous transition-metal carbonyl derivatives, including highly reduced carbonyls, CO-adsorbates and matrix-isolated metal-carbonyl fragments, and it is for this reason that CO is occasionally ranked on a par with or even superior to the isoelectronic cyanide ion, CN^-, in the spectrochemical series [26] even though a fundamental difference becomes immediately obvious: there are now binary metal-cyanide derivatives, mostly complex anions, known with a variety of coordination geometries for all transition metals, and some of the lanthanides and actinides as well [27,28]. Thermally stable binary carbonyls are largely confined to groups 5–10. In addition, stable cyanide complexes form also, where conditions are not conducive to π-back-donation (e.g. where the metal is found in a high oxidation state) or has a d^0 or d^{10} electron configuration (e.g. for post transition- or lanthanide-metal ions). It is apparent that the cyanide ion is also an excellent σ-donor and does not have to rely on π-bonding to form stable metal complexes. These conclusions have been reached by others based on comparative MO calculations [29].

The question may be raised whether thermally stable CO complexes or adducts can be obtained that are comparable with the corresponding cyanide complexes even though, as judged by the experimental criteria summarized above, π-back-donation is either drastically reduced or possibly absent. This question is now examined in detail.

2.2. Carbon monoxide as a σ-donor ligand

There are two principal avenues open for the study of chemical systems, where CO functions largely as a coordinating σ-donor ligand: (i) compounds obtained by the interaction of CO with neutral, molecular Lewis acids, formed by main-group elements that do not have d-electrons for π-back-donation and still form sufficiently stable adducts with the weak Lewis base CO; (ii) the use of selected metal and non-metal cations that cannot or will not engage in π-back-bonding.

2.2.1. CO adducts with boron Lewis acids

In the first group, three 1:1 CO adducts with BH_3, B_4H_8, and BF_3 are known and merit some consideration. The gaseous adduct BH_3CO was first reported in 1937 [30]. Its molecular structure was determined by electron diffraction [31] and microwave spectroscopy [32], and while $\bar{\nu}CO$ is, with 2169 cm^{-1} [33-35], higher than 2143 cm^{-1} for gaseous CO, it appears from a subsequent force-field study [36] using the Wilson FG-matrix method [36a] that the high band position is due in part to vibrational mixing with BH_3 vibrations. The stretching force constant obtained is, with 18.05×10^2 N m^{-1}, lower compared with that of CO (18.6×10^2 N m^{-1}) and calculated stretching frequencies are between 2101 and 2107 cm^{-1} for the ^{10}B, ^{11}B, ^{1}H, and ^{2}D isotopomers.

The bonding in BH_3CO and other BH_3 adducts has been studied by photoelectron spectroscopy [37], where it is concluded that π-back-donation from a filled BH_3 molecular orbital, the HOMO, of e-symmetry to the π^* MO of CO, results in a significant stabilization of the BH_3 CO as suggested previously [38]. In addition, rehybridization of the 4σ and 5σ MOs results in a strengthening of the C–O bond. Hence it appears that π-bonding plays a role in BH_3CO. However, the B–C bond remains weak and the bond energy is estimated to be about 80 kJ mol^{-1} [38].

The chemistry of BH_3CO provides examples of nucleophilic attack either on B or on C, e.g. trimethylamine will displace CO to give the adduct $H_3BN(CH_3)_3$ [30], while NH_3, CH_3NH_2, and $(CH_3)_2NH$ all form 2:1 adducts with BH_3CO [39] where $\bar{\nu}CO$ is lowered to about 1640 cm^{-1}. The adduct with methylamine is formulated as an ionic solid of the type $[H_3NCH_3]^+[H_3BC(O)NHCH_3]^-$ [39] and the molecular structure of this salt has been obtained [39b]. Similar behaviour is found for B_4H_8CO [40] in the reaction with ammonia. It is suggested that the boranecarbamate anion is also present here.

At least BH_3CO is relatively stable with respect to dissociation into CO and BH_3 or B_2H_6. This cannot be said for $BF_3 \cdot CO$, which according to a study [41] by molecular beam resonance spectroscopy is a van der Waals molecule with a B–C bond length of 2.886 Å, compared with 1.540 Å in BH_3CO [32]. Since there do not appear to be any other reasonably stable neutral molecular adducts of CO studied by vibrational spectroscopy, it remains to consider CO complexes or adducts with positively charged species, non-metal or metal cations, which may be viewed as atomic Lewis acids.

2.2.2. The HCO^+ cation

By far the simplest cation and the strongest Lewis acid of this type is the free proton H^+. Its adduct with CO, the formyl cation HCO^+, is the subject of much recent interest. The formyl cation has been suggested as a primary ionic product in the combustion of hydrocarbons. It has also been observed as a reasonably abundant species in interstellar molecular clouds [42], and its microwave spectrum is known [43]. In addition, the formyl cation is postulated as a reactive intermediate in many acid- and superacid-catalysed formylation reactions with CO [44]. Attempts to observe the cation by NMR spectroscopy under stable ion conditions using ^{13}C-enriched CO in superacid solution have been unsuccessful, owing to rapid proton exchange even at low temperatures [44]. However, matrix-isolation experiments have allowed detection of weakly bound molecular complexes of the types $OC \cdots HF$ and $CO \cdots HF$, with the former the most stable [45]. Even though the microwave spectrum of HCO^+ was observed in 1975 for the first time in the laboratory [43b], recording the complete vibrational spectrum became a protracted process [46–48]. By now all three fundamentals are known, and we have recently reported on force-field calculations for HCO^+ in the course of a general study on gold carbonyl derivatives [49] which is discussed in more detail below. While $\bar{\nu}CO$ is, with 2184 cm^{-1} [46], well above the value for $\bar{\nu}CO(g)$ of 2143 cm^{-1} [9], the stretching force constant of 21.3×10^2 N m^{-1} is the highest so far reported [49]. It appears that this value represents the upper limit for a complex with σ-bonded CO in the complete absence of π-back-donation, and the value obtained [49] may be used as a bench mark in judging the extent of π-back-donation in other complexes.

In addition, HCO^+ has played an important role in recent developments in the area of coordinated CO complexes, because it was an attempt to protonate carbon monoxide in the superacid system HSO_3F–$Au(SO_3F)_3$ [50,51] in the search of HCO^+ that resulted in the accidental discovery of $[Au(CO)_2]^+$ and $Au(CO)SO_3F$ [52].

2.3. Noble- and coinage-metal carbonyl derivatives

This group consists of two general interrelated types of derivatives: (i) *carbonyl cations* of the metals Cu, Ag, and Au with the metal in the +1 formal oxidation state, as well as Pd (formal oxidation state +1 and +2) and Pt (oxidation state +2); (ii) *cationic carbonyl complexes* of the same metals in the oxidation states listed above. These carbonyl complexes may be mononuclear and polynuclear, and involve, in addition to CO, an electronegative substituent, e.g. Cl or Br. Where this substituent becomes extremely weakly nucleophilic, we have a transition to carbonyl cations in the resulting compounds.

While noble-metal carbonyl cations were discovered very recently, the cationic complexes have a very long history, as mentioned in the general introduction. This history is reviewed briefly, which allows also the introduction of the principal members of this small and select group of metal-carbonyl complexes.

2.3.1. Noble- and coinage-metal carbonyl halides: early developments

The discovery and separation of the three platinum(II) carbonyl chlorides $Pt(CO)_2Cl_2$, $Pt_2(CO)_2Cl_4$, and $Pt_2(CO)_3Cl_4$ by P. Schützenberger in 1868–1870 [2] predate the first synthesis of nickel (0) tetracarbonyl [23], $Ni(CO)_4$, by 22 years and mark the beginning of metal-carbonyl chemistry. A later report of the corresponding three Pd(II) carbonyl chlorides [53] in 1898 was subsequently found to be erroneous by Manchot and König [54], who argued that the palladium used to prepare the starting material $PdCl_2$ had contained substantial amounts of platinum. A year later the same authors reported the first synthesis of a palladium(II) derivative, $Pd(CO)Cl_2$ [55]. The nearly simultaneous discovery of gold(I) carbonylchloride, Au(CO)Cl, by Manchot and Gall [56] and Kharash and Isbell [57] occurred in 1925 (Kharash and Isbell published their results five years after the initial discovery). It is interesting to note that Au(CO)Cl remained for about 65 years the only mononuclear carbonyl derivative of gold. The principal method of synthesis involved reductive carbonylation of gold(III) chloride.

Manchot and König also pioneered the use of a strong protonic acid, conc. H_2SO_4, in an unsuccessful attempt to obtain a silver(I) carbonyl derivative [58]. A material of the composition $Ag_2SO_4 \cdot CO$, produced in situ, was found to be thermally unstable. Only recently has it been possible to obtain isolable carbonyl complexes of silver(I) (vide infra).

Early postulates regarding the existence of copper carbonyl species go back a long time as well and concern two separate areas: (i) the transport of metallic copper in a CO atmosphere [59] and (ii) the absorption of gaseous CO by solution of

Cu(I) in various solvents [60,61] at a 1:1 stoichiometric ratio (e.g. in aqueous hydrochloric acid). The isolation and structural characterization of Cu(CO)Cl, however, is of very recent date [62].

As is apparent from this brief summary, the roots of the area of non-classical metal carbonyls can be traced well back, often into the last century. This older work has been reviewed extensively in the past; hence a detailed account is not necessary here. Bruce [63] has reviewed early work involving group 11 metals (Cu, Ag, Au). In addition, reviews on carbonyls of the platinum metals (Rh, Ir, Pd, Pt) [64] and on palladium carbonyls [65] are available.

In all early studies the unusual nature of the metal–CO bond was not recognized, and the next section deals with the use of spectroscopic and structural techniques.

2.3.2. *Spectroscopic and structural studies on noble-metal carbonyl derivatives*

The unusual nature of the metal ion–CO bond in these compounds was first revealed in a study of the vibrational and ^{13}C-NMR spectra [66] of Au, Pt, and Pd carbonyl derivatives and the implication that metal ion to CO π-back-donation was substantially reduced was soon recognized by Calderazzo and coworkers [67–69], who made extensive use of aprotic solvents such as $SOCl_2$ both in the synthesis and in the spectroscopic solution studies of noble-metal carbonyl chlorides. In thionylchloride, CO addition to metal halides at relatively mild conditions and low CO pressure (1) is possible [70,71]:

$$2PdCl_2 + 2CO \xrightarrow[120°C]{SOCl_2} Pd_2(CO)_2Cl_4 \qquad (1)$$

and the reaction produces binuclear or mononuclear carbonylchlorides e.g. (2) [72]:

$$PtCl_2 + 2CO \xrightarrow{SOCl_2} cis\text{-}Pt(CO)_2Cl_2 \qquad (2)$$

Also the conversion of the thermodynamically more stable *cis*-$Pt(CO)_2Cl_2$ to the *trans*-isomer via monomer dimer equilibria of types (3) and (4) [73,74],

$$2\ cis\text{-}Pt(CO)_2X_2 \rightleftarrows Pt_2(CO)_2X_4 + 2CO \qquad (3)$$

$$Pt_2(CO)_2X_4 + 2CO \rightleftarrows 2\ trans\text{-}Pt(CO)_2X_2 \quad X = Cl, Br \text{ or } I \qquad (4)$$

and the reductive carbonylation of higher valent metal halides such as $AuCl_3$ [75] or $PtCl_4$ [72b] are now easily accomplished, *via* e.g. (5) [75]

$$AuCl_3 + 2CO \xrightarrow{SOCl_2} Au(CO)Cl + COCl_2 \qquad (5)$$

Finally, addition of $AuCl_3$ to Au(CO)Cl according to (6) [76]

$$AuCl_3 + Au(CO)Cl \rightarrow Au_2(CO)Cl_4 \tag{6}$$

afforded the first binuclear carbonyl derivative of gold with $\bar{\nu}$CO at 2180 cm^{-1}.

In addition to interesting synthetic procedures, the use of $SOCl_2$ and similar solvents allowed various spectroscopic (NMR, vibrational) and calorimetric measurements in solution [67–69]. The spectroscopic results are summarized in Table 3.

The use of $SOCl_2$ and similar aprotic solvents combined with the availability of metal chlorides as suitable starting materials may be seen as a limitation of research in this area to the study of metal-carbonyl chlorides, which nevertheless resulted in the synthesis and characterization of a substantial number of mononuclear and dinuclear, neutral or anionic metal-carbonyl derivatives of Pt, Pd, and Au. In addition, an interesting new synthetic route to $Pt(CO)_2Cl_2$, the reaction of Pt atoms with oxalyl chloride $C_2O_2Cl_2$, has been reported [77], but this approach does not widen the scope of known carbonyl derivatives of the noble metals. The general order of thermal stability of the $M(CO)_nX_m$ derivatives with M = Pt, Pd or Au and X = Cl, Br or I, is found to be Cl > Br > I [69,78], which is a reversal of the order observed for the classical transition-metal carbonyl halides, as discussed above. The reversed stability order for noble-metal carbonyl halides is best illustrated by the known gold(I) complexes. As discussed, Au(CO)Cl [56,57] has been known for more than 65 years, while Au(CO)Br is, according to a recent report [76], thermally unstable and is only characterized in cyclohexene solution, with Au(CO)I so far unknown.

TABLE 3

Selected carbonyl derivatives of group 10 and 11 metals and their spectroscopic properties

Compound	Description	$\bar{\nu}CO_{av}$ (cm^{-1})[a]	δ^{13}C-NMR (ppm)	Reference[b]
cis-$Pt(CO)_2Cl_2$	White solid	2157.5 (2164.5)	151.6 $J(^{195}Pt-^{13}C$ 1576 Hz)	66
cis-$Pt(CO)_2Br_2$	White solid	2143 (2153)	152.0 $J(^{195}Pt-^{13}C$ 1566 Hz)	66
Au(CO)Cl	White solid	2162 (2183)	170.8	66
$[Pt(CO)Cl_5]^-$		2191		80
$Au_2(CO)Cl_4$		2180	170.8	76b
$Pd_2(CO)_2Cl_4$		2166		70, 71
$Pt_2(CO)_2Cl_4$		2146		80
$[Cu(CO)][AsF_6]$		2180		82
CO on ZnO at 77 K		2169–2178		83

[a] The wavenumber in brackets refers to Raman shifts of solid samples, while IR spectra are obtained in solutions in aprotic solvents.

[b] The reference refers to the spectroscopic data not to the synthesis.

Another limitation is posed by the low ionizing ability of thionylchloride, $SOCl_2$, and similar aprotic solvents used in this area in the past on the one hand, and the relatively high nucleophilicity of the halide ligands on the other hand. As a consequence, cationic complexes of the noble-metal carbonyls are virtually unknown. Where molecular structures have become known, as for Au(CO)Cl [79], which is a four-atomic linear monomer, or for Cu(CO)Cl [62], a chloride-bridged polymer, or $Pt_2(CO)_2I_4$ [80], carbonyl cations are not present. Only in two instances, both involving fluorine-containing ligands ($[Cu(CO)][CF_2CO_2]$ [81] and $[Cu(CO)][AsF_6]$ [82]), has the presence of $[Cu(CO)]^+$ been suggested, based on spectroscopic evidence. For the hexafluoroarsenate a rather high $\bar{\nu}$CO value of 2180 cm^{-1} is reported [82], and it is interesting to note that similarly high $\bar{\nu}$CO values are reported for CO adsorbates on solids containing metal cations, as for example, in ZnO where $\bar{\nu}$CO depends on the extent of surface coverage by CO, the value ranges between 2169 and 2177 cm^{-1} according to a study at 77 K [83]. Similar vibrational spectra have been reported for CO adsorbates on cuprous fluoride and on CuO [84a]. In a different approach, CO complexes with monomeric nickel(II) halides were studied by matrix isolation [84b] in an attempt to extend the field of group 10 metalcarbonyl halides [67–69] to nickel. For a complex formulated as $NiF_2 \cdot CO$, $\bar{\nu}$CO was found at 2200 cm^{-1}, the highest reported CO stretch at that time. There is also a theoretical study of the bonding in CO adducts to nickel ions Ni^{2+} and Ni^{3+} [84c].

These examples make a simple point: changing the metal surface [15,16] to a metal salt reduces π-back-bonding in CO adsorbates as well as in matrix-isolated metal-chloride CO complexes, when compared with the use of metal atoms [17,20–22].

In summary, a number of group 10 and 11 metal-carbonyl derivatives including CO adsorbates on metal salts [83,84a] and matrix species [84b] have been known, where vibrational spectra as well as ^{13}C-NMR spectra indicate reduced π-back-bonding. In addition, some of the descriptive features of the molecular compounds show differences to those of the classical transition-metal carbonyl compounds. The oxidation state of the metal ranges from +1 for Cu, Au, Pd, and Pt, to +4 in the case of the anion $[Pt(CO)X_5]^-$, X = Cl or Br, obtained by the oxidative addition of Cl_2 or Br_2 to $[Pt(CO)X_3]^-$ [85]. Oligomerization occurs either through halide bridges or, in the case of some Pd(I) compounds, through bridging CO [64,65] rather than via direct metal–metal bonds, and the effective atomic rule is frequently not observed. The reversed order of thermal stability for noble-metal carbonyl halides has already been discussed.

2.3.3. Recent developments: the use of strong protonic acids and weakly basic anions to generate and stabilize metal–CO cations

In addition to these isolated and characterized neutral or anionic carbonyl derivatives, a number of binary carbonyl cations of Cu(I) and Ag(I) of the type

$[Cu(CO)_n]^+$, $n=1$, 3, or 4, and $[Ag(CO)_n]^+$, $n=1$ or 2, have been generated in strong protonic acids such as H_2SO_4, HSO_3F, HSO_3CF_3, HF, and $BF_3 \cdot H_2O$ [58,86–91]. The method of generation has been the dissolution of Cu_2O or Ag_2O in the protonic acid, the application of relatively high CO pressures frequently at temperatures of −40°C, and measurements of CO uptake by gas/volumetric methods, following closely earlier attempts to synthesize silver(I) carbonyl derivatives in H_2SO_4 by Manchot and König [54]. In addition, IR [86], Raman [87], and ^{13}C-NMR [65] are employed. The results of the spectroscopic measurements suggest reduced π-back-donation in the solvated metal-carbonyl cations, with $\bar{\nu}$CO between 2160 and 2193 cm^{-1}, and $\delta^{13}C$ shifted to lower ppm values relative to CO.

Even though it has not been possible to isolate solid metal-carbonyl salts from the acid solutions, possibly owing to their low thermal stability, two interesting consequences of these studies may be mentioned. (i) It is reportedly possible to coordinate up to 4 mol CO per mole Cu(I) and up to 2 mol CO per mole Ag^+, depending on temperature, CO pressure, and the acid chosen. (ii) CO uptake will decrease with increasing solvating tendency or "basicity" of the acid in the following order: $H_2SO_4 > HSO_3CF_3 > HSO_3F > HF > BF_3 \cdot H_2O$.

Possibly owing to the thermal instability and concomitant high reactivity of the metal ion–CO solutions, extensive use has been made of them in carbonylation reactions of olefins, alcohols, and saturated hydrocarbons [91–94]. The low thermal stability of the solvated silver(I) carbonyl cations must be seen as the principal reason for the failure to isolate solid silver(I) carbonyl compounds until very recently [95], when Strauss and coworkers succeeded in the isolation and characterization by X-ray diffraction of the first complex of the composition $Ag(CO)B(OTeF_5)_4$. The formation reaction

$$AgOTeF_5 + B(OTeF_5)_3 + CO \xrightarrow[25^\circ C,\ 36\ h]{P=200\ Torr} Ag(CO)B(OTeF_5)_4 \tag{7}$$

involves a thermally labile intermediate, $[Ag(CO)_2][B(OTeF_5)_4]$, which decomposes within minutes to $Ag(CO)B(OTeF_5)_4$, but within a few hours the remaining CO is released and the starting materials $AgOTeF_5$ and $B(OTeF_5)_3$ reform.

In spite of the reversible interaction of CO with Ag^+, the molecular structures of $Ag(CO)B(OTeF_5)_4$ [95], and more recently of $[Ag(CO)_2][B(OTeF_5)_4]$ [96], have been obtained at −125 and −100°C respectively, by single-crystal X-ray diffraction. In $Ag(CO)B(OTeF_5)_4$, a nearly linear AgCO group (AgCO = 176 (1)°) is bonded to two oxygen atoms of the $-OTeF_5$ groups. The reported bond distances, a long Ag–C bond of 2.10 Å and a short C–O bond of 1.077(16) Å, as well as the high $\bar{\nu}$CO value of 2204 cm^{-1}, are indicative of substantially reduced π-back-bonding.

In $[Ag(CO)_2][B(OTeF_5)_4]$ [96], a linear $[Ag(CO)_2]^+$ cation (initially identified in acid solution [86,87]) appears to be present, but the large estimated standard deviations do not permit a detailed analysis of the C–O bond distances. High $\bar{\nu}$CO values of 2207 cm^{-1} for the IR-active mode for this compound, and similar high CO stretching frequencies observed in the IR spectra of other silver mono-carbonyl and di-carbonyl complexes with $[Zn(OTeF_5)_4]^{2-}$ as counteranions, are consistent with the presence of coordinated CO ligands with little or no metal-to-CO π-back-donation for these compounds.

It appears that the use of large and complex weakly coordinating anions made up of highly electronegative $-OTeF_5$ (teflate) groups allows for the isolation and structural characterization of various silver(I) carbonyl compounds. The previously [58,86,87] noted thermal instability of silver(I) carbonyls still remains a problem and results in a reversible CO interaction with Ag^+.

A different approach is chosen for the generation of the biscarbonyl gold(I) cation $[Au(CO)_2]^+$ because suitable gold(I) compounds comparable with $AgOTeF_5$ [97] are not available [98,99] and have to be generated in situ. An interesting approach is the oxidation of gold by UF_6 in anhydrous HF as solvent in the presence of carbon monoxide [100] according to

$$Au+2CO+UF_6 \xrightarrow[\text{anhydrous HF}]{25°C} [Au(CO)_2][UF_6] \tag{8}$$

The low thermal stability of the reaction product permits characterization of the $[Au(CO)_2]^+$ cation by IR spectroscopy only. The reduction of gold(III) compounds provides another route to $[Au(CO)_2]^+$ [52]. Again a protonic acid, HSO_3F, is employed as solvent with CO as reducing agent:

$$Au(SO_3F)_3+3CO \xrightarrow[HSO_3F]{} [Au(CO)_2]^+ + SO_3F^- + CO_2 + S_2O_5F_2 \tag{9}$$

The reductive carbonylation of $Au(SO_3F)_3$ in HSO_3F proceeds similarly to the reduction of $AuCl_3$ in $SOCl_2$ [75] with two exceptions: (i) the phosgene analogue $CO(SO_3F)_2$ formed during the reaction is thermally unstable and decomposes to CO_2 and $S_2O_5F_2$ [101], and (ii) the use of a strongly ionizing solvent such as HSO_3F allows the formation of the electrophilic $[Au(CO)_2]^+$ cation and its detection by IR, Raman, and ^{13}C-NMR spectroscopy [49].

Attempts to isolate an $[Au(CO)_2]^+$ fluorosulphate by removing the solvent and the volatile reaction products in vacuo were unsuccessful. It appears that the SO_3F^- ion is sufficiently basic to compete successfully with CO for a coordination site on gold, and $Au(CO)SO_3F$ is isolated in quantitative yield [52] according to

$$[Au(CO)_2]^+_{solv} + SO_3F^- \xrightarrow[HSO_3F]{80°C} Au(CO)SO_3F + CO(g) \tag{10}$$

Gold(I) carbonyl fluorosulphate is thermally stable up to about 190°C, has $\bar{\nu}CO$ at $2197\,cm^{-1}$, and will ionize in HSO_3F to give the $[Au(CO)]^+$ ion in HSO_3F and magic acid, HSO_3F+SbF_5 [49]. According to the vibrational spectra, a strongly ionically polarized, monodentate $-OSO_2F$ group is weakly bonded to gold. Interestingly, $Au(CO)SO_3F$ is, in addition to $Au(CO)Cl$ (reported about 65 years earlier), the only thermally stable Au(CO) derivative. In contrast to the Ag(I)CO derivatives discussed above, the CO uptake is not reversible and the exact decomposition mode is still unclear. The unknown compound $AuSO_3F$ is not obtained by thermal decomposition of $Au(CO)SO_3F$.

A different course of the reduction by CO is observed when low CO pressure is employed. In this case only partial reduction of gold(III) fluorosulphate is observed, according to

$$2Au(SO_3F)_3 + CO \xrightarrow[HSO_3F]{25^{\circ}C} 2Au(SO_3F)_2 + CO_2 + S_2O_5F_2 \text{ [102]} \qquad (11)$$

This reduction by CO has a parallel in the formation of $(AuCl_2)_4$ from $AuCl_3$, where the structure is known [103].

The diamagnetic solid of composition $Au(SO_3F)_2$ is best formulated as a mixed valence gold(I)–gold(III) fluorosulphate. The compound, which may also be obtained by reduction of $Au(SO_3F)_3$ with gold powder, is sparingly soluble in HSO_3F. The resulting paramagnetic solutions contain the solvated Au^{2+} cation according to a recent electron spin resonance study [102,104]. The obviously oligomeric $Au(SO_3F)_2$ and Au^{2+}(solv) are normally not encountered when sufficiently high CO pressure is used and a near-quantitative yield of $Au(CO)SO_3F$ is easily obtained.

The subsequent conversion of $Au(CO)SO_3F$ to $[Au(CO)_2][Sb_2F_{11}]$ is motivated by the intent to replace the fluorosulphate anion by an even less basic antimony(V) fluoro anion [105]. The method chosen, the solvolysis of $Au(CO)SO_3F$ in liquid SbF_5 and with CO present according to

$$Au(CO)SO_3F + CO + 4SbF_5 \xrightarrow[SbF_5]{\text{excess CO, } 25^{\circ}C} [Au(CO)_2][Sb_2F_{11}] + Sb_2F_9SO_3F \qquad (12)$$

follows published precedents, where main-group, organometallic or transition-metal fluorosulphates are solvolysed in an excess of antimony(V) fluoride to permit the syntheses of fluoroantimonate derivatives such as $Br_2[Sb_3F_{16}]$ [106], $[(CH_3)_2Sn][Sb_2F_{11}]_2$ [107] or $Pd[SbF_6]_2$ [108]. This route becomes the preferred synthetic approach, where fluorosulphates are more readily available than are the corresponding fluorides.

Bis(carbonyl)gold(I) undecafluoro antimonate(V), $[Au(CO)_2][Sb_2F_{11}]$, is the first reported example of a compound with a thermally stable, linear metal-carbonyl cation. The material is stable up to 130°C, in contrast to the corresponding biscarbonyl silver(I) cation. The use of ^{13}C and ^{18}O isotopic substitution allows a complete vibrational assignment, a normal coordinate analysis, and general valence force field calculations. The results of the force field calculations permit a comparison with previously reported force constants for the isoelectronic species $Hg(CN)_2$ and $[Au(CN)_2]^-$ [109]. It is found that the strength of the metal-carbon bond decreases from $[Au(CN)_2]^-$ over $Hg(CN)_2$ to $[Au(CO)_2]^+$, while the intra-ligand bond increases in strength in the same order, which reflects decreasing π-back-donation. The stretching force constant f_r for $[Au(CO)_2]^+$ is, with 20.0×10^2 N m^{-1}, below the bench-mark value 21.3×10^2 N m^{-1} for HCO^+ [49]; however the average $\bar{\nu}CO$ is, with 2235.5 cm^{-1}, over 90 cm^{-1} higher than for CO itself.

Within the group of known gold(I) carbonyl derivatives, π-back-donation as judged by $\bar{\nu}CO$ decreases in the order $Br^- > Cl^- > SO_3F^- > UF_6^- > Sb_2F_{11}^-$, which appears to coincide with the order of decreasing anion basicity. Within the group of $[Au(CO)_2]^+$ derivatives inclusive of the solvated cation [52], the thermal stability increases again with decreasing anion basicity: $HSO_3F/SO_3F^- < UF_6^- < Sb_2F_{11}^-$.

These trends suggest positive charges on gold, and consequently polar contributions to the metal–carbon bond play an important role in the formation of thermally stable gold(I) carbonyl compounds. In addition to these polar contributions, the noted ability of univalent gold to form strong covalent bonds [98], in compounds mostly with coordination number 2 and a linear geometry, becomes important as well. Covalent bond strength is possibly aided by relativistic effects [110]. These are said to be at a maximum for gold according to recent calculations for gold(I) halide anions [111], and may explain the striking difference in thermal stability between gold(I) and silver(I) carbonyl derivatives. The reversibility of CO uptake by silver(I) complexes, but not by gold(I) compounds, has a simple explanation: dissociation of CO leads in the case of Ag(I) compounds to existing thermodynamically stable compounds such as $AgOTeF_5$ [97]. The corresponding gold(I) compounds such as $AuSO_3F$, $AuUF_6$, or $AuSb_2F_{11}$ are, just like AuF [99], unknown and evidently not preparable by pyrolysis of the carbonyl precursors discussed. In all instances a more complex decomposition reaction is observed, which results essentially in the formation of elemental gold and various volatile decomposition products [49,52].

While the clean elimination of CO on heating is not observed, the reactivity of the gold–carbon bond is evident from CO cleavage and ligand substitution reactions. Fast CO exchange between $[Au(^{13}CO)_2]^+$ and $[Au(^{12}CO)_2]^+$ is observed at 25°C in HSO_3F using vibrational spectroscopy [49]. Slow exchange between $[Au(^{13}CO)_2]^+$ and $[Au(^{13}CO)]^+$ in HSO_3F or $HSO_3F + SbF_5$, magic acid, is observable by ^{13}C-NMR, where the two single-line resonances 174 and 158–162 ppm respectively coalesce on warming from 17 to 52°C. The formation of a dinuclear intermediate in a bimolecular reaction via a bridging CO group or possibly an isocarbonyl linkage (AuCO···Au) is likely. Ligand exchange is observed inadvertantly during an attempt to recrystallize $[Au(CO)_2][Sb_2F_{11}]$ from acetonitrile, CH_3CN. The reaction proceeds cleanly according to

$$[Au(CO)_2][Sb_2F_{11}] + 2CH_3CN \xrightarrow[CH_3CN]{25°C} [Au(NCCH_3)_2][SbF_6] + SbF_5 + 2CO \tag{13}$$

and the resulting product, $[Au(NCCH_3)_2][SbF_6]$, crystallizes in a cubic NaCl structure with a perfectly linear $[Au(NCCH_3)_2]^+$ cation on the space diagonal of the unit cell. The reaction suggests a wide potential use of $[Au(CO)_2]^+$ in the synthesis of various AuL_2^+ cations, involving ligands with better σ donor ability than CO. Not many examples of this type are known [98] and many precedents for CO-substitution reactions have been reported for Au(CO)Cl [98]. Finally, alternative routes to $[Au(CO)_2][Sb_2F_{11}]$ according to (14) [35] and (15) deserve mention:

$$AuF_3+2SbF_5+3CO \xrightarrow[SbF_5]{25^\circ C,\ 3d} [Au(CO)_2][Sb_2F_{11}]+COF_2 \tag{14}$$

$$Au(SO_3F)_3+6SbF_5+3CO \xrightarrow[SbF_5]{25^\circ C\ 1d} [Au(CO)_2][Sb_2F_{11}]$$

$$+CO_2+S_2O_5F_2+2Sb_2F_9SO_3F \tag{15}$$

Reaction (14) may be of use where AuF_3 is more readily available than $Au(SO_3F)_3$.

The facile formation of $[Au(CO)_2]^+$(solv) and $Au(CO)SO_3F$ by reductive carbonylation of $Au(SO_3F)_3$ in the previously investigated superacid system $HSO_3F+Au(SO_3F)_3$ [36,37] suggests the possible extension of this synthetic approach to the superacid system $HSO_3F+Pt(SO_3F)_4$ [112]. Reductive carbonylation occurs with similar ease, but depending on the reaction conditions two different solid materials are obtained: partial reduction of $Pt(SO_3F)_4$ produces a yellow diamagnetic solid of composition $Pt(CO)_2(SO_3F)_3$ [113], and complete reduction to Pt(II) leads to colourless $Pt(CO)_2(SO_3F)_2$ according to

$$Pt(SO_3F)_4+3CO \xrightarrow[HSO_3F]{60^\circ C} Pt(CO)_2(SO_3F)_2+CO_2+S_2O_5F_2 \tag{16}$$

Vibrational spectroscopy shows that the solid isolated from solution is exclusively *cis*-$Pt(CO)_2(SO_3F)_2$ [114] in analogy to the formation of *cis*-$Pt(CO)_2Cl_2$ in the reductive carbonylation of $PtCl_4$ in $SOCl_2$ [67,69].

Yellow $Pt(CO)_2(SO_3F)_3$ has no precedent among previously reported carbonyl derivatives of platinum [64]. Vibrational analysis suggests formulation as $[Pt(CO)_4][Pt(SO_3F)_6]$ [113] by comparison with reported spectra for the anion $[Pt(SO_3F)_6]^{2-}$ with Ba^{2+} or Cs^+ as cations [112]. The formation reaction according to

$$2Pt(SO_3F)_4+5CO \xrightarrow[HSO_3F]{25^\circ C} [Pt(CO)_4][Pt(SO_3F)_6]+CO_2+S_2O_5F_2 \tag{17}$$

requires lower CO pressure and reaction temperature. The isolation of solid $[Pt(CO)_4][Pt(SO_3F)_6]$ from solution and the separation from *cis*-$Pt(CO)_2(SO_3F)_2$ are facilitated by the limited solubility of the former in HSO_3F. In addition, *cis*-$Pt(CO)_2(SO_3F)_2$ is soluble in SO_2, but $[Pt(CO)_4][Pt(SO_3F)_6]$ is not.

The $[Pt(CO)_4]^{2+}$ cation is also observed in solution of HSO_3F by ^{13}C-NMR. The cation is generated either by redissolving $[Pt(CO)_4][Pt(SO_3F)_6]$ in HSO_3F, or as the initially formed carbonyl species during the reductive carbonylation of $Pt(SO_3F)_4$. Finally, solvolysis of *cis*-$Pt(CO)_2(SO_3F)_2$ under CO pressure in liquid

SbF_5 proceeds in complete analogy to the solvolysis of $Au(CO)SO_3F$ according to

$$Pt(CO)_2(SO_3F)_2 + 2CO + 8SbF_5 \xrightarrow[SbF_5]{40°C} [Pt(CO)_4][Sb_2F_{11}]_2 + 2Sb_2F_9(SO_3F) \quad (18)$$

and results in the formation of a white solid of composition $[Pt(CO)_4]$ $[Sb_2F_{11}]_2$, which again contains the square-planar cation $[Pt(CO)_4]^{2+}$ and is thermally stable up to 120°C [115].

Reductive carbonylation of $Pd[Pd(SO_3F)_6]$ [116,117] proceeds again very readily either in solution of HSO_3F (even though the palladium(III) fluorosulphate is only sparingly soluble) or in the solid state at room temperature and low CO pressure, to yield a yellow solid of composition $Pd(CO)_2(SO_3F)_2$. This can be converted to $[Pd(CO)_4][Sb_2F_{11}]_2$ [115] by solvolysis in an excess of antimony(V) fluoride and a CO atmosphere, like the corresponding platinum(II) compound. Judging by the strong similarity of their vibrational spectra, the compounds appear to be isostructural, which implies that both contain a square-planar $[M(CO)_4]^{2+}$ cation with M = Pd or Pt. Like the linear $[M(CO)_2]^+$ cations M = Au [49,52] or Ag [96], the tetracarbonyl complexes are unprecedented among metal-carbonyl derivatives (including the thermally unstable binary carbonyls of Pd^0 and Pt^0) studied by matrix-isolation techniques [17,20,21]. The vibrational spectrum of $[Pt(CO)_4][Sb_2F_{11}]_2$ is shown in Fig. 1.

There is, however, a strong similarity between the tetracarbonyl cation $[M(CO)_4]^{2+}$ and the isoelectronic pair of tetracyanide anions $[M(CN)_4]^{2-}$ [118] with M = Pd or Pt. Their vibrational spectra in the CO and CN stretching regions are summarized in Table 4, together with data for $[M(CO)_2]^+$ and $[M(CN)_2]^-$, M = Au. The spectra are consistent with a square-planar geometry for both Pd(II) and Pt(II). As found previously [49,109] for the isoelectronic pair of linear ions $[Au(CO)_2]^+$ and $[Au(CN)_2]^-$, the bond stretching force constants for the CO bond are considerably higher than those of the CN bond in the corresponding complex ions. The value of f_r for CO in $[Pt(CO)_4]^{2+}$ of 20.64×10^2 N m^{-1}, obtained according to the method of Cotton and Kraihanzel [119,120], is the highest reported so far and the weighted average of the CO stretching frequencies is, with 2260 cm^{-1} found for both $[Pd(CO)_4]^{2+}$ and $[Pt(CO)_4]^{2+}$ in their respective $Sb_2F_{11}^-$ salt, again without precedent. Even for $[Pt(CO)_4][Pt(SO_3F)_6]$, $\bar{\nu}CO_{av}$ is 2251 cm^{-1}, more than one hundred wavenumbers higher than in gaseous CO [9].

The characterization of the $[Pt(CO)_4]^{2+}$ cation by ^{13}C-NMR on isotopically labelled samples suggests a chemical shift of 140.5 ppm, which is generally lower than reported previously for platinum(II) carbonyl halides [66,69] by about 10–15 ppm, while $J^{13}C–^{195}Pt$ of 1576 Hz compares well with reported data.

Even though the two pairs of compounds *cis*-$M(CO)_2(SO_3F)_2$ and $[M(CO)_4][Sb_2F_{11}]_2$, M = Pd or Pt, give virtually superimposable pairs of vibrational spectra, which in turn suggest isostructural compounds and show comparable thermal stability, there are interesting discrepancies in the first reaction sequence, the

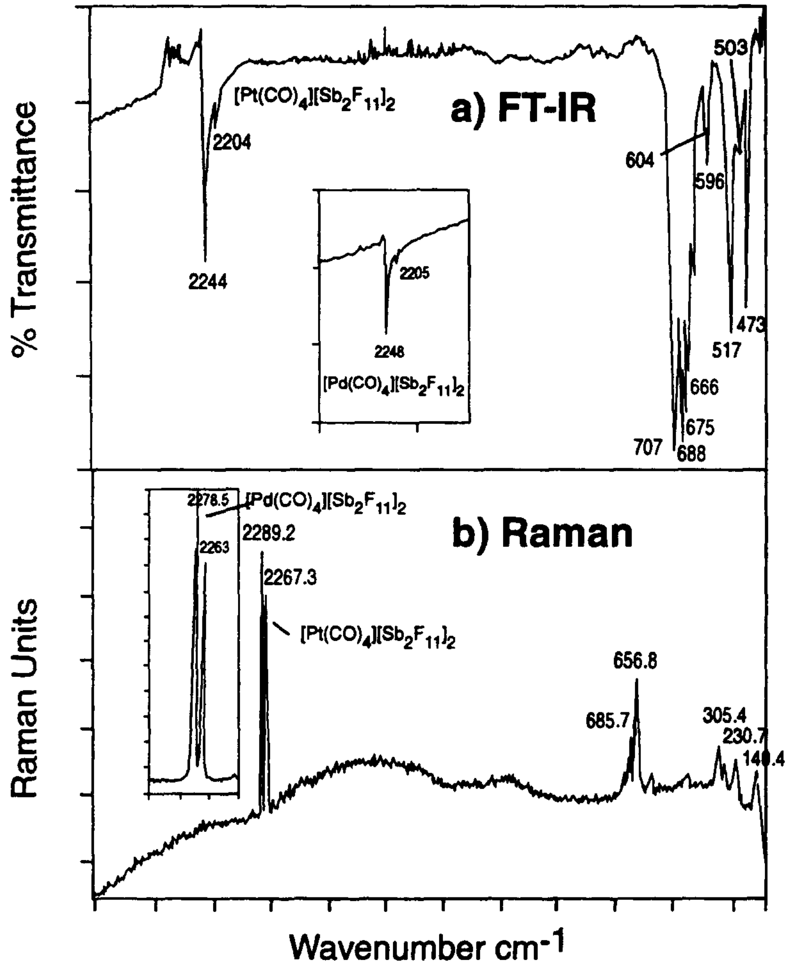


Fig. 1. The vibrational spectra of $[Pt(CO)_4][Sb_2F_{11}]_2$ and $[Pd(CO)_4][Sb_2F_{11}]_2$ (CO-stretching region only).

reductive carbonylation of $Pt(SO_3F)_4$ and $Pd[Pd(SO_3F)_6]$ respectively in HSO_3F. In the former case, the reaction proceeds slowly, and incomplete reduction allows isolation of $[Pt(CO)_4][Pt(SO_3F)_6]$ [113]. More forcing conditions (1–2 atm CO and 80°C) are required to achieve complete reduction and to allow isolation of *cis*-$Pt(CO)_2(SO_3F)_2$ in approximately quantitative yield.

The reductive carbonylation of $Pd[Pd(SO_3F)_6]$ in HSO_3F at approximately 0.5 atm CO and 25°C is complete within 1 h. The observed difference in reactivity towards CO reflects the standard reduction potentials for the M(IV)/M(II) couples which are 1.60 V for Pd and 1.10 V for Pt. The resulting product analyses as $Pd(CO)_2(SO_3F)_2$, but according to the vibrational spectra an isomeric mixture forms with *cis*-$Pd(CO)_2(SO_3F)_2$ as a minor constituent. The second, so far unidentified,

TABLE 4

Co and CN stretching vibrations for $[M(CO)_4]^{2+}$, $[M(CN)_4]^{2-}$, M = Pd or Pt, $[Au(CO)_2]^+$ and $[Au(CN)_2]^-$

Species	Vibrational frequency and assignment	Reference
$[Pd(CO)_4]^{2+}$	Raman 2278 vs (A_{1g}), 2263 s (B_{1g}) IR 2248 ms (E_u) 2205 vw (E_u ^{13}C–O)	115
$[Pt(CO)_4]^{2+}$ in $[Pt(CO)_4][Sb_2F_{11}]$	Raman 2289 (vs) (A_{1g}) 2267 s (B_{1g}) IR 2244 (s) (E_u) 2204 vw (E_u ^{13}CO)	115
$[Pt(CO)_4]^{2+}$ in $[Pt(CO)_4][Pt(SO_3F)_2]$	Raman 2281 (s) (A_{1g}) 2257 ms (B_{1g}) IR ≈2300 (E_u)	113
$[Pd(CN)_4]^{2-}$	Raman 2160 (s) (A_{1g}) 2146 (vs) (B_{1g}) IR 2136 (vs) (E_u) 2090 vw (E_u ^{13}CN)	118
$[Pt(CN)_4^{2-}$	Raman 2168 s (A_{1g}) 2149 vs (B_{1g}) IR 2133 vs (E_u) 2087.2 (E_u ^{13}CN)	118
$[Au(CO)_2]^+$- in $[Au(CO)_2][Sb_2F_{11}]$	Raman 2254 vs (Σ_g^+) IR 2217 s (Σ_u^+) 2176 w (Σ_u^+ ^{13}CO)	49
$Au(CO)_2]^+$ (solv) in HSO_3F	Raman 2246 vs (Σ_g^+) IR 2211 s (Σ_u^+) 2160 vw (Σ_u^+ ^{13}CO)	52
$Au(CN)_2^-$	Raman 2162 vs (Σ_g^+) IR 2142 s (Σ_u^+) 2094 vs (Σ_u^+ ^{13}CO)	148

isomer gives rise to two strong bands of equal intensity in the CO-stretching region at 2179 and 1967 cm^{-1}. The latter band suggests a bridging carbonyl group, which in turn would imply the presence of a CO-bridged oligomer. Monomeric *cis*-$Pd(CO)_2(SO_3F)_2$ appears to be the thermodynamically stable isomer that may be obtained in pure form either by the reductive carbonylation of solid $Pd[Pd(SO_3F)_6]$, or by heating the solution in HSO_3F to about 60°C to give single crystals of the *cis*-isomer on cooling, suitable for X-ray diffraction [121], or by allowing the solid mixture to stand at 25°C for several months.

Attempts to separate the oligomer by recrystallization from HSO_3F at 25°C produce a surprising result: over a period of 3–4 weeks, crystalline needles of composition $Pd(CO)SO_3F$ form, suggesting a reductive decomposition. The crystals allow structure determination by single-crystal X-ray diffraction [122], to be discussed subsequently, that reveals the presence of cyclic $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cations linked by weakly coordinated fluorosulphate groups into a polymeric sheet. It is curious that the same solution, depending on temperature, produces single crystals of two different palladium carbonyl compounds. While there are a number of structurally characterized polynuclear palladium(I) carbonyl derivatives, all with bridging CO ligands [123–126], *cis*-$Pd(CO)_2(SO_3F)_2$ is the first reported thermally stable *bis*-carbonyl compound of palladium(II) [69]. Organometallic derivatives of the type $Pd(CO)_2R_2$, $R = C_6F_5$ or C_6Cl_5, are unstable even at −30°C in a CO atmosphere [127].

There is a structure reported on a dimeric, chloride-bridged Pd(I) *bis*-carbonyl derivative of the type $[Pd(CO)_2\mu\text{-}Cl]_2$ [128] that does not have a precedent among the previously reported and structurally characterized Pd(I) carbonyl compounds [64,65,69], where in oligomers only CO bridges are observed [122–126]. Here terminal CO ligands are present and the Cl are bridging, which is again unusual. Close inspection of the reported unit-cell parameters, internuclear distances and bond angles, IR stretching frequencies in the CO region, and the colour, results in the disturbing observation that these data are identical within error limits to previously reported data of the well known complex $[Rh(CO)_2\mu\text{-}Cl]_2$ [129,130]. A reinvestigation of this structure is suggested.

Finally the high reactivity of $Pd[Pd(SO_3F)_6]$ in reductive carbonylation reactions allows the direct conversion of this compound to $[Pd(CO)_4][Sb_2F_{11}]_2$ by solvolysis in an excess of SbF_5 and in the presence of CO.

In summary, a serendipitous observation during an unsuccessful attempt to obtain the elusive formyl cation HCO^+ by protonation of CO in the superacid $HSO_3F + Au(SO_3F)_3$ [50,51] has led to the development of simple but highly unconventional synthetic routes to a novel group of compounds: thermally stable, cationic noble-metal carbonyl derivatives. Strong protonic acids such as HSO_3F have previously found little or no use as reaction media in metal-carbonyl chemistry. This medium has nevertheless allowed the generation and study of novel binary carbonyl cations of Au(I), Pd(II) and Pt(II). Since CO appears to be of comparable or slightly lower nucleophilicity than the self-ionization ion SO_3F^-, isolation of the cations as fluorosulphates is not observed owing to SO_3F^- vs. CO exchange, and the fluorosulphate derivatives $Au(CO)SO_3F$ [52] and *cis*-$M(CO)_2(SO_3F)_2$, M = Pd or Pt [114], are isolated instead. Substitution of SO_3F^- by the less basic fluoroantimonate(V) anion $Sb_2F_{11}^-$ [105] allows further addition of CO to the metal centres and permits isolation of $[Au(CO)_2][Sb_2F_{11}]$ [49] and $[M(CO)_4][Sb_2F_{11}]_2$ [115].

The characteristic features of the eight compounds and the three cations studied so far in HSO_3F are summarized in Table 5. A ninth compound, oligomeric $Pd(CO)_2(SO_3F)_2$, remains to be fully characterized. All compounds show high thermal stability, usually well above 100°C. This is in marked contrast to the reported silver(I) carbonyl compounds [95,96], which release CO at room temperature. Their synthesis, the addition of CO to thermodynamically stable silver(I) salts with large, poorly coordinating anions at low temperature and high CO pressure, is reversible.

In contrast, the corresponding gold(I), palladium(II), and platinum(II) cations may be generated by reduction of suitable fluorosulphate precursors in HSO_3F as solvent, but they do not appear to be capable of existence in the acid and will require stabilization by coordinating ligands in a medium where only CO and SO_3F^- are available to fill this role. Hence thermal decomposition of the resulting carbonyl compounds in Table 5 is complex and not simply a loss of CO in clearly marked steps.

The binary carbonyl cations $[M(CO)_2]^+$, M = Ag or Au, and $[M(CO)_4]^{2+}$ have allowed an extension of the range of known thermally stable binary carbonyls to the electron-rich metals in groups 10 and 11, just as the highly reduced carbonylate

TABLE 5

Cationic non-classical metal carbonyl compounds of Au, Pd and Pt

Number	Compound	Point group[a]	m.p. (°C)	dec.p. (°C)	$\tilde{\nu}CO_{av}$ (cm^{-1})	Comments	Reference
1	$Au(CO)SO_3F$	C_s	49	190	2197	White solid	52
2	$[Au(CO)]^+$ in HSO_3F	$C_{\infty v}$			2198	$\delta^{13}C$ 162 ppm	49
3	$[Au(CO)_2]^+$ in HSO_3F	$D_{\infty h}$			2231	$\delta^{13}C$ 174 ppm	49
4	$[Au(CO)_2][Sb_2F_{11}]$	$D_{\infty h}$		156	2235.5	White solid	49
5	*cis*-$Pd(CO)_2(SO_3F)_2$[b]	$\approx C_{2v}$		117	2218	Yellow solid	114
6	$[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$[b]	D_{2h}		157	2002	Orange needles	122
7	$[Pd(CO)_4][Sb_2F_{11}]_2$	D_{4h}		155	2259	White solid	115
8	*cis*-$Pt(CO)_2(SO_3F)_6]$	$\approx C_{2v}$		100	2202	White solid	114
9	$[Pt(CO)_4][Pt(SO_3F)_6]$	D_{4h}		140	2251	Yellow solid[c]	113
10	$[Pt(CO)_4][Sb_2F_{11}]_2$	D_{4h}		200	2261	White solid	115
11	$[Pt(CO)_4]^{2+}$ in HSO_3F	D_{4h}				$\delta^{13}C$ 140.5 ppm $J^{13}C\text{–}^{195}Pt$ 1576 Hz	113

[a] Refers to cation or cationic moiety.

[b] Structure determined by single-crystal X-ray diffraction.

[c] Colour due to anion, see ref. 122.

anions have allowed an extension to the early transition metals in groups 4 and 5 [18,19,25,25].

These groups, the highly reduced carbonyls and the noble-metal carbonyl cations, provide a dramatic contrast when compared, even though both are best obtained by reduction reactions: in one case liquid ammonia is used, one of the most basic protonic solvents [131], while the carbonyl cations are generated in the strongest protonic acid, HSO_3F [44,132]. π-Back-donation appears to be enhanced for the super-reduced carbonylate anions, resulting in unusually low $\tilde{\nu}CO$ values. For the cation, π-back-donation is drastically reduced, as the data in Table 5 indicate, where $\tilde{\nu}CO_{av}$ values are generally higher than 2200 cm^{-1}, which had been the upper limit for noble-metal carbonyl halides (see Table 3). Finally the highly reduced carbonyls follow the effective number rule reasonably well, while this rule is irrelevant for the noble-metal carbonyl cations and their derivatives because the role of CO as ligand has changed from an extremely effective π-acid ligand or a Lewis acid to a Lewis base. Hence the geometries of the cations reflect the coordination requirements of the central metal cations, linear for Ag(I) ($4d^{10}$) and Au(I) ($5d^{10}$), and square planar for Pd(II) ($4d^8$) and Pt(II) ($5d^8$).

With a number of molecular structures for carbonyl derivatives of elements in groups 10 and 11 now known, a comparison of the structural features is undertaken in the next section, before a discussion of bonding features to complete this review.

2.3.4. *Structural aspects of noble- and coinage-metal carbonyl derivatives*

The discussion is initially descriptive in nature where all structurally known compounds are briefly introduced. The principal features, the M—C—O segments, are then compared together with the corresponding $\bar{\nu}CO$ values. Finally, two molecular structures where sufficient detail is known to include intermolecular or interlayer contacts in the discussion are described in more detail. These structures involve the two palladium derivatives $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ [122] and *cis*-$Pd(CO)_2(SO_3F)_2$. Even though the exact molecular structure of $[Au(CO)_2]^+$ is not known, the complete vibrational analysis inclusive of ^{13}C and ^{18}O substitution studies, a normal coordinate analysis, and force field calculations using equations developed by Jones [133], have allowed an estimate of both the gold–carbon and the carbon–oxygen distances [49]. Hence $[Au(CO)_2]^+$ is included in the discussion. Also included are two anionic derivatives $[Pd(CO)X_3]^-$, X = Cl or Br [134], even though these complex species have been largely neglected in the preceding part of this review.

2.3.4.1. Descriptive structural features of selected carbonyl derivatives of groups 10 and 11 *Group 11.* The molecular structures of Au(CO)Cl [79] and Cu(CO)Cl [62] provide an interesting contrast. The four-atom molecule Au(CO)Cl is essentially linear. In the unit cell neighbouring molecules are lined up in an inverted position so that two sets of four C···Cl contacts of approximately 3.35 Å are produced, which are slightly shorter than the sum of the van der Waals radii [135]. Linear coordination is extremely common for gold(I) [98].

Cu(CO)Cl [62] is a layered material. Layer formation is effected by fusion of six-membered Cu(I) chloride rings in the chair configuration. Terminal CO groups are found on adjacent layers. Cu is in an approximately tetrahedral environment and Cl acts as a tridentate bridging ligand. The closest non-bonding O···O contacts are, with 3.246(8) Å, longer than the sum of the van der Waals radii.

$AgCOB(OTeF_5)_4$ [95] contains nearly linear Ag–C–O (176(1)°) groups. Silver is also asymmetrically coordinated to two O-atoms of the $-OTeF_5$ (teflate) groups. The structure is reported in a preliminary publication and full details are not consistently provided. Again terminal C–O groups are present and Ag exhibits coordination number 3. Descending down group 11 the coordination number of the metal decreases from 4 (Cu) to 3 (Ag) to 2 (Au).

The structure of $[Ag(CO)_2][B(OTeF_5)_4]$ [96], obtained at −100°C, has two nearly linear $[Ag(CO)_2]^+$ cations at different sites. In a centrosymmetric site Ag···F contacts of 3.0 Å generate a distorted (tetragonally compressed) octahedral environment. The structural report is again a preliminary communication [96].

Group 10. The structures of the anions $[Pd(CO)X_3]^-$, X = Cl or Br [134], and $[Pt(CO)Cl_3]^-$ [137] are unremarkably simple. The central metal atoms are in square planar environments, though there are slight deviations from exact planarity. $[n\text{-}Bu_4N]^+$ is used as counter cation. The CO groups are terminal and no intermolecular contacts are noted that could affect the CO groups.

The molecular structure of *cis*-$Pd(CO)_2(OSO_2F)_2$ [121] is shown in Fig. 2. The coordination of Pd(II) is square planar and the two CO groups are terminal in a *cis*-arrangement. More structural details are discussed below.

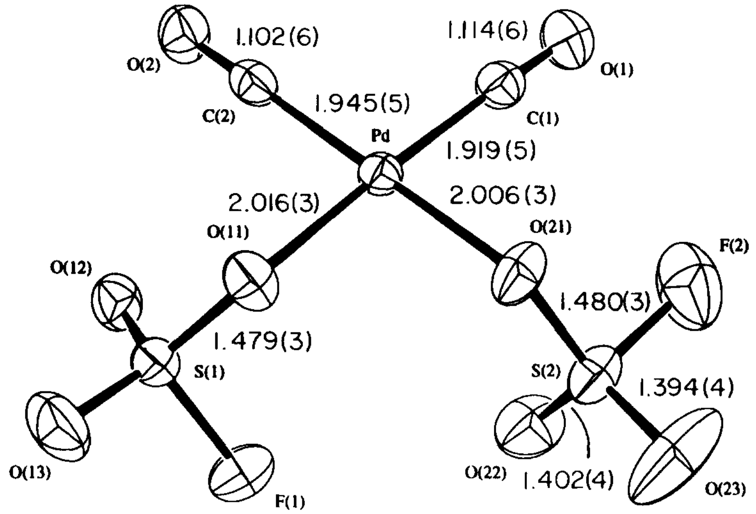


Fig. 2. The molecular structure of *cis*-$Pd(CO)_2(SO_3F)_2$. Selected bond distances (in ångströms) are included.

The molecular structure of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ [122] departs from the others discussed here on two accounts. (i) The CO groups are nearly symmetrically bridging and form a completely planar metallocycle with the palladium atoms. (ii) Based on S–O and S–F distances the fluorosulphate groups are, in analogy to the structure of $(CH_3)_2Sn(SO_3F)_2$ [136], viewed as anions that are packed in a bidentate bridging configuration. They coordinate weakly to the $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cations to give a sheet-like polymer. Ignoring the Pd–Pd bond, the coordination environment of Pd is distorted square planar. A segment of the structure is shown in Fig. 3 and details are discussed below.

Finally, $Pt_2I_4(CO)_2$ [80] is found to be a nearly planar, iodide-bridged dimer. In the centrosymmetrical structure the two terminal CO groups are trans to each other. Interestingly, the internuclear distances of Pt to bridging I^- (2.622(3) Å) are only slightly longer than those to terminal I (2.596(3) Å).

In summary, structural details have become known for eleven carbonyl derivatives, representing all of the relevant metals. In all but one instance terminal CO groups are present and a comparison of structural parameters for the M–C–O moiety should be possible.

2.3.4.2. Comparison of structural data for the M–C–O group In judging the nature of the metal ion–carbon monoxide interaction, three criteria are important: (i) the M–C–O bond angle, which should be approximately 180° for terminal C–O groups; (ii) the M–C bond length, which should be rather long in the absence of π-back-donation (from the listing in Table 2 it can be seen that comparable radii for the metals (metallic, van der Waals, or ionic) do not vary appreciably for the pairs Ag

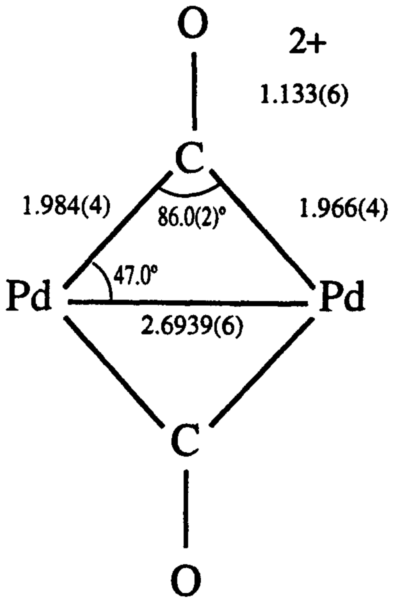


Fig. 3. The molecular structure of the $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cation.

and Au, or Pd and Pt); (iii) the C—O bond distance, which should be less than 1.12819 Å, the distance in unbound CO in the absence of π-back-donation. Because bond-distance variations at high C—O bond orders are small and difficult to determine precisely, $\bar{\nu}$CO, the wavenumber of the CO stretching vibrations, may be used in place of C—O bond lengths.

The data on these four parameters are compiled in Table 6 and allow the following conclusions. In all instances where terminal CO groups are present, the M—C—O moiety appears to be approximately linear, even though for $[Ag(CO)_2]^+$ [96] some variation is observed and the Ag—C—O angle may deviate from linearity by as much as 10°. As expected, all C—O bonds are very short, except for that in $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ [122], and may in fact be shorter than in CO. However, uncertainties due to quoted ESD values and thermal motion corrections cast some doubt on this reasoning. If the $\bar{\nu}$CO values are compared with the νCO(g) value, the silver and gold derivatives and *cis*-$Pd(CO)_2(SO_3F)_2$ [121] have higher values, even though the vibrational spectrum of $[Ag(CO)_2][B(OTeF_5)_4]$ [96] is incomplete.

The metal—carbon distances are long, as is expected in the absence of appreciable π-back-donation. Values are in the approximate range 1.90 Å ± 0.05 Å. However, corresponding data for the two silver(I) carbonyl derivatives appear to be appreciably longer [95,96]. This is consistent with their thermal instability, which sets them apart from all of the remaining noble-metal carbonyl derivatives. The structures were obtained at −100 [95] and −120°C [96] respectively.

TABLE 6

Structural data on the M–C–O group in carbonyl derivatives of Cu, Ag, Au, Pd and Pt

Compound or ion	Angle MCO (deg)	d(M–C) [Å]	d(C–O) [Å]	$\bar{\nu}CO_{av}$ (cm^{-1})	Reference
Cu(CO)Cl	179(1)	1.856(16)	1.112(18)	2127	62
Au(CO)Cl	180[a]	1.93(2)	1.11(3)	2183	79,66
$[Au(CO)_2]^+$	180[a]	2.05[a]	1.11[a]	2235.5	49
$Ag(CO)B(OTeF_5)_4$	176(1)	2.10(1)	1.077(16)	2204	95
$[Ag(CO)_2][B(OTeF_5)_4]$[b]	169(1) to 176(1)	2.06(5) to 2.16(4)	1.07(5) 1.09(5)	2198[c]	96
$[Pd(CO)Cl_3]^-$[d]	178(1)	1.87(1)	1.11(1)	2132	134
$[Pd(CO)Br_3]^-$[d]	175(2)	1.87(3)	1.10(3)	2120	134
cis-$Pd(CO)_2(SO_3F)_2$	178.9(4) and 177.5(4)	1.945(5) and 1.919(5)	1.102(6) and 1.114(6)	2218	121
$[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$	138.2(4)	1.984(4) and 1.966(4)	1.133(6)	2002	122
$[Pt(CO)Cl_3]^-$[d]	178(2)	1.82(1)	1.12(1)	2095	137,66
$Pt_2(CO)_2(\mu\text{-}I)_2I_2$	177(3)	1.88(3)	1.06(4)	2106	80

[a] Estimated parameter.

[b] Molecule has two $[Ag(CO)_2]^+$ in two different sites.

[c] From IR spectrum.

[d] $[n\text{-}Bu_4N]^+$ is the cation.

The three molecular structures reported on the related square planar palladium(II) complexes $[Pd(CO)X_3]^-$ [134], X = Cl or Br, and *cis*-$Pd(CO)_2(SO_3F)_2$ [121] show an interesting contrast. The Pd–C bonds in the anions are appreciably shorter owing to more extensive π-back-donation. Subsequently $\bar{\nu}CO$ is reduced by 80–90 cm^{-1} from the average $\bar{\nu}CO$ for *cis*-$Pd(CO)_2(SO_3F)_2$ of 2218 cm^{-1}. A similar observation is made for the M–C bond length in $Pt_2(CO)_2(\mu\text{-}I)_2I_2$ [80]. The effect of π-back-donation in $[Pt(CO)Cl_3]^-$ [137] becomes evident when the Pt–C bond distance of 1.82(1) Å is compared with values for a number of neutral Pt(II) complexes compiled previously [138] with a variety of carbon-donor ligands, which range from 1.83 to 2.079 Å for *trans*-$PtCl(CH_2SiMe_3)(PPhMe_2)_2$ [139]. Consistent with observation based on vibrational spectroscopy [113], π-back-donation will decrease from anionic to neutral to cationic metal-carbonyl derivatives with a concomitant increased $\bar{\nu}CO$.

It is hoped that molecular structures of $[M(CO)_4][Sb_6F_{11}]_2$ [115], M = Pt and Pd, will become available because $\bar{\nu}CO_{av}$ of 2260 cm^{-1} is unprecedented. The only structurally characterized, thermally stable carbonyl cation is $[Pd_2(\mu\text{-}CO)_2]^{2+}$ [122], but here symmetrically bridging carbonyl ligands are found. The detailed molecular structures of $[Pd_2(\mu\text{-}CO)_2]_2(SO_3F)_2$ [122] and of *cis*-$Pd(CO)_2(SO_3F)_2$ [121] are discussed below.

2.3.4.3. The molecular structures of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ and of cis-$Pd(CO)_2(SO_3F)_2$ Both structures were obtained by us very recently and close attention was paid to intermolecular contacts. The cyclic $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cation (Fig. 3) is stabilized both by weak coordination to the fluorosulphate anions and by O···Pd and Pd···Pd interlayer contacts of 2.653 and 3.477 Å respectively. The O(3) atom of the SO_3F^- group is not involved in direct coordination to Pd where Pd—O is 2.159 and 2.153 Å.

The cross-ring Pd—Pd bond length of 2.6939(6) Å corresponds to a single bond and is identical with reported precedents [124,140–142]. The C—O distance (1.133(6) Å) is slightly longer than in CO, and $\bar{\nu}CO$ (2002 cm^{-1}) is about 250 cm^{-1} higher than observed usually in transition-metal complexes with bidentate-bridging CO ligands [4,7,8]. Hence π-back-donation is reduced, consistent with the rather long Pd—C bonds (see Table 6).

There is a precedent for the presence of the $[Pd_2(\mu\text{-}CO)_2]^{2+}$ group in the acetate derivative $[Pd_4(\mu\text{-}CO)_4(\mu\text{-}O_2CCH_3)_4]\cdot 2CH_3CO_2H$ [123] where two such ions with structural parameters very similar to those of the fluorosulphate are linked by symmetrically bridging acetate groups to give a tetranuclear cluster with a rectangular arrangement of four Pd atoms and alternating pairs of bridging-CO and acetate ligands. The $[Pd_2(\mu\text{-}CO)_2]$ group appears to be also present in $[Pd(CO)Cl]_n$, but the nuclearity of the compound and the exact structure are unknown [143,144]. The rather simple $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cation belongs to point group D_{2h} and a complete vibrational analysis is possible since both IR and Raman spectra down to 50 cm^{-1} have been obtained [122].

For *cis*-Pd $(CO)_2(SO_3F)_2$ the molecular structure shown in Fig. 2 seems simple and straightforward. The unusually high $\bar{\nu}CO_{av}$ value of 2218 cm^{-1} suggests strongly diminished π-back-donation, which would imply primarily σ-donation to Pd from the 5σ pair on carbon and a partial positive charge on C. A closer look at the molecular structure shows that there are a number of intermolecular C···O contacts (four each for each carbon atom) to the terminal oxygen atoms of the fluorosulphate group in the range 2.839(6) to 3.172(6) Å, all significantly shorter than the sum of the van der Waals radii for C and O of 3.24 Å. It appears that in the near absence of π-back-donation, these intermolecular contacts provide a measure of charge compensation in these unusual complexes. As already discussed in the molecular structure of Au(CO)Cl [79], carbon also has four weak intermolecular C···Cl contacts.

It is interesting to note that fluorosulphuric acid, HSO_3F, and thionylchloride, $SOCl_2$, are suitable solvents for noble-metal carbonyl cations such as $[Au(CO)_2]^+$ [49,52] or $[M(CO)_4]^{2+}$, M = Pd or Pt [115], or noble-metal carbonyl halides [67,69]. Both are extremely weak bases, but both may be able to exert a stabilizing effect by weak C···O or C···Cl solvation of the noble-metal carbonyl species in these solutions.

In instances where anions such as $Sb_2F_{11}^-$ are present in solid complexes like $[Au(CO)_2][Sb_2F_{11}]$ [49] and $[M(CO)_4][Sb_2F_{11}]_2$ [115], M = Pd or Pt, fluoro ligands of the anion may act in a similar manner. The reported molecular structure of $Br_2[Sb_3F_{16}]$ [145,146] provides an example for stabilization of an extremely electrophilic cation by Br···F contacts of variable strength. Secondary bonding interactions are quite common in solid, low-valent main-group compounds of groups 13–17 [147]; hence observation of such interactions in $Pd(CO)_2(SO_3F)_2$ should not be surprising.

When an attempt is made at understanding the bonding in this exotic group of compounds, the example of *cis*-$Pd(CO)_2(SO_3F)_2$ underscores the need for complete structural information inclusive of secondary intermolecular or intramolecular contacts. We had previously [114] correctly predicted the *cis*-geometry of the square planar complex and the presence of weakly oxygen-bonded monodentate fluorosulphate groups based on vibrational spectra. In addition $\bar{\nu}CO_{av}$ of 2218 cm^{-1} had provided a better measure of the strength of the C–O bond than the C–O bond lengths of 1.102(6) and 1.114(6) Å [121]. However, it is extremely difficult to detect the weak secondary contacts using only vibrational spectroscopy. It is hoped that as more structures of the noble-metal carbonyl compounds become available, more attention will be focused on these secondary contacts. Likewise, the availability of only the complete IR (including far-IR) and Raman data for $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ would have made it difficult to engage in a complete vibrational analysis of the square planar cation without the help from a molecular structure determination [122].

Finally, it should be noted that emphasis in this account has been placed on synthesis, direct structure determinations, and vibrational spectroscopy, while little use appears to have been made of ^{13}C or heteronuclear NMR. While some use of ^{13}C-NMR has been made recently as well as in the past [49,66,69,113], more use of NMR will be made when the reactivity of the noble-metal carbonyls is probed more deeply. In particular, CO exchange reactions between $[Au(CO)]^+$ and $[Au(CO)_2]^+$ in solutions of strong protonic acids appear to be a promising area of study [49].

2.3.5. *Bonding aspects*

From a start dating back well into the last century, the study of σ-bonded metal-carbonyl derivatives has expanded very recently and some of the more interesting noble-metal carbonyl cations have been reported since 1990, the one-hundredth anniversary of the discovery of $Ni(CO)_4$ [23], the first binary transition-metal carbonyl. It is encouraging to note that these unusual species have attracted attention, and that quantum mechanical ab initio calculations using relativistic core potentials for the metals have been completed [148] for the species $M(CO)_n^+ M = Ag$ or Au and $n = 1$, 2, or 3, where the higher thermal stability of the gold compared with the silver dicarbonyl cations has been postulated. Eventually such calculations will have to go beyond the molecular level to include secondary bonding effects, but nevertheless a start has been made.

Our comments here stay on a much simpler, qualitative level and address two concerns: (i) the real or perceived absence of π-back-donation in these complexes and (ii) the probable cause for the difference in thermal stability between silver and other transient metal-carbonyl cations and those of gold(I), palladium(II), and platinum(III).

2.3.5.1. The role of π-back-donation in metal-carbonyl cations We have argued in this review that internuclear C–O distances are rather poor criteria where large ESD values (see Table 6) and thermal motion cause uncertainties. We have instead recommended vibrational spectroscopic techniques as more suitable, because $\bar{\nu}$CO is usually easily measured and the values are far more sensitive to subtle changes in the CO bond order than d(C–O). As the example of $[Au(CO)_2]^+$ [49] illustrates, the careful use of vibrational spectroscopy requires (a) the recording of the complete IR and Raman spectra in the solid state and solution, (b) an extension of (a) to the study of ^{13}C and ^{18}O isotopomers, (c) the complete vibrational assignment, aided by comparison with isoelectronic cyanide species, where much work has been done in the past [133], (d) a normal coordinate analysis to secure any proposed assignment, and (e) force field calculations to include also species where vibrational mixing can occur.

The stretching force constant for HCO^+, the formyl cation where no π-back-donation is possible, provides a good yardstick with $f_r = 21.3 \times 10^2$ N m^{-1} [49]. In Table 7 vibrational data for a number of carbonyl and cyanide derivatives are

TABLE 7

CO and CN stretching vibrations and force constants for selected noble metal carbonyl- and cyanide-complexes

Molecule or ion	Point group	νCX sym (cm^{-1})	ν'CX sym[a] (cm^{-1})	νCX asym (cm^{-1})	νCX av (cm^{-1})	$f_r \times 10^2$ (N m^{-1})	Reference
$[Pt(CO)_4]^{2+}$ [b]	D_{4h}	2289	2267	2244	2261	20.64[e]	115
$[Pt(CO)_4]^{2+}$ [c]	D_{4h}	2281	2257	2233	2251	20.47[e]	113
$[Pd(CO)_4]^{2+}$	D_{4h}	2278	2263	2248	2259	20.63[e]	115
$[Pt(CN)_4]^{2-}$	D_{4h}	2168	2149	2133	2146	17.38[f]	118
$[Pd(CN)_4]^{2-}$	D_{4h}	2160	2146	2136	2144.5	17.35[f]	118
$[Au(CO)_2]^+$	$D_{\infty h}$	2254		2217	2235.5	20.18[e] 20.1[f]	49
$[Au(CN)_2]^-$	$D_{\infty h}$	2162		2142	2152	17.60[f]	
cis-$Pt(CO)_2(SO_3F)_2$[d]	$\approx C_{2v}$	2219		2185	2202	19.56[e]	114
cis-$Pd(CO)_2(SO_3F)_2$[d]	$\approx C_{2v}$	2227		2208	2217.5	19.87[e]	114
$Au(CO)SO_3F$[d]	$\approx C_s$	2196			2196	19.5[f]	52
CO	$C_{\infty v}$	2143			2143.17	18.6[f]	9,49
CO^+	$C_{\infty v}$	2184			2184	19.3[f]	49
BH_3CO		2165			2165	19.24	36,49
HCO^+	$C_{\infty v}$	2184			2184	21.3[f]	49

[a] ν' refers to the B_{1g} mode; [b] $Sb_2F_{11}^-$ as anion; [c] $[Pt(SO_3F)_6]^{2-}$ as anion; [d] IR bands; [e] Cotton–Kraihanzel values [119,120]; [f] according to Jones [133].

compiled including those with the highest $\bar{\nu}$CO values observed so far. The CO stretching force constants are calculated either according to Jones [133] or using the Cotton–Kraihanzel method [119,120]; the values do not usually differ very much. As can be seen, f_r for HCO^+ remains the highest stretching force constant and it must be concluded that even in $[Pt(CO)_4]^{2+}$, with $f_r = 20.64 \times 10^2$ N m^{-1}, some residual π-back-donation either from the metal or through secondary interaction with the anion must remain and result in a smaller stretching force constant.

It seems to us that all claims of the complete absence of π-back-donation made from time to time by others whenever $\bar{\nu}$CO approaches about 2200 cm^{-1} appear to have been exaggerated. It hence seems that some π-back-donation is still possible in the cationic noble-metal carbonyl derivatives, albeit under grossly reduced circumstances.

2.3.5.2. Contributing factors to the bonding in persistent cationic noble-metal carbonyl derivatives Persistent carbonyl derivatives are formed primarily by Au(I), Pd(I) (in oligomeric complexes), Pd(II), and Pt(II), and the principal coordination geometries are linear and square planar respectively. Of the metals, Au(I) [98], Pt(II) [149], and to a lesser degree Pd(II) [150], have an extensive coordination chemistry where linear coordination is found almost exclusively for gold(I) [98], and square-planar geometry is encountered exclusively for Pt(II) [149].

For both Au(I) and Pt(II) there are many examples of stable complexes with carbon donor ligands among the carbonyl ligands, as evidenced for Pt(II) by the early history [2] and the rich chemistry of the platinum(II) carbonyl cations, two of which, $[Pt(CO)Cl(PEt_3)_2][BF_4]$ [151] and $[Pt(CO)(CH_3C_6H_4)(PEt_3)_2][PF_6]$ [152], have been structurally characterized. Interestingly, in complexes of this type CO appears to function as a "normal" π-acid ligand ($\bar{\nu}$CO between 2040 and 2123 cm^{-1}) [153] when other π-acid ligands are present. We have recently made [122] similar observations regarding Pd(I) complexes with bridging CO ligands [124–126]. It is therefore not surprising that gold(I) and platinum(II) form thermally stable binary carbonyls of the $[Au(CO)_2]^+$ [49,52] and $[Pt(CO)_4]^{2+}$ [115] and that these cations appear to be linear and square planar respectively. It is also interesting that both metal ions form exclusively the isoelectronic cyanide complexes $[Au(CN)_2]^-$ and $[Pt(CN)_4]^{2-}$ respectively, and that cyanide complexes with higher or lower coordination numbers appear to be unknown or unstable [27,28,98,149].

Since relativistic effects [110,111,154,155] are expected to stabilize the 6s orbital (in particular for gold), it seems reasonable to consider both covalent and electrostatic contributions to the bonding in both carbonyl cations $[Au(CO)_2]^+$ and $[Pt(CO)_4]^{2+}$ as the principle reasons for their existence and high thermal stability. Similar conclusions based on ab initio calculations have been reached recently for $[Au(CO)_2]^+$ [147]. Two additional contributions are expected from residual π-back-donation and from secondary bonding features with a carbon Lewis acid site as recently demonstrated for *cis*-$Pd(CO)_2(SO_3F)_2$ [121] and Au(CO)Cl [79]. Secondary coordination should also play a role for the solvated cations and other dissolved carbonyl derivatives in solvents such as HSO_3F and $SOCl_2$.

For cations or cationic derivatives π-back-donation should be rather small. This is easily demonstrated by two simple examples. For the isoelectronic series of octahedral classical transition-metal carbonyls [9] $[V(CO)_6]^-$, $Cr(CO)_6$, and $[Mn(CO)_6]^+$, $\bar{\nu}CO_{av}$ increases from 1897 to 2029 to 2121 cm^{-1}, with the latter value close to the upper limit for terminal CO ligands [4,5], Table 2. The effect on the metal–carbon bond is illustrated for the isoelectronic linear species $[Au(CO)_2]^+$, $Hg(CN)_2$, and $[Au(CN)_2]^-$ [49] where the metal–carbon stretching force constants f_R increase from 2.16 ± 0.03 to 2.59 ± 0.03 to $2.78 \pm 0.03 \times 10^2$ N m^{-1} [49], while the C–X, X = O or N, stretching force constant f_r decreases from 20.1 ± 0.1 to 18.1 ± 0.2 to $17.6 \pm 0.2 \times 20^2$ N m^{-1}.

For Pd(II), which again forms exclusively square planar $[Pd(CN)_4]^{2-}$ complexes [27,28], relativistic effects should be less dominant, and covalent contributions relative to those for Pt(II) complexes should be reduced. This expectation is reflected in the carbonyl halide derivatives of Pd(II), which are smaller in number and of lower thermal stability [68,69] than their Pt(II) congeners. This expected deficiency appears to be compensated for by electrostatic effects in $[Pd(CO)_4][Sb_2F_{11}]_2$ [115] and *cis*-$Pd(CO)_2(SO_3F)_2$ [114,121] which are of similar or higher thermal stability than their platinum(II) congeners [114,115]. The strong similarity of their vibrational spectra suggests a comparably small degree of π-back-donation in both sets of compounds.

For Ag(I), which forms only thermally unstable carbonyl derivatives [95,96] and in which reduced relativistic effects are expected [154,155], the covalent contribution appears to be minimal [147], and strict adherence to coordination number 2 and linear geometries is no longer observed [156]. This is best illustrated by the CN^- complexes, where coordination by C or N may occur and where cyanide complexes such as $[Ag(CN)_3]^{2-}$ and $[Ag(CN)_4]^{3-}$ may exist in addition to $[Ag(CN)_2]^-$ and some binuclear complexes [27,28]. Even in $[Ag(CN)_2]^-$ the Ag–C bond is said to be weaker than Au–C in $[Au(CN)_2]^-$ where the stability constant β_2 is estimated to be 10^{38} compared with 10^{20} for $[Ag(CN)_2]^-$. It is hence not surprising that both $Ag(CO)B(OTeF_5)_4$ [95] and $[Ag(CO)_2][B(OTeF_5)]$ [96] show such low thermally stability. This in our opinion is due to the difference in counteranions because our own attempts to make $Ag(CO)_nSb_2F_{11}$ [157] by reductive carbonylation of $Ag(SO_3F)_2$ [158] in HSO_3F produced a material of compositions $[Ag(CO)][Sb_2F_{11}]$ and $[Ag(CO)_2][Sb_2F_{11}]$, which have no appreciable CO-dissociation pressure at 25°C. Nevertheless, the reported low-temperature X-ray diffraction studies of $Ag(CO)B(OTeF_5)_4$ [95] and of $[Ag(CO)_2][B(OTeF_5)_4]$ [96] indicate that well defined species are present, and the work by Souma and co-workers [86,93,94] shows that the silver(I) carbonyls in protonic acids are very useful carbonylation catalysts.

While our interest has been focused on the thermally stable non-classical carbonyl cations of Au(I), Pd(I), Pd(II), and Pt(II) [49,52,113,115,122] and their fluorosulphate derivatives [52,114,121], it may well be that the thermally unstable carbonyl cations of electron-rich metals will find far wider use in synthesis or in surface chemistry.

A final comment concerns the most unusual spectroscopic feature of these noble-metal carbonyl cations, the unusually high CO stretching frequency with average $\bar{\nu}$CO values now as high as 2261 cm^{-1} for $[Pt(CO)_4][Sb_2F_{11}]_2$ with the highest individual CO stretch (the A_{1g} mode) at 2289 cm^{-1} [115]. It is unlikely that shifts of approximately 120 cm^{-1} from the $\bar{\nu}$CO value of 2143 cm^{-1} for free CO can be explained satisfactorily by the removal of electron density from the 5σ orbital of CO by σ-donation to a metal centre. Removal of a single electron to give CO^+ results in a shift of only 41 cm^{-1} to higher wavenumbers. As suggested previously for $BH_3 \cdot CO$ [37] based on photoelectron spectroscopy, rehybridization involving the 5σ and the bonding 4σ orbital appears to occur where the higher bond strength in the CO bond region is explained by increased s-character of the 4σ orbital, while the 5σ orbital has more extensive p-character. The comments and observations made in this section are at this time necessarily very qualitative and descriptive. It is hoped that sound theoretical work, which has already begun [147], will continue and will provide an appropriate supplement to the synthetic structural and spectroscopic work described in this review.

3. SUMMARY AND CONCLUSIONS

We have travelled a fair distance in this survey from classical main-group chemistry to noble-metal compounds. En route we have touched on a number of exotic species such as HCO^+ (the interstellar ion) [42] and BH_3CO [30], some "oldies" such as *cis*-$Pt(CO)_2Cl_2$ [2] (the first metal carbonyl ever synthesized), and now the latest additions, the carbonyl cations such as $[Pd_2(\mu\text{-}CO)_2]^{2+}$ [122] and $[Pd(CO)_4]^{2+}$ [115] with unusual geometries and spectroscopic properties. The question may be asked how this will all fit into a review dedicated to topics on main-group chemistry. There is of course carbon monoxide, and there are also the principle reagents and reaction media such as SbF_5 and HSO_3F and a synthetic approach that has been applied in the past to the generation and stabilization of main-group cations. The principle noble metals Au and Pt also have many nonmetallic features. Gold, with a strict preference for oxidation states -1, $+1$, $+3$, and $+5$ and many structural analogues, has been likened to iodine [159] and viewed as a pseudo-halogen. The organometallic chemistry of Pt(IV), with a preference for σ bonding, resembles that of Sn(IV), and both elements Au and Pt have electron affinities that are only surpassed by those of the halogens.

However, accepting the fact that both gold and platinum are after all (together with palladium) metals or better transition metals, another point can be made here. The novel binary carbonyl cations $[Au(CO)_2]^+$ [49,52], $[M(CO)_4]^{2+}$, M = Pd or

Pt [115], and $[Pd_2(\mu\text{-}CO)_2]^{2+}$ [122], the first of which was reported in 1990, represent an expansion of the known binary carbonyl species formed by metals of the middle section of the transition series to the electron-rich noble metals and to new, unprecedented coordination geometries. The carbonyl cations discussed in this review and highly reduced binary carbonylate anions reported by Ellis and his group [18,19,24,25], briefly mentioned here, may be viewed as differently coloured bookends to a library section that encompasses important volumes of the organometallic and coordination transition-metal chemistry. It is gratifying to see that this expansion has come about by the use of "old fashioned" non-aqueous, classical reagents [44] and working principles adopted from main-group chemistry, and has resulted in the synthesis of "real", thermally stable compounds with a bright future.

4. OUTLOOK AND FURTHER DIRECTIONS

The developments in recent years have been rapid. Certain aspects such as the role of Brönsted and Lewis superacids [44] have been unpredictable and the findings initially accidental [52]. An obvious extension, the search for other persistent carbonyl cations, should be directed initially towards the 4d and 5d elements in groups 8 and 9. Fluorosulphate derivatives of Rh(III) [160], Ru(III) and Ru(IV) [161], Ir(III) and Ir(IV) [162], and Os(III) [160] are known and some are soluble in HSO_3F. Expanding the series from the known cations, linear $[Au(CO)_2]^+$ to $[Pt(CO)_4]^{2+}$ with a square-planar geometry to a possibly octahedral $[Ir(CO)_6]^{3+}$, becomes a worthwhile challenge. The existence of the corresponding isoelectronic cyanide anions [27,28] provides a guide, in particular where unusually high CN-stretching frequencies for these complexes are found, as for $[Au(CN)_2]^-$ [109] and $[M(CN)_4]^{2-}$, M = Ni, Pd or Pt. It must be admitted, however, that following this analogy, attempts at the synthesis of $[Ni(CO)_4]^{2+}$ have failed so far [163]. It also appears doubtful that there will be as many non-classical carbonyl compounds as there are metal–cyanide complexes. A recent review on transition-metal derivatives of strong protonic acid and superacids [164] may serve as a source book for other suitable derivatives, and a useful reference to strong protonic and superacids [44].

In the search for transient carbonyl derivatives, which may display sufficient thermal stability to be classified as persistent, four approaches may be utilized.

(i) Salts with very large, weakly coordinating anion can be used. The synthesis of $Ag(CO)B(OTeF_5)_4$ [95] and $Ag(CO)B(OTeF_5)_4$ [96] presents precedents and a review on weakly coordinating anions has appeared recently [165].

(ii) HSO_3F [132] and other protonic acids and superacids [44] can be used in the in situ generation of carbonyl cations. HSO_3F has a low melting point [132] and studies down to −90°C are feasible.

(iii) The oxidation of metals can be carried out by for example AsF_5, SbF_5, or UF_6 in the presence of CO. The binary fluorides used in excess could produce weakly nucleophilic counteranions such as AsF_6^-, SbF_6^-, or UF_6^-. The generation of

$[Au(CO)_2][UF_6]$ [100] provides an example. Anhydrous HF, SO_2, or AsF_3 could be used as solvent.

(iv) More extensive use of matrix-isolation techniques applied to metal–halide reactions could be made with CO in various inert matrices. Previous work [166] has resulted in the generation of complexes such as $CuF_2 \cdot CO$ with $\bar{\nu}CO$ at $2210\ cm^{-1}$, and $CaF_2 \cdot CO$ with $\bar{\nu}CO$ at $2178\ cm^{-1}$ has produced a derivative with one of the highest CO stretches and has shown, together with the work on CO adsorbates on ZnO [83], that these non-classical carbonyl complexes may not be restricted to transition metals.

Finally, the complexes prepared so far require more attention. More detailed molecular-structure determination should shed some light on the role secondary interactions play in stabilizing these compounds in the solid state with carbon as Lewis acid sites. Since most of the cations are highly symmetrical, complete vibrational analysis and force field calculations are possible, challenging and, in view of the information obtained from them, very important in judging π-back-donation. Also, greater use of ^{13}C-NMR or heteronuclear NMR needs to be made in the future. Most efforts so far have been directed towards the synthesis and structural characterization of the noble-metal carbonyl cations and their derivatives. With nucleophilic attack possible on the metal centre as well as on carbon, an interesting and rich chemistry is expected to emerge.

A fitting conclusion to this review comes from very recent work by us [167,168] and by Strauss and co-workers [169]. It has been possible to adopt the synthetic methodology discussed here to synthesize $[Hg(CO)_2][Sb_2F_{11}]_2$ according to

$$Hg(SO_3F)_2 + 8SbF_5 + 2CO \xrightarrow[100^{\circ}C,\ 1\ h]{SbF_5} [Hg(CO)_2][Sb_2F_{11}]_2 + 2Sb_2F_9(SO_3F) \qquad (19)$$

The corresponding mercury(I) derivative $[Hg_2(CO)_2][Sb_2F_{11}]_2$ is obtained in a similar manner. The resulting white solids have decomposition points above 100°C and the linear cations feature very high CO stretching frequencies with $\bar{\nu}CO_{av}$ of $2280\ cm^{-1}$ for $[Hg(CO)_2]^{2+}$ and $2248\ cm^{-1}$ for $[Hg_2(CO)_2]^{2+}$. Both are the first examples where a post-transition metal forms thermally stable carbonyl derivatives, and both illustrate the conclusion that where π-back-donation is unimportant, as in this group of carbonyl cations, a restriction to transition-metal centres only for M–CO bonding is no longer necessary. Even more recently the molecular structure of $[Hg(CO)_2][Sb_2F_{11}]_2$ has been obtained by single-crystal X-ray diffraction [168] and details will be published soon. In a different and novel approach, Strauss and co-workers have obtained evidence for the formation of $[Ag(CO)_3]^+$ by employing high-pressure IR spectroscopy [169].

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