Carbonyl Derivatives of Gold and Related Organometallics

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The properties and reactions of simple gold carbonyls and related compounds are described and the bonding within the gold carbonyl molecules discussed in terms of bond dissociation enthalpies.

Although the organometallic chemistry of gold is still rather limited (but see accompanying article in this issue of *Gold Bulletin* by R V Parish (1)) it presents aspects of uniqueness. Some of the properties of gold organometallics may be understood if in the oxidation state I, as is the case in some of the complexes described in this review, the electronic configuration of gold is $5d^{10}$. This means that we are dealing with a non-transition system characterized by a closed-shell configuration, expected to be colourless and diamagnetic.

When carbon-based ligands are considered, we can distinguish one-electron donors (alkyls, aryls; *ie* hydrocarbyls) and two-electron donors. Excellent reviews have appeared (2a, b) concerning hydrocarbyl derivatives of gold(I) and gold(III), including structural aspects (2c) and this subject will not be treated here. We limit the presentation to gold organometallics with two-electron donor carbon-based ligands, namely carbon monoxide, olefins, isonitriles and cyanides.

Generally, within transition metals, bond dissociation enthalpies (BDE) of metal-carbonyl bonds can be discussed in conjunction with metal-methyl bonds (3). For example, for some typical 5d elements such as tungsten or rhenium, BDE's have been evaluated to be (kJ mol⁻¹): W-Me, 160±6 (average in WMe₆); W-CO, 178±1 (average in hexacarbonyltungsten(0)); Re-Me, 220±11, in ReMe(CO)₅; Re-CO, 187±6 (average in Re₂(CO)₁₀). If extrapolation to gold is allowed, something similar would be expected to occur, unless additional factors come into play. It is therefore interesting to see whether or not these expectations are met. The

synthesis of the gold organometallics described to date provides some relevant information.

The carbonyl derivatives of gold(I) reported in the literature all have ligands of high electronegativity or ligands containing electron-withdrawing substituents and it is interesting to note the carbonyl vibrational frequencies in the infrared spectra of the following mononuclear, dinuclear and cationic species: AuCl(CO) which has $\nu_{\text{CO}} = 2162 \text{ cm}^{-1}$ (4); AuBr(CO), $\nu_{\text{CO}} = 2159 \text{ cm}^{-1}$ (4); Cl₃Au(μ -Cl)Au(CO), $\nu_{\text{CO}} = 2180 \text{ cm}^{-1}$ (5); Au(SO₃F)(CO), $\nu_{\text{CO}} = 2195 \text{ cm}^{-1}$ (6); a fluorinated tris(pyrazolyl)borato complex, [HB(3,5-(CF₃)₂C₃H₃N₂)₃]Au(CO), $\nu_{\text{CO}} = 2144 \text{ cm}^{-1}$ (7); [Au(CO)₂][UF₆], $\nu_{\text{CO}} = 2200 \text{ cm}^{-1}$ (8) or [Au(CO)₂][Sb₂F₁₁], $\nu_{\text{CO}} = 2217 \text{ cm}^{-1}$ (9). All these compounds have high ν_{CO} 's, sometimes well above that of uncoordinated carbon monoxide which is 2147 cm⁻¹ (10), thus suggesting little or no π -back donation within the Au-CO bond (11), and we should therefore think of these compounds in terms of the 'σ-bonding only' model typical of the interaction of CO with a metal of d^{10} electron configuration.

SYNTHESIS

The synthesis of the chloro- derivative of gold(I), AuCl(CO), has been studied in detail. In thionyl chloride as medium, the reaction of anhydrous gold(III) chloride with CO gives excellent yields, *via* the dinuclear Cl₃Au(μ -Cl)Au(CO) and the mixed-valence gold(I)-gold(III) chloride Au₄Cl₈ intermediates (12); with carbonyl chloride, COCl₂, being the

oxidation product. The thermodynamics of the reaction involving the formation of carbonyl chloride are so highly favoured ($\Delta G_r^0(\text{CO}_{(g)} + \text{Cl}_{2(g)} \rightarrow \text{COCl}_{2(g)} = -67.7 \text{ kJ mol}^{-1}$ (13)), that any one of the three products can be obtained in high yields depending on the CO:Au(III) molar ratio.

The preparation of the bromo-derivative, AuBr(CO), which is unstable in the solid state, is interesting (4). This bromo-carbonyl can be prepared by reductive carbonylation of gold(III) bromide:

In view of the now thermodynamically unfavourable reaction to carbonyl bromide [$\Delta G_r^0(\text{CO}_{(g)} + \text{Br}_{2(l)} \rightarrow \text{COBr}_{2(g)} = +26.3 \text{ kJ mol}^{-1}$ (13)], a substantially quantitative conversion to the desired product is only obtained when bromine is removed by cyclohexene. AuBr(CO) can also be obtained by direct carbonylation of AuBr.

The gold(I) halides, AuX, may be converted quantitatively to the halocarbonyl AuX(CO) by treatment with CO (4):

The BDE relative to the Au(I)-CO system can be readily calculated (17) to be at least 210 kJ mol^{-1} from some thermodynamic data available in the literature (13)*, and this is in agreement with the results of a recent theoretical calculation (18).

Within the series of halide derivatives, the stability of carbonyls with respect to dissociation ($\text{AuX} + \text{CO}$) decreases in the sequence $\text{Cl} > \text{Br} > \text{I}$: in line with the combined effects of both Au-X and Au-CO BDE's decreasing in the same sequence, if the main contribution to the Au-CO bonding is of the σ -type.

Attempts to isolate carbonyl derivatives of gold(I)

with thiolato or hydrosulfido ligands, by metathetical reactions with AuCl(CO) have failed (19a): the products isolated were sulfido and chloro complexes of gold(I) and coordinated carbon monoxide was lost (19b). Also, both $\text{K}[\text{Au}(\text{CN})_2]$ and Au(CN) are unreactive towards carbon monoxide (19a). In this connection, it is interesting that a cyano-isocyanide complex of gold(I) has been reported, being obtained by electrophilic attack on $\text{K}[\text{Au}(\text{CN})_2]$:

This compound contains substantially linearly coordinated gold(I) (20), with Au-C_{CN} and Au-C_{CNMe} bond distances of 2.01 and 1.98 Å respectively, the angle at gold being 176°.

SPECTROSCOPY AND BONDING

The high ν_{CO} 's, which are a common feature of gold(I) carbonyl derivatives, are increased still further in AuCl(CO) (by about 10 cm^{-1}), when the solvent is changed from hydrocarbon to chlorohydrocarbon (4). Changes of this type have been observed with other carbonyl compounds (17, 21), and are suggestive of a specific weak solvent-solute interaction. The solid-state structure of AuCl(CO), as reported by Jones (22), indicates that the gold atom in this mononuclear compound is linearly coordinated with the chlorine and carbon atoms with Au-Cl and Au-C bond distances of 2.261(6) and 1.93(2) Å, respectively, the bond angle at gold being 180° by symmetry. A re-evaluation of the published data in terms of packing,

Figure Crystal packing of AuCl(CO); recalculated from the data of Reference 22. $' = \frac{1}{2}x, \frac{1}{2}y, 1-z$; $'' = -\frac{1}{2}x, \frac{1}{2}y, 1-z$; $''' = -\frac{1}{2}x, \frac{1}{2}y, -z$; $'''' = \frac{1}{2}x, \frac{1}{2}y, -z$.

* The BDE (at 298 K) for the diatomic molecule Au-Cl, $343 \pm 9.6 \text{ kJ mol}^{-1}$, (see reference 13, Section 9) and the entropy change for the transfer of CO as diluted solution to a metal-bonded carbonyl group ($-145 \text{ J K}^{-1} \text{ mol}^{-1}$, see reference 14), can be combined to give an estimated value of about 210 kJ mol^{-1} for the Au-CO BDE, after considering the Au-Cl_b BDE to be 25% less than the Au-Cl_t BDE (Cl_b and Cl_t designate bridging and terminal chlorides, respectively), *ie* in terms of percentages, the same as that estimated for palladium(II) (15). The entropy loss due to the binding of CO to gold(I) is believed to be compensated by the fragmentation of the polynuclear chloride-bridged structure of solid AuCl (16).

see Figure, indicates that the C...Cl intermolecular contacts of 3.352 Å are in fact at least as important as the Au...Au contacts of 3.380 Å. The molecules appear to be packed in such a way as to minimize the C...Cl non-bonding distances: the deviation of the carbon atom from the best Cl'-Cl''-Cl'''-Cl'''' plane is 0.11 Å, while the deviation of the gold atom from the best Au'-Au''-Au'''-Au'''' plane is 0.450 Å. A similar situation has recently been encountered in the crystal packing of square-planar *cis*-PtCl₂(CO)₂ (23), where the interplanar C...Cl interactions were similarly found to be the most important ones.

CARBON MONOXIDE *vs* OLEFIN COORDINATION TO GOLD(I)

Earlier work (24) had indicated that carbon monoxide is displaced by the cyclic olefin norbornene with a K of 4±1 at 21.5°C, corresponding to a ΔG° of the reaction of about -3 kJ mol⁻¹ and that bonding to the olefin is slightly favoured with respect to carbon monoxide.

This result is at variance with those generally observed for typical transition metals, whereby olefin displacement by CO is highly favoured. It is interesting, in this connection, that the BDE's (kJ mol⁻¹) for the gold(I) cation have been recently calculated (25a) to increase in the order: H₂O (163.4) < CO (209) < NH₃ (289) < C₂H₄ (306). On the other hand, the proton affinity increases from CO (25b) (587.1 kJ mol⁻¹) to C₂H₄ (676.5 kJ mol⁻¹). This suggests again that for gold(I) the main contribution to the bonding of two-electron donor carbon-based ligands is σ in character. The BDE of the gold(I)-methyl bond in AuMe has been recently calculated (26) to be 226 kJ mol⁻¹, similar to the value estimated for the Au(I)-CO bond.

CONCLUSIONS

Undoubtedly gold chemistry has some unusual features of great interest. Relativistic effects are responsible for *ca* 20% contraction in the covalent radius of mercury (27 a-c) and, presumably, for a corresponding increase of the BDE. It has recently been observed (27d) that the radius of gold(I) is smaller than that of silver(I), based

on the structural data for the isostructural [M(Pmes₃)₂]⁺ cations, (M = Ag, Au; mes = 1,3,5-Me₃C₆H₂) obtained from their tetrafluoroborate derivatives*.

Catalytic applications of gold are still rather small in number but are expected to grow in their importance. For example, gold(I) carbonyls formed by the reductive carbonylation of gold(III) chloride in zeolite cages have been found to be catalytically active in nitrogen oxide reduction by carbon monoxide (28a). Also AuCl(CO) was found to be the best catalyst for the thermal chlorination of carbon monoxide to carbonyl chloride in the absence of light (28b).

An example of homogeneous solution catalysis by gold has recently been described in *Gold Bulletin* (29), which has also published a discussion on the potential of gold in heterogeneous catalysis (30).

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* See W S Rapson, *Gold Bull.*, 1996, 29, 143

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