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SYNTHESIS AND REACTIVITY OF CARBON-BONDED TRANSITION ELEMENTS

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Abstract - New experimental results recently obtained in this and other Laboratories are presented.These results suggest the following hints for further research :a) apparently slight modifications in the donor atoms set around a metal can alter the energetic situation considerably at the metal-carbon bond; b) the molecular parameters obtained by diffraction studies should always be complemented by studies of reactivity and/or of spectral behaviour in solution in order to have a reasonable description of a chemical species.

A) Reactions of Coordinated CO - Metals at the end of the periodic table do not easily combine with carbon monoxide to give binary uncharged metal carbonyls under ordinary laboratory conditions (1) . The so-called "matrix isolation technique" has been used at about 20°K for the preparation of thermally unstable carbonyls of palladium (2) , silver (3) and copper (3). On the other hand,anionic carbonyl species of the cluster type have been prepared by Chini and coworkers (4) . Only a limited number of thermally stable carbonyl derivatives of Pt(5) , Cu(6) and Au(6) with positive oxidation numbers is known. It was therefore of interest to investigate the reasons of this apparent low stability of M-CO bonds in this area of the periodic table. This problem is, of course , related to the current interest in catalytica properties of these metals. By using $Pt(CO)_2Cl_2$ and Au(CO)Cl as model compounds, it has been found (5) that these carbonyl derivatives are characterised by high $\nu_{CO}(cm^{-1})$ and unusually low molar extinction coefficients $\varepsilon(mol^{-1} x\ l x\ cm^{-1})$, see Table.

TABLE - I.r. Data in the Carbonyl Stretching Region for $Pt(CO)_2Cl_2$ and Au(CO)Cl

Compound	Solvent	$\nu_{CO}(cm^{-1})$		
$Pt(CO)_2Cl_2$	$SOCl_2$	2177		2136
	CH_2Cl_2	2180		2140
	Et_2O	2172		2125
	THF	2174		2130
	Toluene	2168^a		2127
Au(CO)Cl	$SOCl_2$		2162	
	CH_2Cl_2		2162	
	CCl_4		2152	
	THF		2158	
	Benzene		2153^b	
	Toluene		2153	

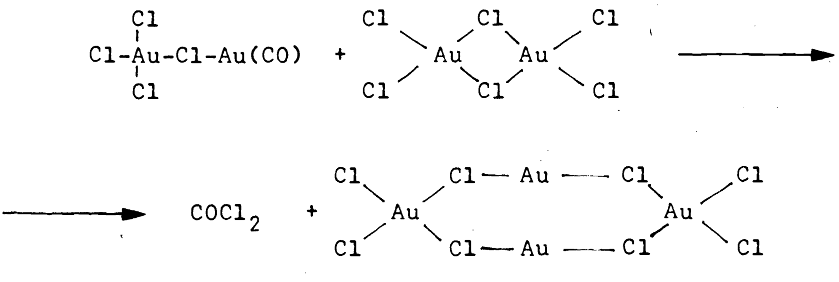
^{a} ε = 1200 $mol^{-1}xlxcm^{-1}$; ^{b} ε = 980 $mol^{-1}xlxcm^{-1}$

The conclusion which can be drawn from the data of the Table is that the degree of π-back bonding from either platinum(II) or gold(I) to the carbonyl groups is low. This may in turn be related to the increased stability of the d orbitals at the end of the periodic table and their consequent lower availability for π-bonding. Decreasing the formal charge on the metal and including the extra stabilisation induced by metal-metal bond (as in the case of anionic metal clusters) , or the use of strong σ-donor ligands may therefore promote the stabilisation of the M-CO bond in this area of the periodic table. Although spectroscopic evidence exists (3b) for an O-bonded carbonyl group on gold in CO and N_2 lattices , linkage isomerism does not appear to be a tenable proposition for the species stable at room temperature (7).

Copper plays an important role in several catalytic processes. Very few carbonyl derivatives of copper(I) are known. Cationic binary species of formula $[Cu(CO)_n]^+$ were reported (8) as thermally unstable , which could not be isolated . All the other stable carbonyl derivatives of copper(I) do include other ligands in addition to CO , most commonly nitrogen donor ligands. Water can also be a suitable ligand for carbonyl derivatives of copper(I) , (9,10).

A structurally characterised (11) compound is that originally reported (12) by Bruce and Ostazewski , in which the CuN_3-CO core is in a distorted tetrahedral geometry .The Cu-C distance (average) is 1.765 Å , which compares well with the value of 1.776 Å found by Floriani and coworkers (13) for $[Cu(dien)CO]^+ BPh_4^-$ (dien= diethylenetriamine) . The corresponding C-O distances are identical in the two complexes , within experimental error (1.120 Å) . The $\tilde{\nu}_{CO}$ are at about 2080 cm^{-1} in both complexes , a value which is on the low wavenumber side for copper(I) carbonyl complexes , as expected in view of the nature of the ligand involved in the coordination. Concerning C-O bond lengths , it is interesting to compare them with those reported (14) in an anionic iron(II) carbonyl complex , i.e., $Na_2Fe(CO)_4 \cdot 1.5$ dioxane . The C-O distances in this case are 1.175(7) and 1.162(8) Å , close to the values reported for the copper(I) derivatives , despite the large difference in $\tilde{\nu}_{CO}$ values. It has already been noted (15) that C-O bond lengths in metal carbonyls vary very little. Chemically significant information about the electronic situation in M-CO systems can better be obtained from carbonyl stretching measurements rather than from C-O bond lengths.

The high $\tilde{\nu}_{CO}$ values for Au(CO)Cl and $Pt(CO)_2Cl_2$ suggest that the carbon of the carbonyl group may undergo easy attack by nucleophilic reagents. An initial attack by the chlorine of Au_2Cl_6 on coordinated CO of the unstable(16) $Au_2Cl_4(CO)$ can be suggested to be involved in the formation of the tetrameric Au_4Cl_8 (17) from Au_2Cl_6 and Au(CO)Cl :



(1)

Secondary amines react (18) with $Pt(CO)_2Cl_2$ according to the following stoicheiometry :

$$Pt(CO)_2Cl_2 + 3\ R_2NH \longrightarrow R_2NH_2^+Cl^- + PtCl(CONR_2)(CO)(HNR_2) \quad (2)$$

(R= Me, Et, ^{i}Pr)

The starting dicarbonyl can be obtained back by treating the carboxamido complex with gaseous HCl in hydrocarbons , as monitored by i.r. spectroscopy in the carbonyl stretching region. The products of reaction (2) are assumed to be monomeric (no MW determinations could be carried out in view of the labile nature of these compounds) ; i.r. evidence exists for the presence of geometrical isomers in solution.The question which now arises is how the isomerisation , which has been shown to occur at a reasonably fast rate, can take place. The molecular structure of one of the two isomers is now under investigation , which definitely will establish the relative position of the CO and $CONR_2$ ligands within the coordination sphere of the metal. This problem is somewhat related to the failure to observe CO insertions in between $M\text{-}NR_2$ bonds (19).

B)Reactions of CO_2 and CO_2-Like Molecules with Compounds of Transition Elements - Insertions of CO_2 on $M\text{-}NR_2$ bonds are , on the contrary , very well established , especially for early transition elements (20). In a more general project concerned with the reactivity of carbon dioxide , we reacted UCl_4 with Et_2NH in the presence of CX_2(X= O,S) in hydrocarbons and obtained good yields of $U(X_2CNEt_2)_4$, (21). The preparation of the O-carbamato derivative by this method considerably simplifies the known procedure which requires the preparation of the amido complex. Two possible pathways can operate in our case:

$$\text{a)}\quad UCl_4 + 8\,R_2NH \longrightarrow U(NR_2)_4 + 4\,NH_2R_2^{+}Cl^{-} \tag{3}$$

$$U(NR_2)_4 + 4\,CO_2 \longrightarrow U(O_2CNR_2)_4 \tag{4}$$

$$\text{b)}\quad 2\,R_2NH + CO_2 \rightleftharpoons R_2NH_2^{+}R_2NCO_2^{-} \tag{5}$$

$$4\,R_2NCO_2^{-} + UCl_4 \longrightarrow 4\,Cl^{-} + U(O_2CNR_2)_4 \tag{6}$$

Gasvolumetric measurements have established that equilibrium (5) is almost completely shifted to the right and , moreover, no amido complex was obtained from UCl_4 and R_2NH .It can therefore be concluded that the operative pathway is b), i.e. chloride exchange by $R_2NCO_2^-$. Uranium tetrakisdiethylcarbamato is expected to be a valuable intermediate for the preparation of uranium(IV) complexes.

A presumably hydrolytic product of formula $U_4O_2(O_2CNEt_2)_{12}$ was isolated (22). This compound contains a central core constituted by a nearly planar U_4O_2 system with tri-coordinate oxygens bridging the uranium atoms. The two central oxygen atoms are at non-bonding distance.

Coordination of CO_2 to transition elements has now been firmly established in a few cases. Work by Floriani and Fachinetti at this Institute has produced the first example of a reversible CO_2 carrier (23a) , presumably C-bonded to cobalt :

$$NaCo(salen) + CO_2 + py \rightleftharpoons (py)Co(salen)CO_2Na \tag{7}$$

I.r. data suggest that the CO_2 ligand is bent in the complex obtained from reaction (7). The X-ray investigation on a CO_2-adduct of a substituted Schiff base cobalt complex is now in progress. Coordination through carbon was suggested for the CO_2-adduct of an iridium(I) complex (23b). The CO_2-adduct of a nickel complex was shown (24) to be C- and O-bonded to the central metal atom. Reversible insertion in between a Cu-OR bond has also been found(25) to form an alkyl-carbonato derivative.

Biscyclopentadienyldicarbonyltitanium(II) reacts with diphenylketene (25) to give , among other products , a dimeric compound of formula $[TiCp_2(Ph_2C_2O)]_2$. The X-ray investigation has revealed that titanium is coordinated through both C and O of the ketene ligand , in agreement with the absence of CO absorptions in the i.r. above 1600(reciprocal cm).It is interesting noting , in this connection , that also two acyl derivatives of titanium (27) and zirconium (28) have been found by Floriani and coworkers to be C- and O-bonded to the central metal atom . Diphenylketene bonded to the metal through the C-C π-system has been suggested for platinum (29) and found for mangane -

se(30) by X-ray diffraction methods.

C) Coordinative Addition of CO and Olefins - The electronic situation in VCp_2 appears to be more favourable for CO coordination than the previously noted cases of Cu(I), Au(I) and Pt(II). The one-electron oxidation of this species by $V(CO)_6$ in the presence of CO to give $[VCp_2(CO)_2]^+$ was reported some years ago (31). VCp_2 manifests its basic character by firmly bonding CO (32) - a remarkably low $\tilde{\nu}_{CO}$ at 1881 cm^{-1} was observed - , CS_2(33,34) and activated olefins (34). The X-ray investigation of the CS_2 adduct has shown that vanadium is C- and S-bonded (35), similar to the corresponding platinum derivative (36).

Interestingly, starting with either diethyl maleate or diethyl fumarate, the same product, VCp_2(olefin), was obtained : on the basis of spectroscopic and chemical evidence, a "trans" structure was assigned to this compound(34).

D) Reactivity of Anhydrous Gold(III) Chloride - C-H bond activation is a subject of considerable interest (37), and auration of aromatic hydrocarbons is a known(38) although somewhat disputed (39,40) reaction. Azobenzene and 4,4'-azotoluene were reported (41,42) to react with Au_2Cl_6 to give simple adducts $AuCl_3(L)$. In this case, contrary to the well known example of ortho-metalation by palladium(II) and platinum(II), (43), no attack by the metal takes place at the more favourable aromatic position. The 4,4'-azotoluene adduct has now been investigated (44) by X-ray diffraction methods : coordination to gold was found to be through one of the nitrogens of the azo-aromatic system. It is interesting to note that the closest Au···H approach calculated for one of the ortho aromatic positions might be taken to suggest an incipient Au-H interaction (about 2.4 Å). This, however, contrasts with the chemical behaviour of the compound, which is rather inert and in no case was it found to undergo ortho-metalation (44).

E) Organic Dichalcogenides as Bridging Ligands for Rhenium(I) Carbonyl Compounds - The "solvent-stabilised intermediate" (45) $Re_2Br_2(CO)_6(thf)_2$, (thf= tetrahydrofuran), is a convenient starting material for the preparation of several rhenium(I) carbonyl derivatives under mild conditions. Diphenyldisulphide (45) and dimethyldisulphide (46) react with the dimeric thf-adduct to give dimeric products $Re_2Br_2(CO)_6S_2R_2$, whose molecular structures present the rather unusual feature of bridging Br and S_2R_2 ligands. Also diphenyldiselenide reacts promptly with the thf-adduct yielding a compound which has been shown by X-ray diffraction methods (47) to be isostructural with the corresponding sulphur analogue. An interesting aspect of these studies is that while the solid-state parameters did not show any dramatic change within this series of compounds $Re_2Br_2(CO)_6E_2R_2$ (E=S, R=Me, Ph ; E=Se, R=Ph), the i.r. data in the carbonyl stretching region do show a slight but definite effect of the nature of the chalcogen atom, including the tellurium derivative (E=Te, R=Ph). Also the equilibrium data for the displacement reaction

$$Re_2Br_2(CO)_6E_2R_2 + 2\ thf \rightleftharpoons Re_2Br_2(CO)_6(thf)_2 + E_2R_2 \qquad (8)$$

are definitely affected by the nature of the chalcogen atom attached to rhenium and/or the nature of the group R. For the phenyl derivatives it has been found that both the $\tilde{\nu}_{CO}$ (reciprocal cm) and the equilibrium constants for reaction (8) decrease regularly from S to Te. The significance of these results is in terms of chemical stability change along a group of donor atoms.

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