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PROPERTIES OF THE METAL-LIGAND BOND AND APPLICATIONS IN CATALYSIS

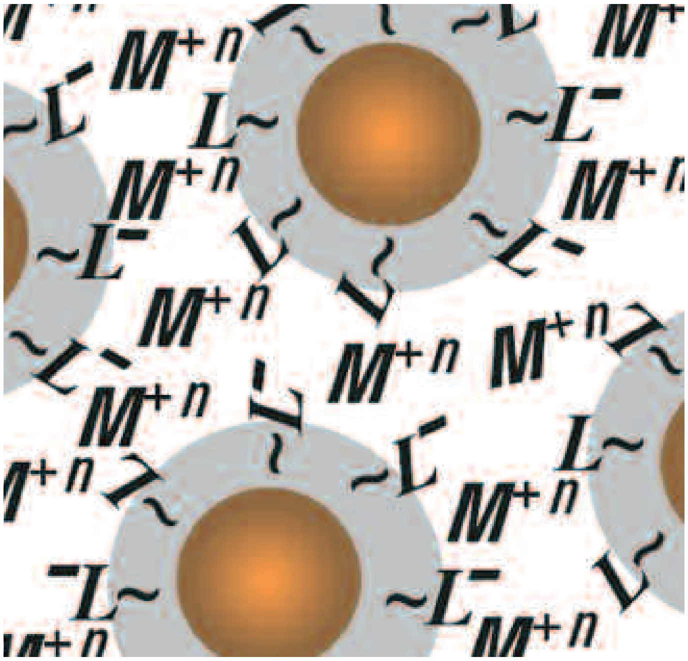
The items covered in this article can be divided in two parts: the properties of the metal-ligand bond as a function of the nature of the metal, preferably in periodic sequences, and insertion of metal cations (or metal particles) on a support. Furthermore, within the first item two further main areas will be discussed, namely: organometallic derivatives, and "classical" coordination compounds.

The nowadays vast area of *Coordination Chemistry* goes back to Alfred Werner, the initiator of this discipline, and the 1913 Nobel Prize winner for his important contributions. A. Werner in 1893 published the first of a long series of scientific contributions, based on his doctorate thesis at the University of Zurich "*Beitrag zur Konstitution anorganischer Verbindungen*" [1]. The term *Koordinationszahl* was introduced and defined at page 326 of this 63-page-long article.

Several Nobel prizes have been awarded to scientists who have carried out their studies in areas related to Inorganic Chemistry in addition to the already mentioned Alfred Werner: in 1912, V. Grignard and P. Sabatier; in 1963, G. Natta and K. Ziegler; in 1973, E.O. Fischer and G. Wilkinson for their studies "on the chemistry of organometallics, so-called sandwich compounds"; in 2001, W.S. Knowles, R. Noyori, K.B. Sharpless; in 2005, Y. Chauvin, R.H. Grubbs, R.R. Schrock.

Properties of the metal-ligand bond

In order to position the observed experimental facts within an appropriate context, we can first consider a simple parameter, namely the enthalpy change connected to the transfer into the gas phase of one mol of the chemical elements from their state at 298 K. If we include some of the Main Group elements into this frame, we soon realize that two elements occupy a leading position within the Periodic Table, namely tungsten among transition *d* metals [$W_{(s)} \rightarrow W_{(g)}$, 849.kJ mol^{-1}] and carbon among Main Group ele-



ments [$C_{(s)} \rightarrow C_{(g)}$, 717 kJ mol^{-1}]. Taking into consideration that a thermodynamic cycle leading to products requires the transfer of the element from its standard state at 298 K to the gas phase, this primary information leads to the conclusion that wolfram and carbon are very good candidates, within the Periodic Table, to form strong bonds in their compounds. This consideration is normally substantiated by experiment.

Stringent requirements for a metal-containing system to perform well in a catalytic cycle are that it should:
a) not combine irreversibly with the substrate to be converted;
b) provide a low-energy path for the formation of the activated (or intermediate) complex;
c) not lead to kinetically or thermodynamically stable intermediates.

Catalysis by transition metals is of course related to the typical reactivity of the metal. Therefore, an important parameter to take into consideration derives from kinetic studies in substitution processes. When *usual oxidation states* are considered, substitution rate constants of first-order processes *decrease* in the order 3*d*>4*d*>5*d* [2]. However, for inorganic systems characterized by a central metal atom in *a low oxidation state*, the reactivity in substitution processes follows a trend whereby the compounds containing a central metal atom belonging to the second *d* (4*d*) transition series are generally more kinetically labile than the corresponding 3*d* and 5*d* counterparts.

Organometallic derivatives

Consistent with the previous observations, derivatives of 4*d* elements *frequently* are more efficient than the corresponding 3*d* and 5*d* counterparts for processes carried out using reducing gaseous substances such as carbon monoxide and dihydrogen, *e.g.* the hydroformylation reaction and related processes [3], and the CO/olefin co-polymerization [4]. The Fischer-Tropsch reaction [5] converting the CO/H_2 mixture to hydrocarbons and operating on supported metal-containing catalysts, will not be considered here, although this process is presumably due to become of great importance in the near future in order to compensate for the expected decrease of oil production.

The kinetics of the hydroformylation reaction, as represented in eq. (1) for an internal symmetrical olefin (in order to avoid the further complication due to the presence of positional isomers in the product), in 1952 were found [6a-c] to depend in a unexpected way on carbon monoxide pressure: by operating at constant dihydrogen pressure, the rates of the reaction would go through a maximum situated around 10 atm of CO pressure, as reported in a detailed study by Natta, Ercoli and Castellano [6d] based on a series of experiments with cyclohexene as substrate.

$$RCH{=}CHR + CO + H_2 \rightarrow RCH_2\text{-}CH(CHO)R \qquad (1)$$

At that time a few low-valent carbonyl species of cobalt were known: $Co_2(CO)_8$, $Co_4(CO)_{12}$ and $CoH(CO)_4$ and the following

equilibria were therefore of the outmost interest for mechanistic considerations on the catalytic reaction :

$$2\ Co_2(CO)_8 \rightleftarrows 4\ CO + Co_4(CO)_{12} \qquad (2)$$

$$Co_8(CO)_8 + H_2 \rightleftarrows 2\ CoH(CO)_4 \qquad (3)$$

As early as 1954 [7a] Ercoli and Barbieri-Hermitte established that the formation of $Co_4(CO)_{12}$ from $Co_2(CO)_8$ is an *endothermic* reaction. This result was later confirmed by Bor and coworkers who also extended their study to the corresponding rhodium complexes [7b-d], thus concluding that also in the rhodium case the formation of the tetranuclear cluster is endothermic, although less so than in the case of cobalt.

One of the fundamental steps in the hydroformylation reaction is believed to be the transformation from a cobalt-bonded alkyl group to the corresponding cobalt-acyl derivative. It is important to point out that the so-called carbon monoxide insertion reaction, see eq. (4), was shown [8] for $MnMe(CO)_5$ to be based on an alkyl migration to an adjacent manganese-bonded CO group. From a thermodynamic viewpoint, the carbonyl insertion reaction in 2,2'-diethoxydiethyl ether was found [9] to be characterized by negative enthalpy- and entropy changes, their absolute values both decreasing with increasing number of carbon atoms in the alkyl chain from C_1 to C_3.

$$MnMe(CO)_5 + CO \rightleftarrows Mn(CO)Me(CO)_5 \qquad (4)$$

Most important was the observation [10] that the kinetics of the carbonyl insertion reaction promoted by PPh_3 in a series of alkyl carbonyl compounds $Mn(C_nH_{2n+1})(CO)_5$ reach a maximum for n=3, the rate of carbonylation being almost unchanged from n=3 to n=17. It is believed that this result is relevant not only for this specific reaction, but also for other related processes, which are believed to proceed *via* insertion steps.

From transformations taking place in carbonyl compounds of transition metals, most important are the properties of the M-CO bond and several reviews on this subject are available in the literature. More recently, the properties of M-CO bonds have been studied for metals on the right-hand side of the transition *d* series, for non-transition elements and for transition *f* metals. It is appropriate at this point to remind that the first carbonyl derivative of a transition *d* element, namely *cis*-$[PtCl_2(CO)_2]$, whose molecular structure was solved recently [11a], was prepared about 140 years ago [11b]. This compound, whose central metal atom has a $5d^8$ configuration, and accordingly has the properties of a transition system, is characterized by high CO stretching vibrations (around 2,150 cm^{-1}), which suggests a low degree of π-back donation. Metal carbonyl derivatives can also be found with metal cations with a closed-shell electronic configuration [*e.g.*, Au(CO)Cl, crystallographically characterized; $Ca(C_5Me_5)_2CO$; $B(CF_3)_3CO$, crystallographically characterized], while more recent literature acquisitions concern the isolation of carbonyl derivatives of f^n metal cations, namely $Yb(C_5Me_5)_2CO$, and $U(C_5Me_4H)_3CO$.

For industrial processes involving CO and olefins as reagents, see above, of the outmost importance is a detailed knowledge of the relative affinity of these molecules for metal centers along the Periodic Table. If this information becomes fully available, which is hardly the case at the present time, then it will be possible to better describe energy profiles by extending to transition (or intermediate) states the *differences* observed for the conventional thermodynamic data of ground-state molecules. Some years ago our Laboratories started to collect some bond enthalpy data, thus finding that the position of the metal cation within the Periodic sequence is of importance for this purpose. Thus, for example, an olefin such as norbornene and CO have a comparable tendency to coordinate to the $5d^{10}$ system of AuCl(CO) [12a], while CO remains firmly coordinated to the $3d^3$ system of bis(cyclopentadienyl)vanadium(II) in the presence of olefins [12b]. Moreover, the platinum(II) system of *cis*-$[PtCl_2(CO)_2]$ shows a definite preference for CO with respect to olefins such as cyclohexene and 1-octene. The bond of CO to gold(I) in AuCl(CO) [13a] has been evaluated to be rather strong, close to that calculated for the cationic species $[Au(C_2H_4)]^+$ [13b].

Palladium and the adjacent element silver occupy a special position within the Periodic Table, as they are characterized by a rather low enthalpy of atomization. It was therefore rather intriguing the fact that $Pt(CO)_4$, as prepared by the atom vaporization technique at low temperature, has a very short lifetime at room temperature,

while the olefin complexes of platinum(0), of general formula Pt(olefin)$_3$ [14a] have been isolated, and some have been even structurally characterized. However, it has recently been shown [14b] that the olefin complexes are unstable under a CO atmosphere, even in the presence of a substoichiometric amount of CO, thus forming platinum metal "decorated" with CO on the surface.

We have now some new information which may be useful to explain the facts observed in the course of some catalytic processes.

If $CoH(CO)_4$ was formed according to equilibrium (2) under the operating conditions of the hydroformylation reaction, then the possibility exists that intermediate alkyl derivatives $CoR(CO)_4$ are present, which may undergo the carbonyl insertion reaction to $Co(COR)(CO)_4$, followed by hydrogenolysis to aldehydes and $CoH(CO)_4$. The negative effect of the CO pressure on rates has been attributed to the presence of active uncharged intermediates with a lower content of carbon monoxide, for example of the type $\{Co(COR)(CO)_3\}$. An alternative explanation could consider the presence in solution, under the operating conditions of the hydroformylation reaction, of ionic species resulting from equilibria of the type shown below, involving Lewis bases L [14c, d], namely:

$$3Co_2(CO)_8 + 2nL \rightleftarrows 2[CoL_n][Co(CO)_4]_2 + 8CO \qquad (5)$$

If the active intermediate originates within the cationic part of the complex resulting from the disproportionation equilibrium (5), then the effect of the partial pressure of CO would be equally well explained with no need of invoking the presence of *neutral* unsaturated cobalt species.

The palladium-catalyzed CO/olefin copolymerization [4] requires a perfectly alternating insertion of CO and the olefin within the Pd-OMe bond formed primarily in methanol as medium from the palladium(II) precursor. Assuming that an initial insertion of the olefin (for simplicity we consider ethylene) is followed by the insertion of CO, the sequence $Pd\text{-}COCH_2CH_2OMe$ would be formed. At this point evidently a second CO insertion is less favorable than the ethylene insertion, the sequence $Pd\text{-}CH_2CH_2COCH_2CH_2OMe$ being preferred to $Pd\text{-}COCOCH_2CH_2OMe$. Support to this hypothesis comes from some considerations on *ground-state* molecules containing carbonyl functions. Although only a limited number of data are available for this kind of molecules, the dissociation enthalpies for the indicated bonds in MeC(O)-C(O)Me and PhC(O)-C(O)Ph are 282.0 and 277.8 kJ mol^{-1}, respectively. On the other hand, the bond enthalpy in Me-C(O)Ph is 355.6 kJ mol^{-1}, thus suggesting a considerably stronger bond in this type of molecule. Moreover, the C-C distance in MeC(O)-C(O)Me is a rather long 1.540(6) Å [15].

"Classical" coordination compounds

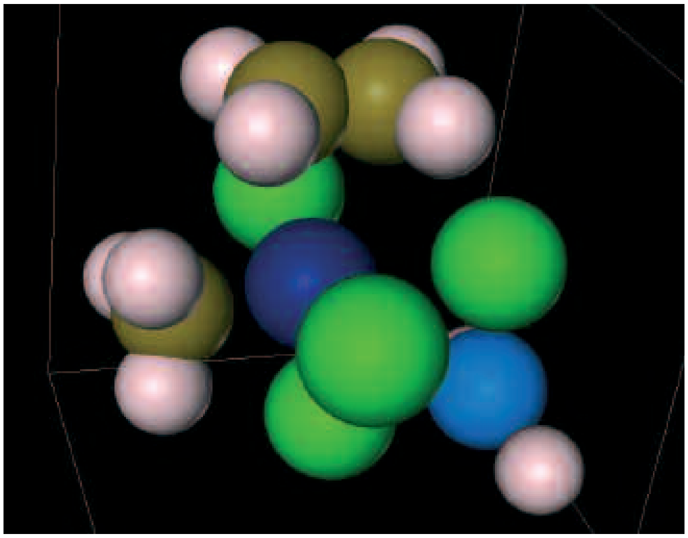
This section will cover *N,N*-dialkylcarbamato metal complexes, which were extensively studied by this research group [16]. The corresponding ligating function of the mononegative group $[O_2CNR_2]^-$ is, from a structural viewpoint, similar to other well-established ligands such as the carboxylato $[O_2CR]^-$, the hydrogencarbonate $[O_2COH]^-$, or the carbonate $[O_2CO]^{2-}$, all being planar and with similar binding properties.

Only the most recent developments in this field will be discussed here, while details on this subject and on earlier studies can be found elsewhere [16]. Preparative and structural data on *N,N*-dialkylcarbamic acids can be found in a recent paper [17]. *N,N*-dialkylcarbamic acids are thermodynamically stable products under atmospheric pressure of carbon dioxide, and some dialkylamines are consequently converted to the corresponding acids HO_2CNR_2. In the case of R=benzyl, the $HN(CH_2C_6H_5)_2/CO_2$ reaction was followed spectroscopically and the carbamic acid $HO_2CN(CH_2C_6H_5)_2$ was found to be the primary product of the reaction, as formed in a slow step, followed by the reaction with excess amine to give $[NH_2(CH_2C_6H_5)_2][O_2CN(CH_2C_6H_5)_2]$. However, $HO_2CN(CH_2C_6H_5)_2$ was established to be the thermodynamic product as it was spectroscopically detected at the end of the process.

The already mentioned review-articles [16a,b] report the synthetic procedures adopted for the preparation of this class of compounds and the reader should therefore refer to those for further details. On the other hand, a rather exotic preparative method was recently found [18], as applied to the preparation of the crystallographically established *trans*-$Cu(O_2CNBz_2)_2(O_2CN(CH_2C_6H_5)_2$. This compound originates from a biphasic system consisting of a Cu^{2+} aqueous solution undergoing fast extraction into the hydrocarbon layer containing the amine under carbon dioxide at atmospheric pressure. The space filling model of this molecule shows the inner core to contain the carbamic functional groups, while the periphery is decorated with the alkyl groups, thus explaining the rather good solubility of this compound in hydrocarbon solvents.

A recent acquisition from our laboratories deals with the preparation and crystallographic analysis of the two tetranuclear cerium derivatives [19] of formula $Ce_4(O_2CN^iPr_2)_{12}$ and $Ce_4(\mu_3\text{-}O)_2(O_2CN^iPr_2)_{12}$. The important point is that the latter product derives from the former by oxidation with dry dioxygen, which represents a quite unique situation, in view of the observation that most of the μ-oxo derivatives originate from *hydrolysis* of the metal-containing carbamate precursor [16b], *vide infra*.

Work has recently been performed on *N,N*-dialkylcarbamato complexes of the lanthanide (Ln) elements [20]: their crystallographic characterization has allowed us to collect a set of precise bonding parameters. This has been utilized to verify *the lanthanide contraction* along a series of *isostructural* complexes [monoclinic, space group *C2/c*] spanning 12 atomic numbers and, for each compound, with four different types of Ln-O bond distances. The plots of the Ln-O bond distances as a function of the electronic $4f^n$ configuration flatten out, the minimum being, of course, observed at lutetium(III). This information may be extrapolated to present an important conclusion, namely that the bonds from the donor atom to the lanthanide become stronger along the series, and presumably this can be generalized to several types of donor atoms. This observation may be related to some catalytic data available for lanthanides. As a matter of fact, diene polymerization was found to be more efficiently catalyzed by neodymium- than by lutetium organometallic complexes [21a]. Fluorenyl-allyl complexes of neodymium catalyze the polymerization of styrene, the efficiency being maximum at neodymium [21b]. An article by a research group from mainland China has also pointed out that the efficiency in the polymerization of dienes along the lanthanide series has two maxima, one at neodymium and the second one at gadolinium [21c].



N,N-dialkylcarbamato metal complexes are readily attacked by water, giving the appropriate μ_n-oxo derivative, in a particularly chemoselective way, provided the exact amount of water is used in the reaction.

The reaction can be exemplified for the case of the aluminum complex, which undergoes hydrolysis [22a] according to the stoichiometry of eq. (6):

$$4Al(O_2CN^iPr_2)_3 + 2H_2O \rightarrow Al_4(\mu_3\text{-}O)_2(O_2CN^iPr_2)_8 + 4CO_2 + 4NH^iPr_2 \quad (6)$$

The anaerobic treatment of the carbamate precursor of iron(II) with the stoichiometric amount of water, see eq. (7), led to the synthesis [22b] of one of the few known examples of a μ-oxo derivative of *iron(II).*

$$8Fe(O_2CN^iPr_2)_2 + 2H_2O \rightarrow Fe_8(\mu_3\text{-}O)_2(O_2CN^iPr_2)_{16} + 4CO_2 + 4NH^iPr_2 \quad (7)$$

Insertion of metal cations (or metal particles) on a support

In general, for the interaction between a support and a molecular complex, the factors influencing the final result were predicted to be: (a) the nature of the metal-containing precursor; (b) the nature of the support, and, (c) the presence of a solvent, if any. The experimentally verified reactivity of *N,N*-dialkylcarbamato metal complexes with water led us to verify the possibility of grafting metal cations on oxide supports, *i.e.* containing hydroxyl groups of even low acidity. Our expectation has been fully verified [16b]. For example, zirconium(IV) has been grafted on dehydrated, at a moderately high temperature ≡SiOH), by using the mixed carbamato-cyclopentadienyl derivative $Zr(C_5H_5)(O_2CNEt_2)_3$ as starting material, see eq. (8).

$$Zr(C_5H_5)(O_2CNEt_2)_3 + \equiv SiOH \rightarrow \equiv SiO\text{-}Zr(\eta^5\text{-}C_5H_5)(O_2CNEt_2)_2 + CO_2 + NHEt_2 \qquad (8)$$

The stoichiometry of the reaction was established gasvolumetrically, while the nature of the grafted products was secured by CP MAS ^{13}C spectrometry [23a]. Also, gold(I) complexed to PPh_3 in $Au(O_2CNR_2)PPh_3$ was supported on silica [23b].

Lately the interest of this research group was addressed to the possibility of grafting metals and metal cations on amorphous carbon. For this purpose, Carbon Vulcan XC 72 was selected as the support and, with an appropriate choice of the metal containing precursor, finely dispersed metal-containing particles, as established by TEM measurements, were thus obtained [24].

Ackowledgements: The expertise of the coworkers who appear in the list of references is gratefully acknowledged. The collaboration with Professor Marcello Mellini of the University of Siena was essential for the TEM measurements of several new products. Financial support was provided by: MIUR Programmi di Interesse Nazionale 1999-2006; the University of Pisa; Pirelli Labs, Milano; Novara Technology, Novara.

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