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# PROPERTIES OF THE METAL-LIGAND BOND AND APPLICATIONS IN CATALYSIS

Understanding the properties of the metal-ligand bond will help us considerably in the rationalization of the known catalytic phenomena and in predicting the feasibility of new ones.

The following series of compounds will be taken into consideration: a) organometallic derivatives for central metal atoms belonging to the same group of the periodic table; b) coordination compounds of the lanthanide series, with special reference to the *N,N*-dialkylcarbamato derivatives and to solvated lanthanide chlorides. The properties of nanometric metal-containing particles on a given support will be discussed.

**S**ynthetic procedures aimed at preparing new or already known classes of inorganic compounds are still of the utmost importance. Simpler purification methods and sometimes solventless preparations should be taken into considera-

tion. Moreover, the properties of the metal/ligand system are better studied for series of compounds whereby coordination numbers and geometries are kept constant within certain limits, the nature of the metal atom thus becoming the most important variable. For this purpose the fol-

lowing systems will be considered:

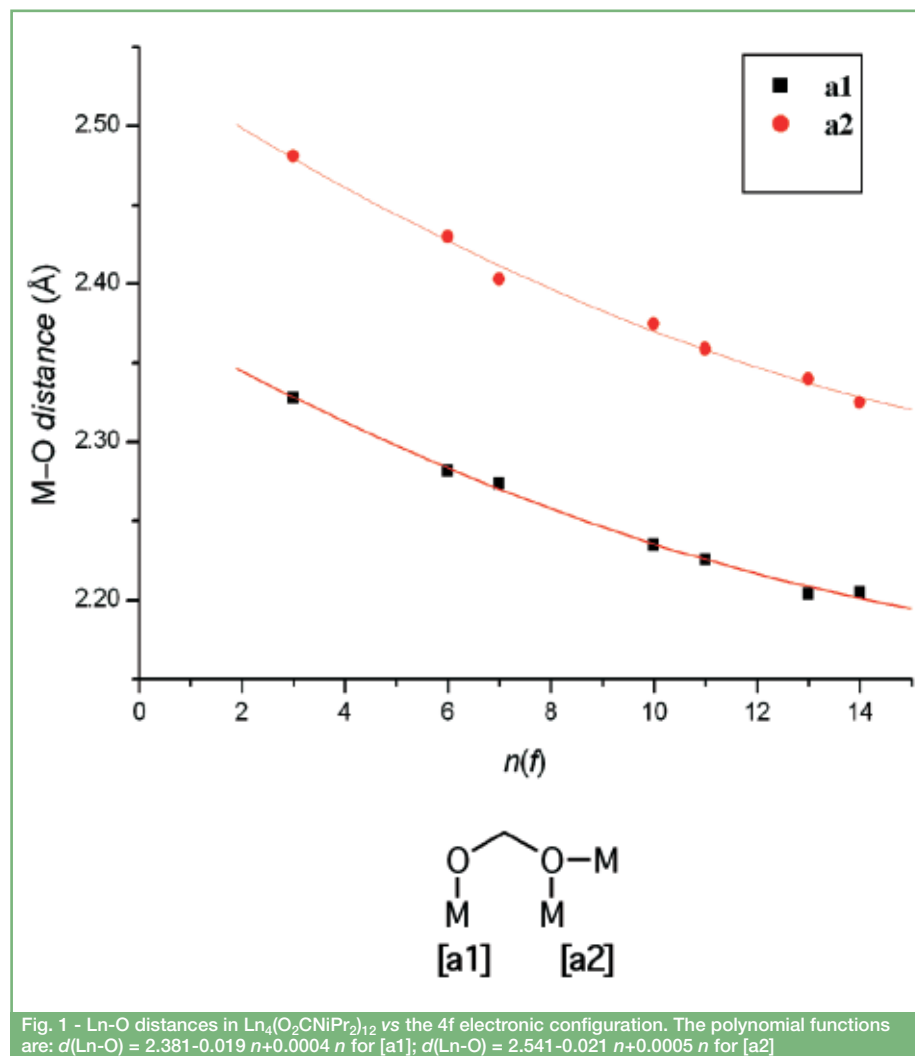
a) organometallic compounds with central metal atoms belonging to the same vertical sequence of transition *d* elements;  
b) coordination compounds of the lanthanides. Furthermore, the properties of metal particles will be discussed, as produced on different supports.

a) An interesting comparison in connection with catalytic properties is that between

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finely divided palladium and platinum, metals which are of the utmost importance in catalysis. Although palladium is much less expensive than platinum, it is less frequently used than its intragroupal partner in catalytic hydrogenations. The activity of palladium was reported to be similar to, if not even higher than, that of platinum [1], in the liquid phase, in terms of turnover frequency for the hydrogenation of cyclohexene at 298 K. The palladium/platinum comparison requires knowing the properties of these elements, the starting point being the atomization enthalpies, *i.e.* for the process  $M_{(s)} \rightarrow M_{(g)}$  [ $376.6 \pm 2.1$  kJ mol<sup>-1</sup> for Pd and  $565.7 \pm 1.3$  kJ mol<sup>-1</sup> for Pt].

Also relevant is the more labile character of palladium(II) complexes with respect to the platinum(II) analogues in substitution reactions. For example, the <sup>13</sup>CO/<sup>12</sup>CO exchange in  $[MCl_3(^{13}CO)]^-$ , M=Pd, Pt, has a rate constant of  $5.7 \times 10^{-1}$  and  $3.4 \times 10^{-3}$  s<sup>-1</sup>M<sup>-1</sup> for palladium and platinum, respectively [2]. Furthermore, the ligand exchange with pyridine in *trans*-M(PEt<sub>3</sub>)<sub>2</sub>(*o*-tolyl)Cl, M=Pd, Pt, has rate constants of  $9.7 \times 10^{-3}$  s<sup>-1</sup>, for M=Pd, and  $4.4 \times 10^{-7}$  s<sup>-1</sup>, for M=Pt [3a]. The lower atomisation enthalpy corresponds to weaker intermetallic bonds in solid palladium, while faster processes for palladium indicate that the 4*d* element labilizes its bonds more readily than platinum does. Several years ago we have pointed out [4a] that the higher tendency of platinum to bond formation is probably to be detected in both high-valent and low-valent complexes. In the case of palladium(II), the Pd-CO bond enthalpy in the chloride-bridged dimer Pd<sub>2</sub>Cl<sub>4</sub>(CO)<sub>2</sub> was evaluated to be about 100 kJ mol<sup>-1</sup>. A carbonyl derivative of silver(I) with a fluorinated tris(pyrazolyl)borato ligand was reported to exhibit a  $\nu_{CO}$  at 2,153 cm<sup>-1</sup> [5].



The low tendency of 4*d* and 5*d* elements of group 10 to form uncharged binary carbonyl derivatives is well evidenced by the low stability of the tetracarbonyls. As a matter of fact, the tetracarbonyls  $M(CO)_4$ , once synthesized *via* the MOCVD methodology at low temperature, have been shown [6a] to undergo ready decomposition. However, the cationic tetracarbonyls  $[M(CO)_4]^{2+}$ , M=Pd, Pt, are now known as their  $[Sb_2F_{11}]^{2-}$  derivatives [6b], stabilisation in these systems presumably arising from

both the lattice energy and the positive charge reinforcing the M-CO  $\sigma$ -bond.

At an earlier stage we have pointed out [6c] that the dinuclear carbonyl derivatives of palladium(II) and platinum(II)  $M_2Cl_4(CO)_2$ , are characterized by a high  $\nu_{CO}$  [ $2,166$  cm<sup>-1</sup> for M=Pd, and  $2,139$  cm<sup>-1</sup> for M=Pt], thus suggesting a low degree of  $\pi$ -back donation. Similar conclusions were drawn [6c] for the carbonyl derivatives of gold(I),  $AuX(CO)$ , X=Cl, Br. The average CO stretching frequencies for  $M(SO_3F)_2(CO)_2$ , M=Pd, Pt, are at

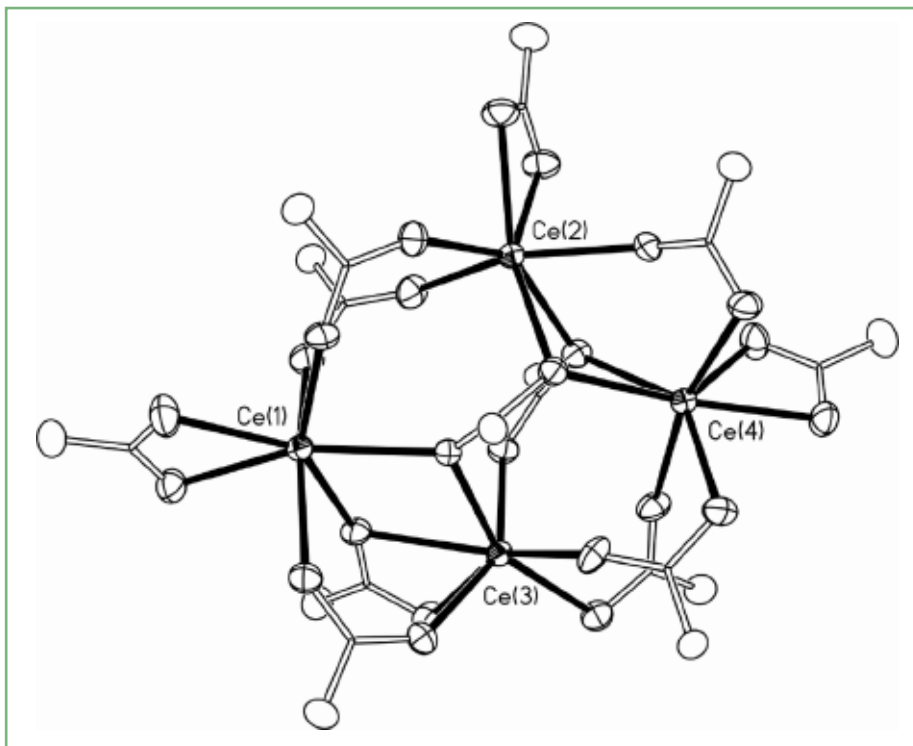


Fig. 2 - Molecular structure of  $Ce_4(O_2CNiPr_2)_{12}$

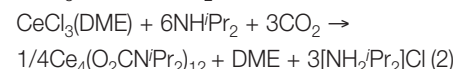
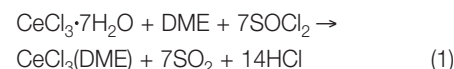
2,217 and 2,201  $cm^{-1}$ , respectively [7]. An interesting problem is the CO/olefin competition for a given metal centre, in connection with catalytic processes such as the CO/olefin copolymerization, the hydroformylation, the hydrocarboxylation and the hydroesterification of olefins. Thus, in CO/olefin competition experiments [8], palladium and platinum in their oxidation state II generally prefer CO. This tendency is also valid for copper(I) in

pyrazolylborato complexes. Palladium occupies a central role in catalytic phenomena connected with the formation of carbon-carbon bonds [9].

b) Attention has recently been paid in these Laboratories to *N,N*-dialkylcarbamate derivatives [10] of lanthanides (Ln). We have found that the tetranuclear *iso*-propyl derivatives  $Ln_4(O_2CNiPr_2)_{12}$  are isostructural over a range of 12 atomic numbers. The products were prepared [11] starting from

the solvento species [12]  $LnCl_3(ether)_x$ , ether = THF or dimethoxyethane. The internal parameters of the  $Ln_4(O_2CNiPr_2)_{12}$  complexes were accurately determined by X-ray diffraction methods and the variation of the Ln-O distance as a function of the position of the central metal in the series is shown in Fig. 1. If the reasonable assumption is made that the radius of the lanthanide-bonded oxygen is constant over the series, the data correspond to the experimental check of the well-established lanthanide contraction for a series of *isostructural* compounds.

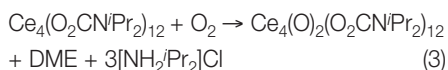
More recently, the di-*iso*-propylcarbamate derivative of cerium(III), see eqns. (1) and (2), has been synthesized together with the product of its oxidation with dioxygen, see eqn. (3), a rare case of oxidation in this type of products [13]. As a matter of fact, the large majority of the  $\mu$ -oxo derivatives of the dialkyl-carbamate family originate from hydrolytic processes [10]. Both compounds have been characterized by X-ray crystallography, thus showing that the parent compound, see Fig. 2, has a similar molecular arrangement with respect to the oxidized derivative, see Fig. 3. The interatomic non-bonding O...O distance is 2.579 Å.



### Proprietà del legame metallo-legante e applicazioni alla catalisi

Comprendere le proprietà del legame metallo-legante può essere di grande aiuto nel razionalizzare fenomeni catalisi conosciuti e nel predire la fattibilità di quelli nuovi. Verrà presa in considerazione la seguente serie di composti: a) derivati organometallici per atomi centrali metallici appartenenti allo stesso gruppo della tavola periodica; b) composti di coordinazione della serie dei lantanidi, con particolare riferimento ai derivati dell'*N,N*-dialchilcarbamato e ai cloruri di lantanidi solvatati. Saranno inoltre illustrate le proprietà di particelle nanometriche contenenti metalli su un opportuno supporto.

RIASSUNTO



A further point of interest is represented by the possibility of using molecular well-defined metal-containing precursors to generate metal particles on a given support. Preliminary to this type of study is the identification of the appropriate match between the nature of the support and the metal to be grafted, as a function of the metal precursor. On continuation of our earlier results on this subject [14], we have recently developed a proprietary method for the formation of nanometre-sized metal particles on carbon [15]. Details of these results will be presented.

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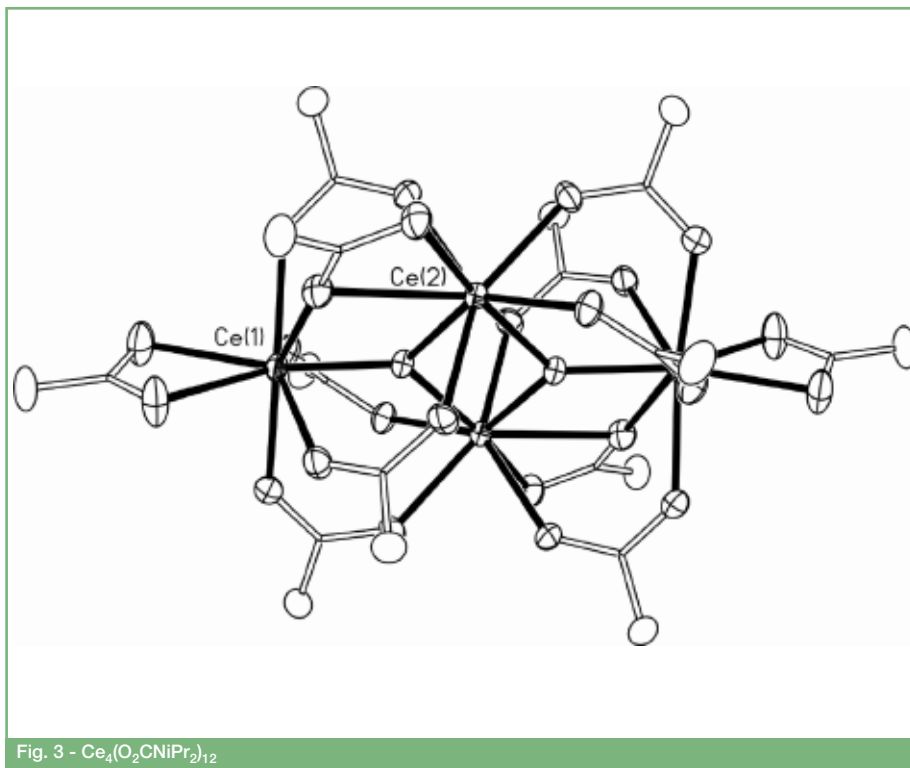


Fig. 3 -  $\text{Ce}_4(\text{O}_2\text{CNiPr}_2)_{12}$

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