study systematically a representative series of phosphine Lewis bases and their Lewis acid adducts by means of PES before any useful basicity trends can be delineated.

A final noteworthy feature of the PES data (Table I) is the observation that in general the ionization potentials for the P-C, P-H, and P-Cl σ bonds follow the trends which are anticipated on the basis of the electronegativity sequence $CF_3 > Cl > H$;[26] e.g., for P-C bonds the ip's are in the order $(CF_3)_3P > (CF_3)_2PH, CF_3PH_2$, for P-H bonds the order is $(CF_3)_2PH > CF_3PH_2 > PH_3$, while for P-Cl bonds the sequence is $(CF_3)_2PCl > CF_3PCl_2 > PCl_3$. It is of interest to note that the above orderings have also been found to apply to the P-H and P-C vibrational spectroscopic force constants of trifluoromethyl-substituted phosphines and chlorophosphines.[31]

Acknowledgment. The authors are grateful to the National Science Foundation (Grant GP 38027X), the Air Force Office of Scientific Research (Contract F44620-71-C-0119), and the Robert A. Welch Foundation for generous financial support. Thanks are also due to Professor Hans Bock for helpful discussion.

References and Notes

(1) It has come to our attention that the photoelectron spectra of trifluoromethyl-substituted phosphines (and arsines) have also been studied at the University of Frankfurt, and the Technische Hochschule, Darmstadt, W. Germany. We extend our thanks to Professor H. Bock, Ms. S. Elbel, and Professor J. Grobe for their courtesy in discussing these results prior to publication.

(2) G. R. Branton, D. C. Frost, C. A. McDowell, and I. A. Stenhouse, *Chem. Phys. Lett.*, **5**, 1 (1970).

(3) A. W. Potts and W. C. Price, *Proc. R. Soc. London, Ser. A*, **326** 181 (1972).

(4) A. W. Potts, H. J. Lempka, D. G. Streets, and W. C. Price, *Philos. Trans R. Soc. London, Ser. A*, **268**, 59 (1970).

(5) I. H. Hillier and V. R. Saunders, *Trans. Faraday Soc.*, **66**, 2401 (1970).

(6) P. J. Bassett and D. R. Lloyd, *J. Chem. Soc., Dalton Trans.*, 248 (1972).

(7) C. R. Brundle, N. A. Kuebler, M. B. Robin, and H. Basch, *Inorg. Chem.*, **11**, 20 (1972).

(8) S. Cradock and D. W. H. Rankin, *J. Chem. Soc., Faraday Trans. 2*, **68**, 940 (1972).

(9) D. W. Goodman, M. J. S. Dewar, J. R. Schweiger, and A. H. Cowley, *Chem. Phys. Lett.*, **21**, 474 (1973).

(10) S. Cradock, E. A. V. Ebsworth, W. J. Savage, and R. A. Whiteford, *J. Chem. Soc., Faraday Trans. 2*, **68**, 934 (1972).

(11) T. P. Debies and J. W. Rabalais, *Inorg. Chem.*, **13**, 308 (1974).

(12) A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and M. C. Padolina, *J. Am. Chem. Soc.*, **96**, 3666 (1974).

(13) S. Elbel, H. Bergmann, and W. Ensslin, *J. Chem. Soc. Faraday Trans. 2*, **70**, 555 (1974).

(14) A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and J. R. Schweiger, *J. Am. Chem. Soc.*, **95**, 6506 (1973).

(15) A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and M. C. Padolina, *J. Am. Chem. Soc.*, **96**, 2648 (1974).

(16) A. H. Cowley, M. J. S. Dewar, J. W. Gilje, D. W. Goodman, and J. R. Schweiger, *J. Chem. Soc., Chem. Commun.*, 340 (1974).

(17) W. Schäfer, A. Schweig, G. Märkl, H. Hauptmann, and F. Mathey, *Angew. Chem., Int. Ed. Engl.*, **12**, 145 (1973).

(18) A. B. Burg, *Acc. Chem. Res.*, **2**, 353 (1969).

(19) F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).

(20) G. S. Harris, *J. Chem. Soc.*, 512 (1958).

(21) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).

(22) P. Bishop, M. J. S. Dewar, and D. W. Goodman, to be submitted for publication. D. W. Goodman, Ph.D. Dissertation, The University of Texas at Austin, Austin, Texas, Dec 1973.

(23) H. J. M. Bowen, *Trans. Faraday Soc.*, **50**, 463 (1954).

(24) I. Y. M. Wang, C. O. Britt, A. H. Cowley, and J. E. Boggs, *J. Chem. Phys.*, **48**, 812 (1968).

(25) A. D. Walsh, *J. Chem. Soc.*, 2296 (1953).

(26) J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965), calculates the (Pauling) electronegativity of the CF_3 group to be 3.46. The Pauling electronegativities for Cl and H are 3.16 and 2.2, respectively.

(27) R. W. Rudolph and R. W. Parry, *J. Am. Chem. Soc.*, **89**, 1621 (1967).

(28) R. W. Parry and T. C. Bissot, *J. Am. Chem. Soc.*, **78**, 1524 (1956).

(29) R. W. Rudolph, R. W. Parry, and C. F. Farran, *Inorg. Chem.*, **5**, 723 (1966).

(30) A. B. Burg and G. Brendel, *J. Am. Chem. Soc.*, **80**, 3198 (1958).

(31) H. Bürger, J. Cichon, R. Demuth, and J. Grobe, *Spectrochim. Acta, Part A* **29**, 47, 943 (1973).

Influence of Metal Particle Size on the Chemisorption Properties of Supported Platinum. Analogy with Cluster Compounds

M. Primet, J. M. Basset,* E. Garbowski,[1] and M. V. Mathieu

Contribution from the Institut de Recherches sur la Catalyse, C.N.R.S., 69100 Villeurbanne, France. *Received June 14, 1974*

Abstract: A series of catalysts, $Pt-Al_2O_3$, with various particle size distributions has been studied by electron microscopy and infrared spectroscopy and chemisorption measurements. Well-characterized narrow distributions have been obtained in the range 15-35 Å. The stretching vibration of NO irreversibly adsorbed on these supported metals is particle size dependent: the larger the size, the lower the ν(NO) vibration. This result is interpreted by assuming that the extent of the back-donation to the π^* orbitals of NO^+ depends on the collective properties of the crystallites. This interpretation is corroborated by the spectroscopic results obtained with platinum carbonyl clusters.

In a previous publication[2] we have adopted a (σ,π) type of bonding for the Pt-CO bond in the case of carbon monoxide adsorption on platinum deposited on alumina. This concept, which is derived from the Chatt-Dewar model[3] in coordination chemistry, takes into account most of the experimental data obtained when CO is adsorbed on platinum: increase of the ν(CO) vibration with increasing platinum coverage (the number of electrons available for backbonding per CO adsorbed decreases as the coverage increases), decrease of the ν(CO) vibration upon adsorption of Lewis bases on a surface previously covered with a small amount of CO.[2,4] The shift toward low wave numbers increases as the coverage by the Lewis base increases which suggests a "long distance interaction".

However, the analogy existing between the metal-CO bonding in classical coordination complexes and in supported metals is far from being fully satisfactory. The observation of a long-distance effect, between a Lewis base and carbon monoxide adsorbed on the same particle, requires the participation of the collective properties of the crystallite. This is also corroborated by the fact that the ν(CO) vibration depends on the surface coverage. Therefore one

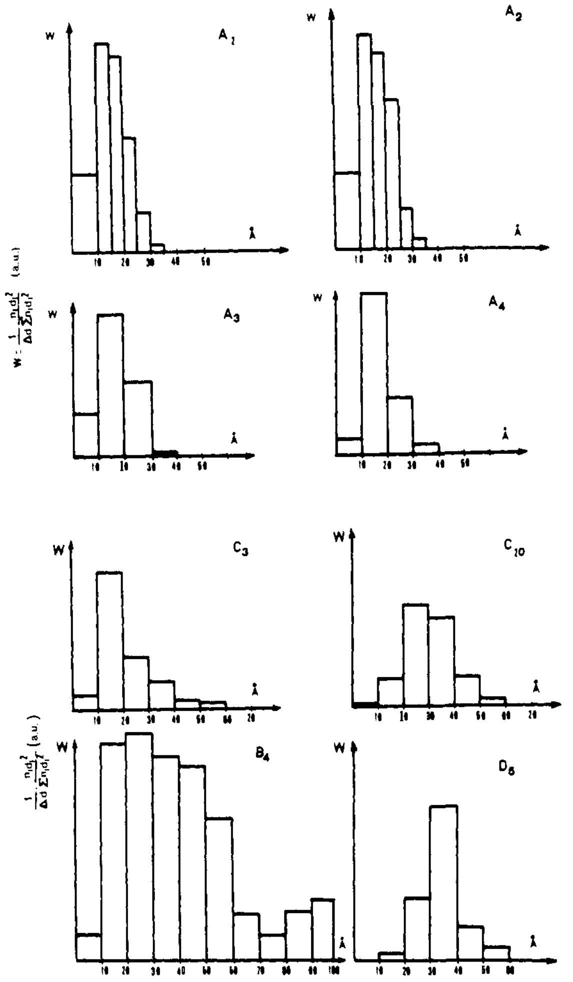


Figure 1. Particle size distribution on the surface for various catalysts.

might expect that the strength of the metal-adsorbate bond should depend on the particle size for a given surface coverage; in effect, if the size of a particle increases, the ratio of the number of atoms on the surface to the number of atoms in the bulk decreases approximately as the inverse of the particle radius, as mentioned by Poltorak et al.[5] Therefore one should theoretically observe that the larger the particle diameter, the higher the back-bonding on a π accepting ligand.

In order to check the validity of this prediction, we have studied the adsorption of nitric oxide on various Pt-Al_2O_3 catalysts. The choice of NO was mainly related to the fact that this ligand, when acting as NO^+, has π accepting properties. The filling of its π^* antibonding orbitals is easily detected by the valence vibration ν(NO) which shows greater variations in nitrosyl complexes[6,7] than the ν(CO) vibration in carbonyl complexes.

Experimental Section

a. Catalysts. Various sets of catalysts were prepared. Some properties are listed in Table I. The catalysts are indexed as follows: A1 represents a catalyst of series A with 1% Pt. Catalysts A were obtained by impregnation of a γ alumina, with an area of 300 m^2/g, with H_2PtCl_6. After a treatment at 100° under vacuum they were reduced at 500° under flowing hydrogen followed by a vacuum treatment at the same temperature. Catalyst B was obtained by impregnation of the same γ alumina with the complex $Pt(NO_2)_2(NH_3)_2$. After a treatment at 100° under air, the complex was decomposed under vacuum by increasing the temperature slowly (5°/min) from room temperature to 570°. A subsequent reduction at 570° under hydrogen for 16 hr was followed by a vacuum treatment at the same temperature. Catalysts C were obtained in the same way as catalyst of series A except that the carrier was a δ alumina (Degussa alumina oxid P) of 90 m^2/g. Catalyst D was a commercial catalyst (Matheson Coleman). It contained 5% Pt deposited on an alumina support of 100 m^2/g.

Table I. Catalyst Properties

Cat.	Wt % Pt	Alumina surface (m^2/g)	Pt dispersion % chemisorption	Metallic surface (m^2/g of catalyst)	Average particle size (Å) Chemisorption	Average particle size (Å) Electron microscopy
A1	1.0	300	67	1.85	15	15.5
A2	2.0	300	65	3.60	15.5	15.4
A3	3.0	300	67	5.50	15	16.8
A4	4.0	300	47	5.20	22	17.5
B4	4.0	300	12.1	1.33	84	(87) 30.5 Å
C3	3.00	90	47.5	3.93	21.3	21
C10	10.00	90	34	9.38	29.8	30.3[a]
D5	5.0	105	17.8	2.50	57	35

[a] This value was corroborated by low angle X-ray scattering (33 Å).

b. Metallic Surface Site Determination. The number of surface platinum atoms was determined by O_2-H_2 titration performed in a gravimetric system. The balance was an ultra-high vacuum CAHN RG electrobalance able to work under a controlled atmosphere over a wide range of temperatures and pressures. All the metallic parts of the balance were gold plated and contamination by grease was avoided by means of a liquid nitrogen trap situated between the balance and both vacuum and gas storage system. All the measurements were made under the same conditions of pressure (10^{-4} Torr) corresponding to species irreversibly adsorbed at room temperature (Pt-O, Pt-H).

The pretreatment procedure was the following. Reduced sample (300 mg) was outgassed at room temperature under a vacuum of 10^{-5} Torr during 1 hr. Then the temperature was raised slowly (1°/min) to 500°. After 20 hr under vacuum at 500°, 50 Torr of hydrogen was introduced into the balance over a period of 10 hr. Finally, the catalyst was evacuated under 10^{-5} Torr, 20 hr, at the same temperature. After cooling to room temperature many titration cycles were performed at 25°.

The following cycles were done. First oxygen was introduced to 50 Torr and the equilibrium was reached in 3-4 min. After evacuation a new equilibrium was obtained in 10 min which gave the amount of oxygen irreversibly adsorbed. Then hydrogen was adsorbed under 50 Torr and evacuated. The procedure was repeated five to six times. Due to the gravimetric procedure employed only oxygen titration uptakes were used for dispersion determination.

c. Electron Microscope Technique. The catalysts were examined using an electron microscope JEOL 100 B. Two techniques of sample preparation were used: direct examination and extractive replica technique.[8] In the direct method, a portion of the catalyst was ground in a mortar and dispersed in butyl alcohol by ultrasonic treatment. A drop of this suspension was put on a carbon collodion film and dried.

The extractive replica technique consisted of evaporating under vacuum a carbon film onto the catalyst. After immersing in dilute HF, the carbon film was separated from the alumina carrier and the platinum particles remained on the carbon film. It was shown that by means of this technique all the platinum particles were extracted from the support. Platinum particles having a diameter as low as 5 Å could be detected.

The pictures were taken at an enlargement of 120,000-180,000. The subsequent photographic enlargements resulted in a final magnification of 500,000 ± 5%.

Many pictures of each sample were taken (at least 20), and the distribution of particle size was determined by measuring the size of at least 1000 particles.

Supposing that the particles are spherical and denoting the particle diameter by d_i and the number of particles of each diameter increment by n_i, the surface average diameter is given by

$$\bar{d}_s = \frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2}$$

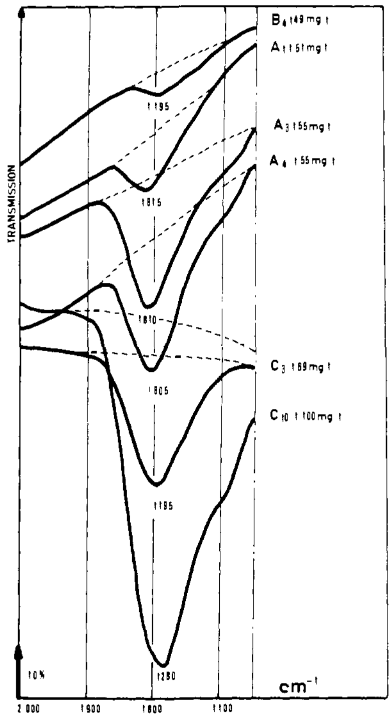


Figure 2. Infrared spectra of NO irreversibly adsorbed at room temperature on Pt–Al_2O_3. The dotted lines correspond to the background before the introduction of NO (the weight of the disk in brackets is given in parentheses).

d. Infrared Spectroscopy. This spectroscopic method was used to identify the state of adsorption of NO over the platinum surface. The technique used for the preparation of the disks of catalyst has already been described.[9] In order to avoid contamination of the catalyst, we used sample holders made of quartz. For the same reason the seal of the CaF_2 disks was obtained with Viton O Rings or with epoxy resin (Torr Seal from Varian).

Nitric oxide was supplied by Air Liquide. Before use, it was frozen in liquid nitrogen and purified by repeated vacuum sublimation from −195 to −78°.

In all cases the standard treatment was the following: 500° under hydrogen for 16 hr followed by a vacuum treatment at the same temperature. The adsorptions were performed after cooling the sample to room temperature.

Results

A. Characterization of the Catalysts. The diameter distribution function, deduced from electron micrographs, has been determined for all the catalysts (Figure 1). In the case of platinum deposited on γ alumina (e.g., H_2PtCl_6), the distribution is very narrow with an average diameter ranging between 15 and 18 Å; in this case 90% of the platinum surface corresponds to particles having a diameter lower than 25 Å. In the case of Pt-aluminum oxid P, there is also a narrow distribution and the average particle size goes from 21 to 30 Å when the platinum content increases from 3 to 10%. For the C3 catalyst, 75% of the metallic surface is due to particles having a diameter included between 10 and 30 Å, whereas with the C10 catalyst 75% of the surface corresponds to diameter ranging between 20 and 40 Å.

The commercial catalyst D5 also has a relatively narrow distribution with an average size of 35 Å; about 70% of the surface is due to particles ranging between 25 and 45 Å.

The catalyst B4 obtained by impregnation with $Pt(NO_2)_2(NH_3)_2$ is less homogeneous. The amplitude of the platinum size distribution in surface is wide, and some multiple distributions are visible. The samples contain both very small particles ($\phi < 10$ Å) and larger ones ($\phi > 60$ Å). In the case of multiple distribution, the average particle size deduced from the full range 10–500 Å has no meaning; the value obtained (87 Å) corresponds to the least abundant diameter. Therefore we have taken into account only the range 10–60 Å which represents more than 60% of the platinum surface. This gave us an average particle size of 30 Å.

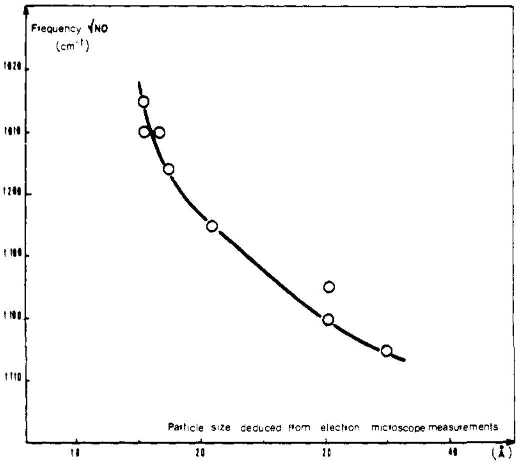


Figure 3. Variations of the frequency of the ν(NO) band vs. the particle size deduced from electron microscope measurements.

The platinum surface of all the catalysts has been determined by the O_2–H_2 titration according to the equations proposed by Boudart et al.[10] We have assumed that each surface platinum was able to chemisorb one oxygen atom and that the surface of one platinum atom was equal to 8.9 $Å^2$.[10] The results obtained are given in Table I.

B. Infrared Spectroscopy. The introduction of 50 Torr of NO on the Pt–Al_2O_3 catalysts gives a band situated between 1820 and 1775 cm^{-1} with other bands near 1600 cm^{-1} of much weaker intensity which will be explained later.[11] Upon evacuation of the gaseous phase only the ν(NO) bond close to 1800 cm^{-1} remained but with various intensity, frequency and shape depending on the catalyst. In almost all cases (Figure 2) these ν(NO) bands are not symmetrical and are broadened toward low frequencies. Such bands are not obtained upon adsorption and desorption at room temperature of NO on the alumina carrier, as previously observed by other authors;[12] this result indicates that NO in fact is irreversibly adsorbed on Pt.

The most significant result concerns the variation of the frequency ν(NO) with the platinum particle size. This variation is shown on Figure 3 vs. the mean particle size $\bar{d}_s$ deduced from electron microscope measurements.

We have chosen $\bar{d}_s$ deduced from electron microscope measurements instead of the average particle size deduced from chemisorption for the following reason. So far there is still controversy concerning the stoichiometry of the O_2–H_2 titration equation of supported platinum.[16] Hall et al.[17] claim that for small particle size the ratio O/Pt_s depends on the diameter of the particle. Consequently one gives more confidence to the results obtained from a physical technique such as electron microscopy, although there is a fairly good agreement between both techniques (Table I). In some cases the average particle size was also corroborated by low angle X-ray scattering measurements.

The general feature shows an increase of the vibration ν(NO) when the particle size decreases. This variation could arise from a difference of coverage of the metallic surface by NO as we have already observed in the case of CO/Pt–Al_2O_3,[1] although a decrease in coverage from 1 to 0.5 gives a ν(CO) shift of less than 10 cm^{-1}. The optical density of the ν(NO) bands has been determined for each sample of constant weight and plotted vs. the metallic area

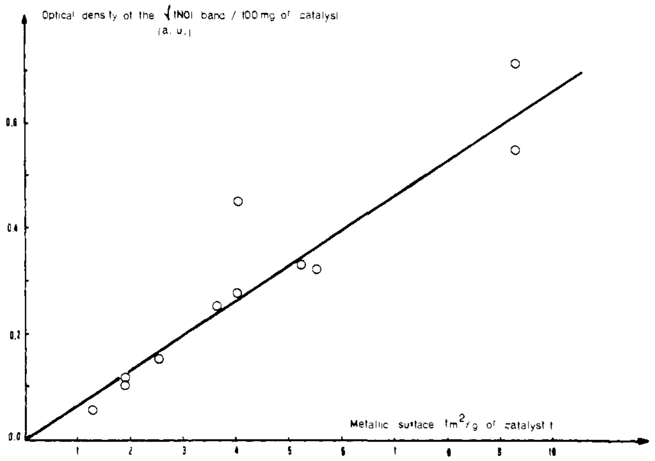


Figure 4. Evolution of the optical density of the ν(NO) band with the metallic particle size.

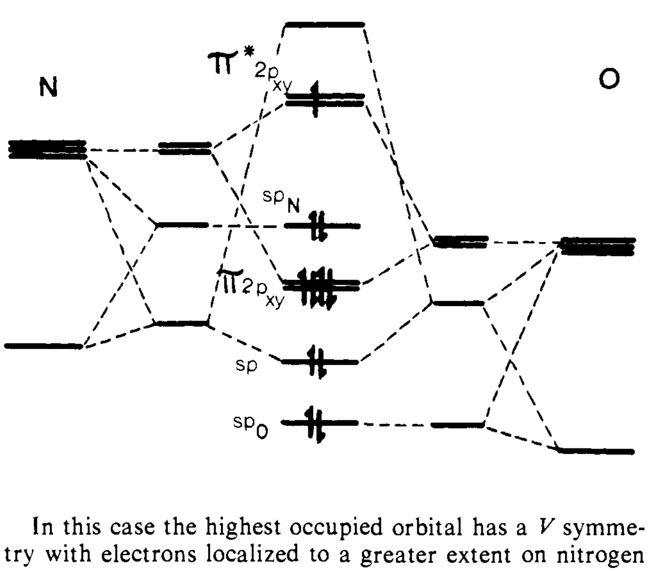
deduced from chemisorption measurements (Figure 4). The amount of adsorbed NO increases almost linearly with the metallic surface of the samples indicating a constant coverage of the metal by NO. Therefore the frequency ν(NO) of adsorbed NO seems to depend for a same carrier (alumina) only on the size of the metallic particle.

Discussion

Before trying to discuss our results it is necessary to consider the type of bonding occurring in nitrosyl complexes of transition metals. From X-ray studies and infrared spectroscopy[6] it seems possible to distinguish two main types of bonding: a linear and a bent form.

Preliminary theoretical studies[13] have shown that the coordination mode of NO essentially depends on the relative energies of the π^* orbital of NO and of the d metal orbitals; NO has low lying π^* orbitals which can be energetically above, close to, or under the d orbitals of the metal resulting in NO^+ and NO^- in the two limiting cases.

The complex with a linear metal -N-O bond corresponds to the ligand acting as NO^+. It shows similar properties to those of analogous carbonyl complexes. (NO^+ and CO are isoelectronic and have the same configuration i.e., $(\sigma ls)^2$ $(\sigma ls^*)^2$ $(\sigma sp_O)^2$ $(\sigma sp)^2$ $(\pi 2p_{xy})^4$ $(\sigma sp_N)^2$.)



In this case the highest occupied orbital has a V symmetry with electrons localized to a greater extent on nitrogen than on the oxygen atom; the occupancy of this orbital is energetically favored resulting in a linear form.

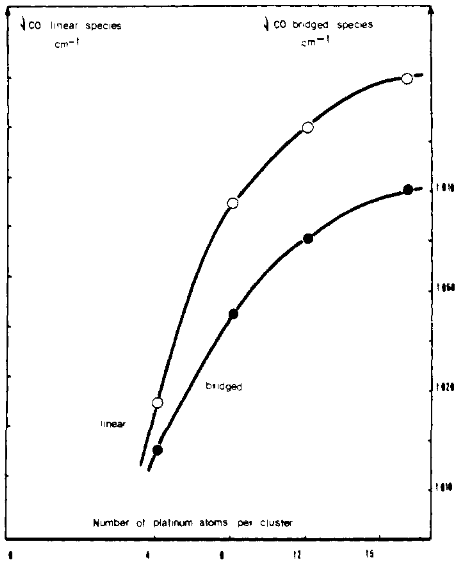


Figure 5. Position of the bands ν(CO) (linear and bridged forms) for the clusters $[Pt_3(CO)_6]_n{}^{2-}$ when n increases from 2 to 6, according to Chini et al.[14]

Bonding of NO as NO^+ allows the metal to back-donate electrons to the empty π^* orbital causing the M-N bond to gain considerable multiple bond character with a shorter M-N distance. Usually this linear form gives an infrared absorption above 1700 cm^{-1}.[6]

When NO is acting as NO^-, corresponding to the bent form, the M-N-O angle is equal to 120°. In this case the metal is acting as an electron donor toward the NO molecule. The NO bond has lost energy by gaining a more pronounced π^* character. (There are now two electrons in a doubly degenerate π^* orbital.)

The loss of the bonding character results in an increase of the N-O distance and in a shift of the vibration ν(NO) toward low wave numbers (in $[Co(NH_3)_5(NO)]^{2+}$, NO is anionic and absorbs at 1195 cm^{-1}). The stability of the complex between the metal atom and NO^- seems to be due to the sp^2 hybridization of the nitrogen atom which explains the 120° angle observed by X-ray studies.

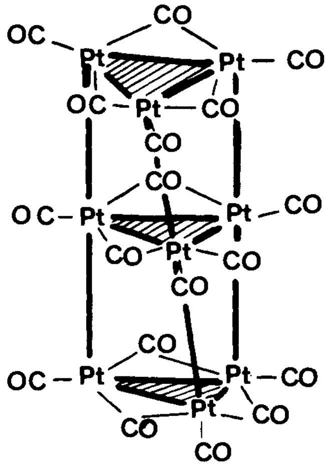
Moreover a back-donation occurs from NO^- π^* orbitals to the d metal orbitals. The N-O bond has now a more bonding character and the frequency of the ν(NO) vibration increases up to the range 1700-1400 cm^{-1}.[6]

Returning to the case of NO adsorbed on platinum, the high stretching frequency suggests that we are dealing with a kind of surface complex in which NO acts as a NO^+ ligand, but in order to explain the decrease of the ν(NO) vibration with increasing particle size two different effects can be advanced: geometric and electronic effects.

One could consider the geometric effect to be predominant especially if one assumes that each infrared band is the overlap of many individual peaks corresponding to NO chemisorbed on various crystallographic positions of the metal, namely, edges, corners, and facial positions, the position of the maximum depending on the relative number of these crystallographic sites. However, if this was the correct explanation then according to the Blyholder's model (ref 2) one would expect the lowest ν(NO) frequency for the platinum sites having the lowest coordination number to correspond to the highest electron density and the highest heat of adsorption. These unsaturated sites are the most numerous on very small particles, and it is on these particles that the ν(NO) frequency is the highest. Consequently the geometric factor seems to be rejected at the expense of the electronic factor: NO^+ is acting as a π accepting ligand and the number of electrons available for the back-donation will depend on the particle size for a given coverage. Since the amount of adsorbed NO is proportional to the platinum surface it seems that the coverage of Pt by NO does not depend on the particle size in the range studied. Therefore the most simple explanation can be advanced: the smaller the particle size, the smaller the number of electrons available for back-donation, and the higher the ν(NO) frequency.

Therefore we consider that this result is a good confirmation of the (σ,π) type of bonding but with participation of the collective properties of the metallic phase. Besides the correlation observed between the ν(NO) frequency and the average particle size, this can be considered as a new technique for determining particle size in supported metals.

The main objection to our model would be related to the fact that no specific d orbitals are expected at the surface of metals. However, recent results obtained by Chini et al.[14] in the field of coordination chemistry reinforce our conclusion. The later have recently published new syntheses of triangular clusters of platinum $[Pt_3(CO)_6]_n^{2-}$. The X-ray structure showed a monomeric unit of triangular configuration of three platinum atoms with a linear and a bridged carbonyl per platinum. The distance Pt-Pt is then very close to that of bulk platinum. When n increases from 2 to 5 the cluster is formed by piling the monomeric unit with new Pt-Pt bonds perpendicular to the initial triangle as shown by the following structure for $[Pt_9(CO)_{18}]^{2-}$. As can be seen on Figure 5 the ν(CO) frequencies for linear and bridged forms increase with the number of platinum atoms per cluster, to reach a value of 2060 cm^{-1} for the linear CO which corresponds to the frequency of CO adsorbed on bulk platinum.[1] Considering that the 2− charge is equally shared in the metal lattice, when n is equal to 2, the two negative charges are shared by six platinum atoms and the ν(CO) frequency is very low corresponding to considerable back-bonding, whereas when n is equal to 5, the 2− charge is shared by 15 platinum atoms and the ν(CO) vibration has almost the same frequency as for bulk platinum.



In this model compound it is not the ratio of surface platinum/bulk platinum which varies but the ratio of the number of negative charges per number of platinum atoms indicating the appearance of collective metallic properties for these small clusters. It is interesting to notice that above 15 atoms the 2− charge is very diluted in the clusters. This roughly corresponds to the range of particle size where the electronic effect is varying the most in the case of supported platinum (i.e., below 15 Å).

Therefore we consider that our results together with those of Chini et al.[14] are the first spectroscopic examples of the influence of a particle size on the strength of a metal-adsorbate bond. We believe this phenomenon must be of relevant interest in the field of catalysis on metals or on clusters. We have now given some proof that, in the field of small particles, besides the geometric factor which is observed in catalysis over metals, an electronic factor is certainly occurring in the range of particle size lower than 40 Å. Then it is possible to observe variations of chemisorption properties of supported metals and some results have already been obtained in the case of palladium prepared by reduction of Pd^{2+} Y zeolites by hydrogen at low temperature. In this case, the chemisorption properties of the metal almost atomically dispersed are quite different from those of bulk palladium.[15]

Acknowledgment. The authors are very grateful to Professor Chini for permission of publication of results in press and for helpful discussions. Thanks are due to Dr. Dalmai-Imelik for taking electron micrographs and to Mr. Mutin for measuring the metallic area of the catalysts.

References and Notes

(1) U.E.R. de chimie-biochimie, Université de Lyon I.
(2) M. Primet, J. M. Basset, M. V. Mathieu, and M. Prettre, *J. Catal.*, **29**, 213 (1973).
(3) J. Chatt, *J. Chem. Soc.*, 2939 (1953); G. J. Blyholder and M. C. Allen, *J. Am. Chem. Soc.*, **91**, 3158 (1969).
(4) R. Queau and R. Poilblanc, *J. Catal.*, **27**, 200 (1972). A. Pazalov, *J. Catal.*, **30**, 13 (1973).
(5) O. M. Poltorak, U. S. Boronin, and A. N. Mitrofanova, IVth International Congress on Catalysis, Moscow, 1968, paper no. 68.
(6) N. G. Conelly, *Inorg. Chim. Acta Rev.* 47 (1972).
(7) D. M. Adams, "Metal Ligand and Related Vibrations", Edward Arnold Publications, London, 1967.
(8) G. Dalmai-Imelik and C. Leclercq, *J. Microsc.*, 306 (1972).
(9) M. Primet, J. M. Basset, M. V. Mathieu, and M. Prettre, *J. Catal.*, **28**, 368 (1973).
(10) J. E. Benson and M. Boudart, *J. Catal.*, **4**, 704 (1965).
(11) M. Primet and A. Ghorbel, to be submitted.
(12) N. D. Parkyns, *Proc. Int. Congr. Catal.*, **1**, 255 (1973).
(13) D. M. P. Mingos, *Inorg. Chem.*, **12**, 1209 (1973).
(14) G. Longoni, P. Chini, S. Martinengo, A. Cavellieri, J. Calabressi, and L. Dahl, VI Convegno Nazionale di Chimica Inorganica, Firenze, paper A. 27, 29, Sept 1973; *J. Am. Chem. Soc.*, (in press).
(15) P. Gallezot and B. Imelik, *Adv. Chem. Ser.*, **No. 121**, 66 (1973); C. Naccache, M. Primet, and M. V. Mathieu, *ibid.*, **No. 121**, 266 (1973).
(16) D. E. Mears and R. C. Hansford, *J. Catal.*, **9**, 125 (1967).
(17) G. R. Wilson and W. K. Hall, *J. Catal.*, **17**, 190 (1970).