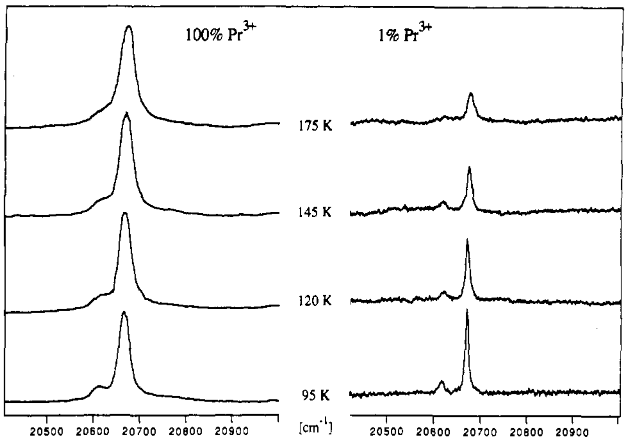


Figure 6. Temperature dependent unpolarized absorption spectra of the $^3H_4 \rightarrow {}^3P_0$ absorption in $Pr(CH_3COO)_3{\cdot}H_2O$ and $Ce(CH_3COO)_3{\cdot}H_2O{:}1\%\ Pr^{3+}$.

roughly corresponds to the sum of the two single excitations, thus leading to a high-energy sideband of the $^3H_4(0) \rightarrow {}^3P_0$ electronic origin. In the discussion of the cross-relaxation mechanism, we mentioned earlier that the acetate bridges offer efficient pathways for exchange interaction, and it is therefore likely that such interactions, in addition to multipole interactions, are also active for the double excitations.[27] Figure 6 provides a nice confirmation for the double-excitation mechanism in the undiluted acetate. It shows the $^3H_4 \rightarrow {}^3P_0$ absorptions for both the diluted and undiluted system as a function of temperature. The diluted spectra show the expected decrease with increasing temperature of the $^3H_4(0) \rightarrow {}^3P_0$ line. In contrast, the undiluted crystal shows an increase accompanied by a broadening of this line. This can be understood by contributions, at high temperatures, of the following double excitations: $^3H_4(i) \rightarrow {}^3P_0 + {}^3H_4(0) \rightarrow {}^3H_4(i)$. Independent of i, their energy is roughly equal to the energy of the $^3H_4(0) \rightarrow {}^3P_0$ single-ion origin. The observed broadening is due to the fact that many double excitations with higher as well as lower energy than $^3H_4(0) \rightarrow {}^3P_0$ become possible with increasing temperature.

5. Conclusions

In this investigation, we have shown that long-range energy migration is not observable in $Pr(CH_3COO)_3{\cdot}H_2O$ or its deuterated analogue. Localized nonradiative relaxation processes are highly competitive. By chemical variation without variation of the crystallographic structure, deuteration on the one hand and dilution in $Ce(CH_3COO)_3{\cdot}H_2O$ on the other, it was possible to identify and analyze the relevant processes in detail. A single-ion multiphonon relaxation mechanism is accompanied by a cooperative cross-relaxation mechanism in the undiluted compounds. Similarly, a single-ion and a cooperative intensity mechanism contribute to the sideband structure of the $^3H_4 \rightarrow {}^3P_0$ absorption in $Pr(CH_3COO)_3{\cdot}H_2O$.

Energy migration phenomena in lanthanide acetates with chain structures are not likely to be observable for the Ln^{3+} other than Gd^{3+}, Eu^{3+}, and Tb^{3+}. The latter ions have much larger energy gaps and correspondingly much smaller nonradiative relaxation rates. Energy migration processes may therefore become competitive. The compounds $[Ln(CH_3COO)_2(H_2O)_3]Cl$ ($Ln = Gd^{3+}$, Eu^{3+}, Tb^{3+}) form chain structures, and we are presently investigating their properties.

Acknowledgment. We thank G. Meyer and T. Schleid for their help with the synthesis and crystal growth and G. Blasse for useful discussions in the data analysis. Financial support by the Swiss National Science Foundation is acknowledged.

---

[27] Gondaira, K. I.; Tanabe, Y. *J. Phys. Soc. Jpn.* **1966**, *21*, 1527.

Contribution from the Dipartimento di Chimica Inorganica e Metallorganica,
Centro CNR, Via Venezian 21, I-20133 Milano, Italy

Electronic and Geometrical Structures of Nitroso Ligands Coordinated to Transition-Metal Atoms. A Nonempirical Theoretical Study of $Pt(PH_3)_2(CF_3NO)$ and $Pt(PH_3)_2(CH_3NO)$

P. Fantucci,* M. Pizzotti, and F. Porta

Received June 5, 1990

The modifications of the molecular geometry and electronic structure of CF_3NO and CH_3NO caused by coordination to a Pt(0) center have been studied by means of nonempirical MO-LCAO theoretical calculations on the model complexes $Pt(PH_3)_2(RNO)$. The η^2 coordination mode of RNO, in which the N-O group acts as a side-on σ-donor and π-acceptor, is found to be more favorable than the η^1 mode, in which only the N atom directly interacts with the metal center. The bonding characteristics of the RNO ligands are compared with those of the isoelectronic dioxygen ligand by investigating the electronic structure of the $Pt(PH_3)_2(\eta^2\text{-}O_2)$ complex.

Introduction

In recent years, the catalytic carbonylation of organo nitro compounds has attracted much interest[1] because of the potential applicability of the catalysts to the industrial processes leading to the preparation of quite a broad class of compounds like amides, amines, carbamates, ureas, and isocyanates. The latter can be obtained in the single-step reaction

$$RNO_2 + 3CO \rightarrow RNCO + 2CO_2$$

which seems particularly interesting because it avoids the use of an energy-demanding, poisonous, and corrosive reagent like phosgene, necessary, on the contrary, in the classical two-step synthesis

$$RNO_2 + 3H_2 \rightarrow RNH_2 + 2H_2O$$

$$RNH_2 + COCl_2 \rightarrow RNCO + 2HCl$$

The formation of isocyanates proceeds in the presence of group VIII metal catalysts at high temperature and pressure. The nitroso compounds RNO can be considered as intermediates of the reaction

$$RNO_2 + CO \rightarrow RNO + CO_2$$

which react further with CO

$$RNO + 2CO \rightarrow RNCO + CO_2$$

The interaction of the nitroso ligands with a group VIII metal center has been studied mainly from an experimental point of view.

---

[1] Cenini, S.; Pizzotti, M.; Crotti, C. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; D. Reidel: Dordrecht, The Netherlands, 1988; Vol. VI; see also references therein.

0020-1669/91/1330-2277$02.50/0 © 1991 American Chemical Society

These studies have led to the determination of molecular structures for the coordinated RNO ligand and the approximate assignment of the vibrational frequencies for N–O bond stretching. Three basic coordination geometries have been identified by means of X-ray diffraction studies of complexes isolated in the solid state. The N–O η^2 coordination (hereafter referred to as I) is analogous to that of other unsaturated ligands like dioxygen, alkenes, and carbon dioxide, and its occurrence has been demonstrated in the case of the $Pt(PPh_3)_2(PhNO)$ complex.[2] In this case, the metal atoms involved are usually in a low oxidation state and possess good π-back-bonding capabilities. The coordination mode η^1(N) (hereafter referred as II) has been found experimentally in the *trans*-dichlorobis(nitrosobenzene)palladium(II)[3a] complex, while the geometry η^1(O) seems to be favored only in the case of hard metal centers, like tin(IV).[3b]

In I the electrons available for the metal–ligand bond are those associated with the π-bonding molecular orbital (MO) of the N–O group, while the π^*_{NO} MO may be involved in the metal-to-ligand back-bonding. Both mechanisms can decrease the order of the N–O bond, a view that is supported by the analysis of the experimental N–O bond distances and ν(N–O) stretching frequencies.[4] In coordination mode II only the lone pair on the N atom is available for the σ-donation mechanism, while the π-back-bonding interaction is expected to be weaker than in I and to mainly involve the π orbitals located on the N atom.

All the above qualitative arguments are insufficient to establish which bonding mechanism is dominant in the coordination of the RNO ligand and to explain why, and to what extent, coordination I is preferred in the case of Pt(0) complexes. These questions, which are of a very general nature in the coordination chemistry of nitroso compounds, have never been previously addressed in theoretical studies. This paper presents results on the electronic structure of platinum complexes containing nitroso ligands obtained from theoretical calculations carried out according to the nonempirical Hartree–Fock (HF) method.

The RNO ligands employed in the synthesis of Pt(0) complexes are those with R = Bu^t, Ph, or CF_3, together with aromatic phosphines, e.g. PPh_3.[2] However, since a nonempirical MO study of complexes of type $Pt(PPh_3)_2(PhNO)$ would be computationally very demanding, our investigation has been limited to relatively small model compounds in which the aromatic phosphines have been substituted with PH_3. In addition, only the two simple trifluoronitrosomethane (CF_3NO) and nitrosomethane (CH_3NO) ligands have been considered.

Some exploratory calculations carried out on the $Pt(PH_3)_2(CF_3NO)$ complex considered in the η^1(O) coordination mode have shown that this arrangement is highly improbable in the case of a Pt(0) metal atom: the complex has been found unstable with respect to the dissociation limit Pt + $2PH_3$ + CF_3NO, and such a coordination mode has not been further investigated.

Since the RNO ligand is isoelectronic with dioxygen, it would be interesting to carry out the theoretical investigation also of the complex $Pt(PH_3)_2(\eta^2\text{-}O_2)$. The comparison of the theoretical data for RNO and O_2 complexes can serve to elucidate whether the coordination of RNO can be classified as an oxidative-addition reaction. This is usually assumed to be the case of the dioxygen adduct with a coordinated "peroxide" anion.[5]

Computational Method

The geometrical and electronic structures of the ligands in their free state and in the platinum–phosphine complexes have been determined according to the restricted Hartree–Fock method. A standard basis set of contracted Gaussians of type 3-21G[6] has been employed for the H, C, N, O, and P atoms. The effective core potential (ECP) approach is used for the Pt atom, for which only the outermost 5s, 5p, 5d, 6s, and 6p orbitals, expanded in a basis set of type (311/32/21),[7] are considered as valence orbitals. Atomic calculations give an energy value of −118.22405 au for the ground state of the Pt atom (^{3}D, ...5d^{9}6s^1). The ECP operator of ref 7 also includes relativistic effects, which can cause a significant contraction of the valence 6s shell and the expansion of the 5d one, leading to shorter computed bond distances and higher binding energies than those given by nonrelativistic methods.[8]

The adopted basis sets are of split-valence type and describe the valence orbitals by a combination of two functions of different spatial extensions. This flexibility is necessary to account for charge-transfer and rehybridization processes occurring in the formation of the coordinative bond. However, the inner core shells on the ligand atoms are poorly described and can be affected by an important basis set superposition error (BSSE). The influence of the BSSE on the computed stabilities of the complexes will be discussed in the next sections, adopting an error estimate proposed by Boys and Bernardi.[9] As is well-known, the HF method cannot take into account the interelectronic correlation effects, usually evaluated according to the configuration interaction (CI) method, which however suffers from severe computational limitations. In particular, when this method is applied to large composite systems like transition-metal complexes, it might be difficult to estimate the interaction energy among the fragments. An alternative can be offered by the use of density functionals, which assume that the correlation energy is a local (or nonlocal) function of the electron density only. In the present study, we have adopted the nonlocal functional, proposed by Colle and Salvetti[10] and reformulated recently by Lee, Yang, and Parr (LYP),[11] for the simplest case of one-determinant wave functions. The reliability of the LYP correlation formula has recently been proved by means of a direct comparison with the results of conventional CI treatments.[12] The Colle–Salvetti (or LYP) formula is size-consistent, contains nonlocal corrections, and implicitly avoids self-interactions. However, the functional cannot overcome the inadequacies that are characteristic of all the independent-particle models. This is obviously the case of LYP calculations based on HF densities. Thus, in this sense, the values of correlation energy reported in the present study must be considered as approximate. Details of a computational scheme suitable for estimating the LYP correction can be found in ref 12. The inclusion of the BSSE correction and the LYP contribution to the total energy make the present theoretical approach reliable enough to allow meaningful comparisons of the computed stabilities of the complexes.

The electron distribution in the free and coordinated ligands will be discussed on the basis of the conventional Mulliken analysis. The approach was recently strongly criticized[13] (especially in connection with transition-metal complexes), claims being made that the method cannot be strictly justified from a theoretical point of view. In Mulliken's original papers,[14] he pointed out that the population analysis has mainly a qualitative meaning. In the present context, we believe that the Mulliken analysis is still a valuable (and qualitatively correct) tool for interpreting the electronic wave functions, particularly when one is interested only in trends and variations in charge distribution caused by the coordination process.

The optimum HF geometries of the free ligands PH_3, O_2, CF_3NO, and CH_3NO have been determined by using the 3-21G basis sets. In the case of CF_3NO and CH_3NO, all the C–F and C–H distances are assumed to be equal. In the case of the platinum complexes, the geometries of the PH_3, CH_3, and CF_3 groups are taken as coincident with those found in free molecules. In addition, the two symmetry-independent Pt–P distances are kept equal in all the complexes. The molecular geometry optimization, based on analytical gradient techniques and carried out by means of a modified version of the GAMESS program,[15] has been limited

---

(2) Pizzotti, M.; Porta, F.; Cenini, S.; Demartin, F.; Masciocchi, N. *J. Organomet. Chem.* **1987**, *330*, 265.

(3) (a) Little, R. G.; Doedens, R. I. *Inorg. Chem.* **1973**, *12*, 537. (b) Matsubayashi, G.; Nakatsu, K. *Inorg. Chim. Acta* **1982**, *64*, L163.

(4) Cameron, M.; Growenlock, B. G.; Vasapollo, G. J. *J. Organomet. Chem.* **1989**, *378*, 493.

(5) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley: New York, 1980.

(6) Pietro, W. J.; Francl, M. M.; Here, W. J.; De Frees, D. J.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 3039.

(7) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(8) (a) Pyykko, P. *Relativistic Theory of Atoms and Molecules*; Springer-Verlag: New York, 1986. (b) Balasubramanian, K. *J. Phys. Chem.* **1989**, *93*, 6585 and references therein.

(9) Boys, S. F.; Bernardi, F. *J. Mol. Phys.* **1970**, *19*, 553.

(10) Colle, R.; Salvetti, O. *J. Chem. Phys.* **1983**, *79*, 104 and references therein.

(11) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(12) Fantucci, P.; Polezzo, S.; Bonacic-Koutecky, V.; Koutecky, J. *J. Chem. Phys.* **1990**, *92*, 6645.

(13) Cioslowski, J.; Hay, P. J.; Ritchie, J. P. *J. Phys. Chem.* **1990**, *94*, 148.

(14) Mulliken, R. A. *J. Chem. Phys.* **1955**, *23*, 3428 and references therein.

(15) Dupuis, M.; Spangler, D.; Wendoloski, J. J. *Natl. Res. Comput. Chem.* **1980**, Program QG01 (version modified by M. Schmidt and S. Elbert). The program was further modified for ECP and LYP correlation energy calculations by P.F.

to a few internal coordinates in order to keep the computational cost, which would be very high for complexes of low or null symmetry, within acceptable limits.

The correlation energy has been evaluated with the LYP formula (E_{LYP}) in the minimum HF geometry, with an associated energy E_{HF}. Values of total energy defined as $E_T = E_{HF} + E_{LYP}$ will be reported in the next sections for complexes and free ligands. However, in order to evaluate the stability of the complexes in a more reliable way, the total energy for ligands must be corrected for the BSSE contribution (E_{BSSE}). E_{BSSE} values have been determined by assuming that the overall geometry of the dummy centers (with basis functions but without electrons and nuclear charges) is identical with the optimum geometry of the complex, while each of the fragments considered (PH_3, O_2, CH_3NO, and CF_3NO) is in its best free-ligand geometry.

Electronic and Geometrical Structures of PH_3, O_2, CF_3NO, and CH_3NO Free Ligands

As stated above, our results for the free ligands cannot be considered as qualitatively accurate. Much more sophisticated studies have been published for dioxygen[16] and phosphine[17] molecules, while investigations on CF_3NO[18] and CH_3NO[19] are much less numerous.

Theoretical data for ligands obtained at the same level of accuracy adopted for the Pt complexes are essentially important to discuss the origin of the electronic and geometrical modifications that accompany the coordination to the platinum atom.

For the PH_3 molecule, the HF method gives the equilibrium values P–H = 1.423 Å and ∠HPH = 96.1°, which are in acceptable agreement with the experimental values, 1.421 Å and 93.3°, respectively.[20] The HF energy (E_{HF}) is −340.704 52 au, the correlation energy (E_{LYP}) is −0.667 82 au, and the total energy (E_T) is −341.372 34 au. According to the Mulliken analysis, the P–H bond is only slightly polar, with a positive charge on P equal to 0.1. The ground-state geometry of O_2 ($^3\Sigma_u^+$) has been computed by using the restricted HF method for open shells. The equilibrium O–O distance is 1.237 Å, 0.03 Å longer than the experimental value.[21] The corresponding energy values are $E_{HF} = -148.755\,22$ and $E_T = -149.320\,01$ au. The HF calculation gives a harmonic vibrational energy 384 cm^{-1} higher than the experimental one (1580.2 cm^{-1}).[21]

The optimum molecular geometries computed for the two nitroso ligands CF_3NO and CH_3NO (see Figures 2a and 3a) are in acceptable agreement with the available experimental data.[22,23] In the two molecules CF_3NO and CH_3NO the C–N distances (1.49 and 1.51 Å, respectively) as well as the N–O distances (1.21 and 1.22 Å) differ by less than 0.02 Å. Also, the valence angles do not differ by more than about 1°. However, the similarity is partially due to an artifact of the HF method, which in the case of CF_3NO gives a C–N distance shorter than the experimental one.[22] It has been shown[18] that only a multiconfigurational treatment can remove the shortcoming. The Mulliken analysis gives the values −0.246, −0.034, 1.379, and −0.367 for the net atomic charges on O, N, C, and F atoms, respectively, in CF_3NO. The corresponding results for CH_3NO are −0.341, 0.055, −0.458, and 0.248 for O, N, C, and H, respectively. This shows that inversion of the sign of the charge on the carbon atom occurs, caused by the electron-withdrawing character of the CF_3 group. The difference between CF_3 and CH_3 groups also affects the O–N bond, and in particular the composition of its π bond, which is more polarized in CH_3NO than in CF_3NO.

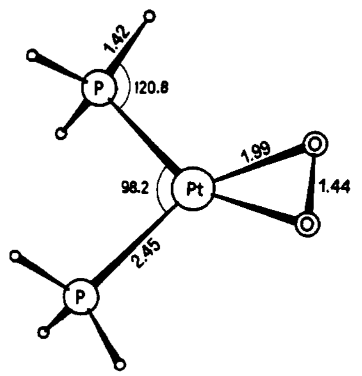


Figure 1. Optimized geometry for $Pt(PH_3)_2(\eta^2\text{-}O_2)$ (bond distances in angstroms; valence angles in degrees).

Electronic and Geometrical Structures of Dioxygen and Nitroso Pt(0) Complexes

The stability of the platinum complexes can be measured in terms of the energy required to promote the dissociation of $Pt(PH_3)_2(X)$ (X = O_2, CF_3NO, CH_3NO) into the fragments Pt + $2PH_3$ + X considered in their ground-state geometry. Three different definitions can be introduced for different levels of approximation: $-\Delta E_{HF} = E_{HF}(C) - \sum_F E_{HF}(F)$, $-\Delta E_{HF\text{-}BSSE} = E_{HF}(C) - \sum_F (E_{HF}(F) + E_{BSSE}(F))$, and $-\Delta E_T = E_T(C) - \sum_F (E_{HF}(F) + E_{BSSE}(F) + E_{LYP}(F))$, where C and F stand respectively for the complex and fragment and $E_T(C)$ is the LYP correlated energy of the complex, $E_T(C) = E_{HF}(C) + E_{LYP}(C)$. Comparison of ΔE_{HF} with $\Delta E_{HF\text{-}BSSE}$ gives a measure of the limitations of the adopted basis sets. Contributions of the correlation energy to the complex stability can be estimated by comparing $\Delta E_{HF\text{-}BSSE}$ with ΔE_T. Of course, ΔE_T is the best estimate of the complex stability, within the limits of the present computational scheme.

$Pt(PH_3)_2(\eta^2\text{-}O_2)$. The best geometry parameters obtained for the dioxygen adduct are displayed in Figure 1. The complex is assumed to possess a C_{2v} symmetry, and its stability values have been computed to be equal to ΔE_{HF} = 134.6 kJ·mol^{-1}, $\Delta E_{HF\text{-}BSSE}$ = 49.8 kJ·mol^{-1}, and ΔE_T = 244.6 kJ·mol^{-1}. The large BSSE correction is almost entirely due to the O_2 fragment for which the STO 3-21G basis seems to be particularly poor. The BSSE correction for the PH_3 ligands is relatively small and amounts to 6.3 kJ·mol^{-1}, even smaller is the contribution associated with the Pt atom (2.1 kJ·mol^{-1}). The computed optimum O–O and Pt–O distances are 1.44 and 1.99 Å, respectively, in good agreement with the values found experimentally (1.45–1.51 Å for O–O and 2.01 Å for Pt–O) in an analogous complex with aromatic phosphines.[24] The Pt–P bond distance has been evaluated equal to 2.45 Å, about 0.2 Å longer than the value found in the $Pt(PPh_3)_2(O_2)$ complex (2.23 Å).[24] Such a large error seems to be present in our and other theoretical studies of phosphine complexes. For instance, a full HF geometry optimization carried out on $Pt(PH_3)_2(X)_2$ (X = CH_3, H) complexes[25] gave Pt–P distances ranging from 2.44 to 2.46 Å. A detailed investigation of the problem[26] revealed that the error is almost entirely due to basis set limitations and can be overcome by a careful choice of the d orbitals located on the P atoms. However, the use of much more flexible basis sets does not change the description of the features of the Pt–P bond with respect to that obtained in the present study. The optimum ∠PPtP angle is equal to 98.2°, only slightly smaller than the experimental one found in the $Pt(PPh_3)_2(O_2)$ complex[24]

---

(16) Klatz, R.; Peyerimoff, S. *Mol. Phys.* **1986**, *57*, 573 and references therein.

(17) (a) Kutzelnigg, W.; Wallmeier, H. *Theor. Chim. Acta* **1979**, *51*, 261. (b) Marymick, D. S.; Dixon, D. A. *J. Phys. Chem.* **1982**, *86*, 914 and references therein.

(18) Tse, J. S.; Goddard, J. D. *J. Mol. Struct.* **1986**, *139*, 165.

(19) (a) Adeney, P. D.; Bouma, W. J.; Radom, L.; Rodwell, W. R. *J. Am. Chem. Soc.* **1980**, *102*, 4069. (b) Dognon, J. P.; Puchan, C.; Dargelos, A. *Chem. Phys. Lett.* **1983**, *99*, 316.

(20) Bartell, L. S.; Hirst, L. C. *J. Chem. Phys.* **1959**, *31*, 449.

(21) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure, Constants of Diatomic Molecules*; Van Nostrand: New York, 1979.

(22) (a) Davis, M. I.; Boggs, J. E.; Coffey, D., Jr.; Hanson, H. P. *J. Phys. Chem.* **1965**, *69*, 3272. (b) Bauer, S. H.; Andreassen, A. L. *J. Phys. Chem.* **1972**, *76*, 3099. (c) Turner, P. H.; Cox, A. P. *Chem. Phys. Lett.* **1976**, *39*, 585.

(23) Turner, P. H.; Cox, A. P. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 533.

(24) Cheng, P.-T.; Cook, C. D.; Nyburg, S. C.; Wan, K. Y. *Can. J. Chem.* **1971**, *49*, 3772. Kashiwagi, T.; Yasuoka, N.; Kasai, N.; Kakudi, M. *Chem. Commun.* **1969**, 743.

(25) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 6115 and references therein.

(26) Fantucci, P. Unpublished results.

Table I. Stability[a] and Charge Charge Distribution[b] in $Pt(PH_3)_2(O_2)$

ΔE_{HF}	$\Delta E_{HF\text{-}BSSE}$	ΔE_T
147.5	62.6	257.4

	s	p	d	Q
Pt	2.502	6.040	8.828	0.630
P	5.712	9.345		−0.057
H[c]	0.979			0.021
O	3.967	4.382		−0.349

[a] Stability of the complex ($kJ \cdot mol^{-1}$) with respect to the dissociation into Pt + $2PH_3$ + O_2 (see text for definitions). [b] Orbital occupancies (s, p, d) and net atomic charge (Q) obtained from Mulliken analysis. [c] Values averaged over nonequivalent atoms.

(101.2°) and very similar to that found in other theoretical studies.[25,27]

A separate optimization of the $Pt(PH_3)_2$ fragment (D_{3h} symmetry) gave a Pt–P distance equal to 2.35 Å, a value which closely reproduces the results quoted by Noell and Hay (2.36 Å)[27] and by Low and Goddard (2.32 Å)[25] and is shorter than that found in the dioxygen adduct. This suggests that the coordination of O_2 to the $Pt(PH_3)_2$ fragment may lead to an increase of the Pt–P distance and, correspondingly, to a weakening of the Pt–P bonding interaction.

The Mulliken analysis data of Table I show that the formation of the Pt–P bond is not accompanied by any important ligand-to-metal charge transfer. On the contrary, it is possible to correlate the large negative charge (0.72 electron) localized on the O_2 group with an elongation of the O–O bond of 0.24 Å. The dioxygen ligand acts as a strong π-acceptor, causing a large increase of the positive charge on the Pt atom, which was found to be slightly negative in $Pt(PH_3)_2$. Therefore, the coordination of O_2 can be rationalized in terms of an oxidative addition. The occurrence of an important π-back-bonding effect is clearly documented also by the fact that the excess of electronic charge on the coordinated oxygen atoms is almost completely associated with the p orbitals, while the occupancies of the s orbitals remain nearly the same as in the free O_2 molecule.

$Pt(PH_3)_2(RNO)$ Complexes. In order to reduce the number of internal coordinates to be optimized in $Pt(PH_3)_2(RNO)$ (R = CF_3, CH_3) complexes, which are characterized by low or null symmetry, we have assumed for ∠PPtP a value of 98.2°, i.e. the optimum value computed for $Pt(PPh_3)_2(\eta^2\text{-}O_2)$. We have proved, however, that such an assumption does not lead to an important loss of stability. For instance, in the case of $Pt(PH_3)_2(O_2)$, the variation of ∠PPtP from the optimum value 98.2° to 106.5° (the experimental value found in $Pt(PPh_3)_2(PhNO)$[2]) is accompanied by an increase in the total energy of 6.2 $kJ \cdot mol^{-1}$ only.

(a) $Pt(PH_3)_2(CF_3NO)$. The best geometry parameters for the trifluoronitrosomethane complex considered in the two different conformations I and II are reported in Figure 2. The first conformation (I) is characterized by the stability values ΔE_{HF} = 265.8 $kJ \cdot mol^{-1}$, $\Delta E_{HF\text{-}BSSE}$ = 179.9 $kJ \cdot mol^{-1}$, and ΔE_T = 360.9 $kJ \cdot mol^{-1}$, which are all strongly reduced (ΔE_{HF} = 105.8 $kJ \cdot mol^{-1}$, $\Delta E_{HF\text{-}BSSE}$ = 43.3 $kJ \cdot mol^{-1}$, and ΔE_T = 200.9 $kJ \cdot mol^{-1}$) when CF_3NO is oriented according to coordination mode II. The Pt–P bond distances in I and II have values of 2.46 and 2.53 Å, respectively, similar to but slightly higher than the value computed for the dioxygen adduct. In the two coordination geometries I and II the PH_3 ligands behave quite differently: in I they act as weak donors with respect to the Pt atom (0.13 electron), and in II they act as weak acceptors (0.09 electron).

In I the platinum atom strongly interacts with the π* component of the N–O bond, and the most evident effects of the coordination are the important increase of the N–O distance (1.43 Å), about 0.22 Å longer than the value of the free ligand, and the occurrence of a large charge donation from the Pt atom to the CF_3NO ligand (0.73 electron; see Table II). The back-bonding mainly involves the π* orbital of the NO group (0.68 electron) and to a small extent also the CF_3 substituent, which reduces its global positive charge from 0.28 (the free-molecule value) to 0.23. Since the π^*_{NO} has larger amplitude on N than on O, the back-donation produces accumulation of a negative charge on N (−0.401) much larger than that computed for the free ligand (−0.034). The net charge on the Pt atom amounts to 0.55.

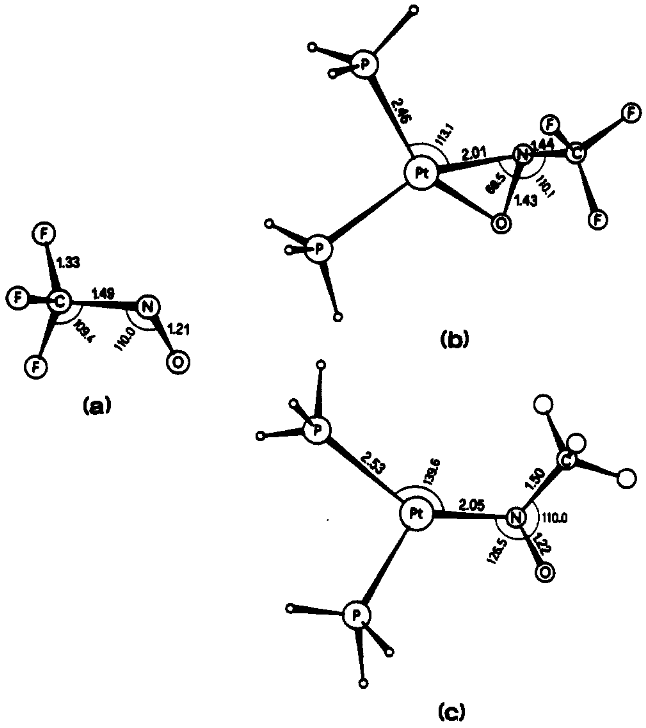


Figure 2. Optimized geometries for (a) CF_3NO, (b) $Pt(PH_3)_2(\eta^2\text{-}CF_3NO)$, and (c) $Pt(PH_3)_2(\eta^1\text{-}CF_3NO)$ (bond distances in angstroms; valence angles in degrees). In (b) the CF_3 group lies above the Pt–O–N plane; the C atom has a torsion angle C–N–O–Pt of 120°.

Table II. Stability[a] and Charge Distribution[b] in $Pt(PH_3)_2(CF_3NO)$

	ΔE_{HF}	$\Delta E_{HF\text{-}BSSE}$	ΔE_T
coordn I	255.8	179.9	360.9
coordn II	105.8	43.1	200.9

	s	p	d	Q
Pt	2.506	6.054	8.846	0.595
	2.474	6.047	9.356	0.123
P[c]	5.706	9.325		−0.032
	5.736	9.294		−0.030
H[c]	0.967			0.033
	1.005			−0.005
O	3.968	4.459		−0.426
	3.978	4.249		−0.227
N	3.737	3.798		−0.535
	3.760	3.423		−0.183
C	2.906	1.706		1.389
	2.751	1.837		1.412
F[c]	4.000	5.385		−0.386
	4.000	5.354		−0.354

[a] Stability of the complex ($kJ \cdot mol^{-1}$) with respect to the dissociation into Pt + $2PH_3$ + CF_3NO (see text for definitions). [b] Orbital occupancies (s, p, d) and net atomic charge (Q) obtained from Mulliken analysis. [c] Values averaged over nonequivalent atoms.

The properties of the CF_3NO ligand involved in coordination II are markedly different from those of the η^2 adduct (see Table II). The elongation of the N–O bond with respect to the free-ligand value is very small (0.01 Å), while the best Pt–N distance (2.05 Å) is very close to that computed for the η^2 mode (2.01 Å) (see Figure 2). The platinum atom carries a small positive charge (0.12), while the global charge on the CF_3NO ligand is equal to −0.134. This proves that in coordination II the π-acceptor properties of CF_3NO are strongly reduced with respect to the case of η^2 coordination. This also explains the fact that the computed

---

(27) Noell, J. O.; Hay, P. J. *Inorg. Chem.* **1982**, *21*, 14.

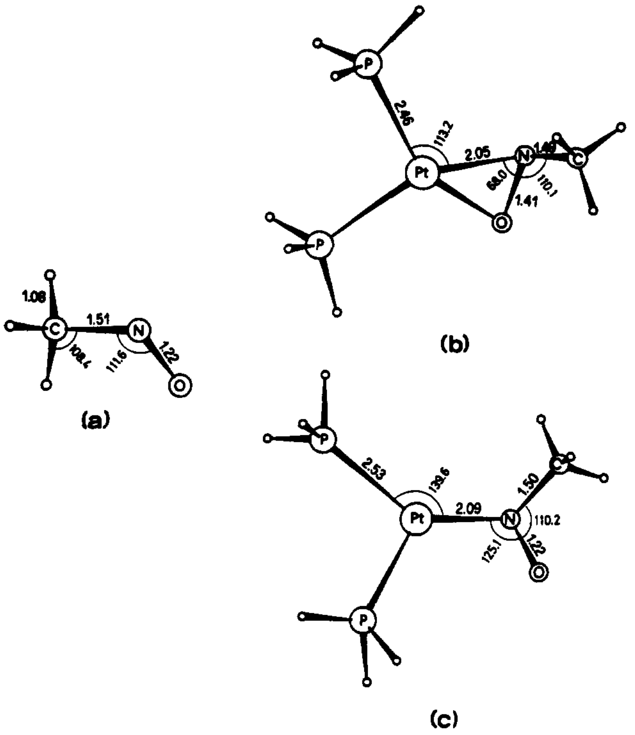


Figure 3. Optimized geometries for (a) CH_3NO, (b) $Pt(PH_3)_2(\eta^2\text{-}CH_3NO)$, and (c) $Pt(PH_3)_2(\eta^1\text{-}CH_3NO)$ (bond distances in angstroms; valence angles in degrees). In (b) the CF_3 group lies above the Pt–O–N plane; the C atom has a torsion angle C–N–O–Pt of 117°.

geometric distortions with respect to the free-ligand situation are much smaller for coordination mode II than for I. In the η^1 coordination the Pt atoms cannot appreciably interact with the O atom, the Pt–O distance being equal to 3.02 Å, which is much longer than that found in I, 2.01 Å.

(b) $Pt(PH_3)_2(CH_3NO)$. The results of the geometry optimization concerning the nitrosomethane derivative in coordination modes I and II are reported in Figure 3a,b. Again, the most evident characteristic of the η^2-coordinated ligand is the increase of the N–O distance (1.41 Å), longer than in the free molecule (1.22 Å) and very close to that found in the η^2 adduct of CF_3NO. The stability values of the η^2-nitrosomethane derivative are $\Delta E_{HF} = 150.1$ kJ·mol^{-1}, $\Delta E_{HF\text{-}BSSE} = 86.2$ kJ·mol^{-1}, and $\Delta E_T = 258.1$ kJ·mol^{-1}. In analogy with all other previous cases, the elongation of the N–O bond can be correlated with the amount of charge back-donated by the Pt atom to the π^*_{NO} MO (about 0.53 electron). This is essentially concentrated on the N atom, which raises its negative charge to −0.34.

The computed stability values for the analogous CH_3NO complex in coordination mode II are smaller than the corresponding values of I: $\Delta E_a H_F = 93.3$ kJ·mol^{-1}, $\Delta E_{HF\text{-}BSSE} = 45.9$ kJ·mol^{-1}, and $\Delta E_T = 202.2$ kJ·mol^{-1}. The best N–O distance, in this case, is found to be coincident with the distance of the free ligand (1.22 Å). Also, the data of the Mulliken analysis (see Table III) show that the Pt–ligand back-bonding mechanism can be considered as completely absent: in fact the CH_3NO ligand carries a small positive charge (0.030), comparable in magnitude with that of the Pt atom (0.065). This is an evident indication that the σ-donation mechanism is more important than the metal-to-ligand charge transfer.

Table III. Stability[a] and Charge Distribution[b] in $Pt(PH_3)_2(CH_3NO)$

	ΔE_{HF}	$\Delta E_{HF\text{-}BSSE}$	ΔE_T
coordn I	150.1	86.2	258.1
coordn II	93.3	45.9	202.2

	s	p	d	Q
Pt	2.514	6.053	8.953	0.480
	2.488	6.054	9.393	0.065
P[c]	5.714	9.316		−0.030
	5.731	9.275		−0.006
H(P)[c]	0.982			0.018
	1.014			−0.014
O	3.961	4.482		−0.443
	3.969	4.319		−0.288
N	3.808	3.531		−0.339
	3.723	3.323		−0.046
C	3.417	2.974		−0.391
	3.436	2.980		−0.416
H(C)[c]	0.786			0.214
	0.740			0.260

[a] Stability of the complex (kJ·mol^{-1}) with respect to the dissociation into Pt + $2PH_3$ + CH_3NO (see text for definitions). [b] Orbital occupancies (s, p, d) and net atomic charge (Q) obtained from Mulliken analysis. [c] Values averaged over nonequivalent atoms.

Table IV. Electronic Charge Exchange between the Pt Atoms and Ligand Groups in $Pt(PH_3)_2X$ (X = O_2, CF_3NO, and CH_3NO) and Complex Stability

X	$q(PH_3\text{–}Pt)$[a]	$q(Pt\text{–}X)$[b]	ΔE_T/kJ·mol^{-1}
η^2-CF_3NO	0.134	0.730	360.9
η^2-CH_3NO	0.048	0.531	258.1
η^2-O_2	0.066	0.698	257.4
η^1-CH_3NO	−0.096	−0.030	202.9
η^1-CF_3NO	−0.090	0.060	200.9

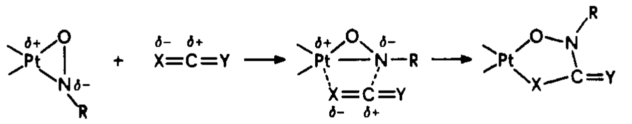
[a] Positive values indicate donation from PH_3 to Pt. [b] Positive values indicate donation from Pt to X.

Discussion and Conclusions

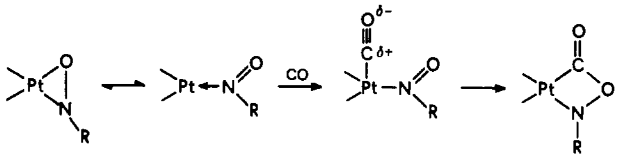
The theoretical results reported above allow the comparison of the bonding capabilities of the two nitroso ligands considered in the present study with that of the isoelectronic molecular dioxygen. The results concerning the stability of the complexes are compared in Table IV with the amount of electronic charge involved in the PH_3–Pt and Pt–X (X = O_2, CF_3NO, and CH_3NO) exchanges. The complex stability correlates well with the Pt → X donation: in the presence of an efficient back-bonding mechanism, which occurs in the η^2 complexes, the stability is much higher than in the case of the η^1(N) adducts where the ligands are forced to interact with the Pt center mainly according to a σ mechanism. In the absence of back-donation, the oxidation state of the Pt atom is very low and, as a consequence, the RNO ligands cannot behave as good donors. According to the Mulliken analysis, the CF_3NO ligand in the η^1 complexes may act only as a very weak acceptor and the CH_3NO ligand as a very weak donor.

In the case of η^2-X complexes, the positive charge on the Pt atom and the global negative charge on the ligand X are of comparable magnitude. Therefore, if one accepts that the formation of the O_2 adduct can be classified as an oxidative addition, such a classification should be extended also to the η^2-RNO complexes. The η^2-CF_3NO adduct has been found definitely more stable than the CH_3NO adduct, while no appreciable difference has been computed for the corresponding η^1 derivatives. The larger stability in I can be explained in terms of a better π-acceptor ability of CF_3NO with respect to CH_3NO. This point clearly differentiates the chemical behavior of the two ligands, and it is worthy of a detailed comment. The amount of Pt → RNO back-donated charge that can be formally assigned to the CF_3 fragment (0.050 electron) is very similar to that located on the CH_3 group (0.035). This means that the withdrawing power of the CF_3 substituent is not enhanced by the coordination process. In fact, the group is unable to delocalize the excess of charge back-donated by the Pt atom and mainly concentrated on the N atom. Therefore, the better π-accepting power of CF_3NO with respect to CH_3NO must be explained only in terms of a pure electrostatic effect originating from the gross atomic charge of the carbon atom. The largely positive charge on C due to the presence of the fluorine atoms allows a charge accumulation by the neighboring N atom, with an inductive stabilizing effect. On the contrary, in the case of the CH_3NO η^2 adduct, a large accumulation of negative charge by the nitrogen atom bound to a negatively charged C atom is a less favorable phenomenon. In this respect, the electronic effects

Scheme I



Scheme II



caused by the CF_3 and CH_3 substituents are different from those occurring in the aromatic derivatives (e.g. PhNO), where the excess of charge back-donated to the π^*_{NO} MO can be effectively delocalized because of a strong conjugative effect.

It is important to note that the carbon atom of the CF_3 or CH_3 group in the η^2 complexes does not belong to the Pt–N–O plane, being characterized by a torsion angle (C–N–O–Pt) of about 120° (see Figures 2 and 3). On the contrary, the planarity is a characteristic of the η^1 coordination. This means that the N atom has a hybridization close to sp^3, which is consistent with the single-bond character of the N–O bond. The small ligand perturbation caused by the η^1 coordination does not appreciably alter the sp^2 hybridization of the N atom and the N–O bond, which still has double-bond character.

The identification of the electronic structure internal to the coordinated ligands that has been clarified by our theoretical results can also serve to rationalize the mechanism of the reaction of the nitroso complexes with alkenes, CO_2, or CO_2-like molecules to give stable compounds in which the entering molecule inserts into the Pt–N bond, with formation of a C–N bond.[2,28,30]

The attack of the electrophilic carbon atom of the entering molecule takes place according to Scheme I (X = S, Y = S, NPh; X = O, NPh, Y = O), which is based on the assumption that the reactants can lead to a dipolar addition to the platinum and nitrogen atoms of the complex. Our results confirm that the nitrogen atom in η^2-coordinated nitroso ligands increases substantially its negative charge with respect to the free molecule, and therefore its nucleophilic character. The hypothesis of a dipolar mechanism seems to be consistent also with theoretical evidence.

The reaction of CO with coordinated nitroso ligands is particularly interesting because it could correspond to the final step of the catalytic deoxygenation of nitro compounds. As discussed in detail in refs 1 and 2, in the case of $Pt(PPh_3)_2(PhNO)$ this reaction leads to the formation of nonstoichiometric quantities of CO_2. A possible reaction intermediate has been postulated according to Scheme II. The cyclic intermediate due to the insertion of CO into a Pt–O bond is not completely consistent with the experimental results.[2,29] The existence of the cyclic species could be postulated by assuming that an equilibrium between η^2 and η^1 coordination modes takes place. Our results do not agree with this view, especially in the case of the CF_3NO ligand, since the two coordination modes I and II differ in stability by about 160 kJ·mol^{-1}. However, one cannot exclude the idea that the η^1 coordination of RNO is favored in the presence of a coordinated CO group, which can be competitive with RNO in the back-donation mechanism. Further theoretical studies would be in order to elucidate such a hypothesis.

Acknowledgment. This work has been supported by the Italian CNR and by the Italian Ministry of Education. We thank Prof. S. Cenini for stimulating discussions.

---

(28) Cenini, S.; Porta, F.; Pizzotti, M.; La Monica, G. *J. Chem. Soc., Dalton Trans.* **1984**, 355.

(29) Cenini, S.; Porta, F.; Pizzotti, M. *J. Chem. Soc., Dalton Trans.* **1985**, 163.

(30) Demartin, F.; Pizzotti, M.; Porta, F.; Cenini, S. *J. Chem. Soc., Dalton Trans.* **1987**, 605.

Contribution from the School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.,
Dipartimento di Chimica, Universita di Sassari, via Vienna 2, 07500 Sassari, Italy, and Dipartimento di Chimica Inorganica,
Chimica Fisica e Chimica dei Materiali, Universita di Torino, via P. Giuria 7, 10125 Torino, Italy

Vibrational Spectra of the μ_2-Hydride Ligands in $[H_4M_4(CO)_{12}]$ (M = Os, Ru)

Christopher E. Anson,[†] Upali A. Jayasooriya,[†] Sidney F. A. Kettle,[*,†] Pier Luigi Stanghellini,[‡]
and Rosanna Rossetti[§]

Received March 27, 1990

The vibrational spectra of the hydride ligands in the title compounds are interpreted in terms of D_{2d} molecular symmetry. The pseudo-D_{4h} symmetry of the four hydrides (if the rest of the cluster is neglected) and the spherical symmetry of the hydride 1s orbital are shown to have a profound effect on the Raman intensities of some of the hydride modes.

Introduction

It is now usually relatively easy to identify those bands in the vibrational spectra of metal clusters that are associated with modes involving bridging hydride ligands. Such features shift to lower frequency on deuteration and sharpen markedly on cooling. However, in many cases the detailed interpretation of the spectra themselves is far from clear. The present communication deals with one such case, that of the clusters $[H_4M_4(CO)_{12}]$ (M = Ru, Os).

X-ray diffraction analyses[1] indicate that the clusters have very similar D_{2d} molecular symmetry; the four metal atoms define a tetrahedron elongated along one 2-fold axis, resulting in four long and two short metal–metal bonds. Neutron diffraction studies[2] of phosphite derivatives show the same bond length pattern for the metal skeleton, with the hydrides each bridging one of the longer bonds; average MHM angles are 112.2° (Os) and 114.2° (Ru).

---

[*] To whom correspondence should be addressed.

[†] University of East Anglia.

[‡] Universita di Sassari.

[§] Universita di Torino.

(1) Wilson, R. D.; Wu, S. M.; Lowe, R. A.; Bau, R. *Inorg. Chem.* **1978**, *17*, 1271. Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Zuccaro, C. *Acta Crystallogr.* **1981**, *B37*, 1728.

(2) Orpen, A. G.; McMullan, R. K. *J. Chem. Soc., Dalton Trans.* **1983**, 463. Wei, C. Y.; Garlaschelli, L.; Bau, R.; Koetzle, T. F. *J. Organomet. Chem.* **1981**, *213*, 63.