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Delocalization of the unpaired spin density in some niobocene complexes with σ-donor, π-acceptors

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Abstract

Extended Hückel calculations and qualitative MO have been used to analyze the EPR data relevant to the localization of the unpaired spin density in several paramagnetic niobocene complexes with σ-donor π-acceptors, acetylene, aldehyde, ketene, ketenimine, and carbon disulfide.

Key words: Niobium; Metallocenes; Paramagnetism; Extended Hückel calculations; Electron spin resonance; Cumulene

1. Introduction

There are numerous examples [1] of ESR spectra of paramagnetic niobocene complexes $[Cp_2NbX_2]$ (X = alkyl, halide, or hydride) which indicate that the unpaired spin density is centered mainly on the niobium atom.

However, in the course of our studies on the reactivity of the niobocene species with unsaturated compounds, we characterized both chemically and electrochemically niobocene paramagnetic species such as $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PhC{\equiv}CPh\text{-}C,C')]$, with ESR spectra which suggest appreciable delocalization of the unpaired spin density onto the ligands. In order to analyze the phenomenon, we have carried out extended Hückel calculations.

2. Results and discussion

We have published several studies on the reactivity of bis(silylcyclopentadienyl)niobocene moieties with different unsaturated molecules such as ketene [2], ketenimine [3], acetylene [4], aldehyde [5], and carbon disulfide [6]. In the course of this work, we have prepared several paramagnetic species with characteristic ESR spectra. On electrochemical or chemical one-electron reduction, the following niobium(V) species, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2\text{-}PhC{\equiv}CPh\text{-}C,C')]$ (X = Cl or Br; $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2\text{-}Ph_2C{=}C{=}O\text{-}C,O)]$) (X = Cl or Br; $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl\text{-}(Ph_2C{=}C{=}NPh\text{-}C,N)]$), lose halide to give the paramagnetic niobium(IV) species. We have prepared the analogous complexes with Ph_2CHCHO and CS_2 through the two-electron reduction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]$ in the presence of one equivalent of Ph_2CHCHO and CS_2, respectively. The ESR spectra of all these species are depicted in Fig. 1. The g and hyperfine splitting, $\langle a \rangle$, values by the ^{93}Nb nucleus (100% natural abundance, $I = 9/2$) are also given in Table 1.

Compared to most paramagnetic niobocene species [7*], our complexes exhibit smaller $\langle a \rangle$ values. The simple explanation is a diminished unpaired spin density at the niobium, consistent with delocalization onto the ligands. There are also differences in the line

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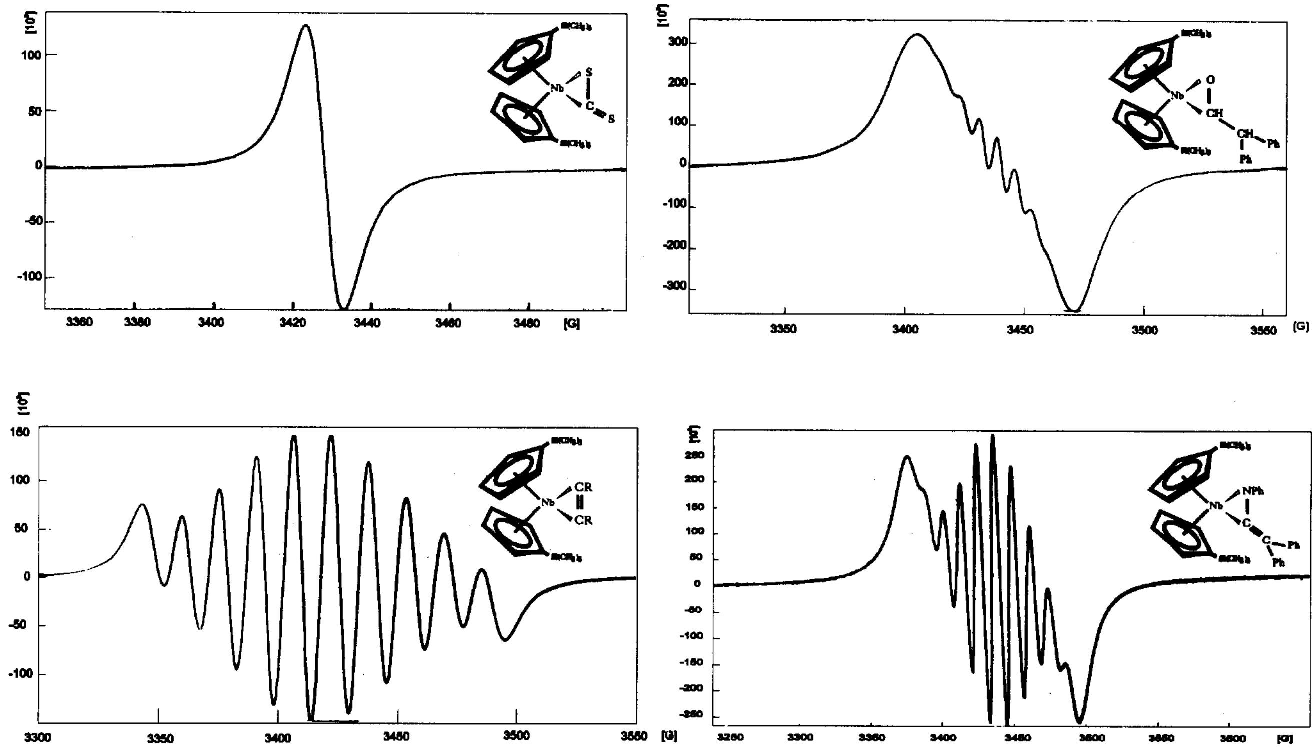

Fig. 1. ESR spectra of some paramagnetic niobocene complexes.

widths. The outer lines are considerably broadened relative to the inner lines, which may be the result of large rotational correlation times [8] in our radicals.

However, an important question to answer concerns the role of the electronic properties of the ligands in the electron delocalization which has been observed in the spectra. To gain more insight into this, we have examined the orbital interaction diagrams for $[Cp'_2Nb(\eta^2\text{-}L)]$ (L = PhC≡CPh, $Ph_2C{=}C{=}O$, $Ph_2C{=}C{=}NPh$, Ph_2CHCHO, or CS_2) although in the calculations the phenyl groups have been replaced by H.

Figure 2 shows the main interactions between the Cp_2Nb fragment and a bent η^2-HC≡CH fragment. The frontier orbitals of the Cp_2Nb fragment, on the left of Fig. 2, have basically metal d character [9]. For the acetylene, we have represented only the π and π^* orbitals, that are in the *yz* plane. The stabilization of the η^2-acetylene complex arises both from the donation of electron density from the filled π orbital to the unfilled metal orbital $2a_1$ and from back-donation from the metal b_2 orbital to the π^* orbital of the ligand. This back-donation lowers the energy of the metal orbital b_2 to below the $1a_1$ orbital. Thus, the unpaired electron lies in an orbital, $1a_1$, which is mainly a metal orbital (see Table 2).

TABLE 1

Complex	g_{iso}	⟨a⟩ (G)
$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PhC{\equiv}CPh)]$	2.014	16.5
$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Ph_2C{=}C{=}O)]$	1.997	18.1
$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Ph_2C{=}C{=}NPh)]$	1.999	11.0
$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Ph_2CHCHO)]$	2.003	8.3
$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CS_2)]$	2.004	–

This pattern of orbital interactions is repeated in complexes with a η^2-ketene and η^2-aldehyde [10*] where the π_{CO} and π^*_{CO} orbitals play the role of the ligand donor and acceptor orbitals.

As the π_{CO} orbital is quite low in energy because of the electronegativity of the oxygen atom, back donation is the most important interaction [11,12]. There is also a less important oxygen lone pair → metal orbital $a'(2a_1)$ interaction. Thus, the HOMO is again the metal orbital $a'(1a_1)$. This situation is also repeated for the η^2-ketenimine complex with the ligand orbitals concerned being π_{CN} and π^*_{CN} (see Table 2).

Finally, Figure 3 shows the main orbital interactions between the Cp_2Nb fragment and η^2-CS_2. For bent CS_2, three orbitals in the *yz* plane (there are three more equivalent orbitals perpendicular to them) have been considered, labelled π, π^n and π^* [13]. In this case, the MO resulting from back-donation from the

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* Reference number with asterisk indicates a note in the list of references.

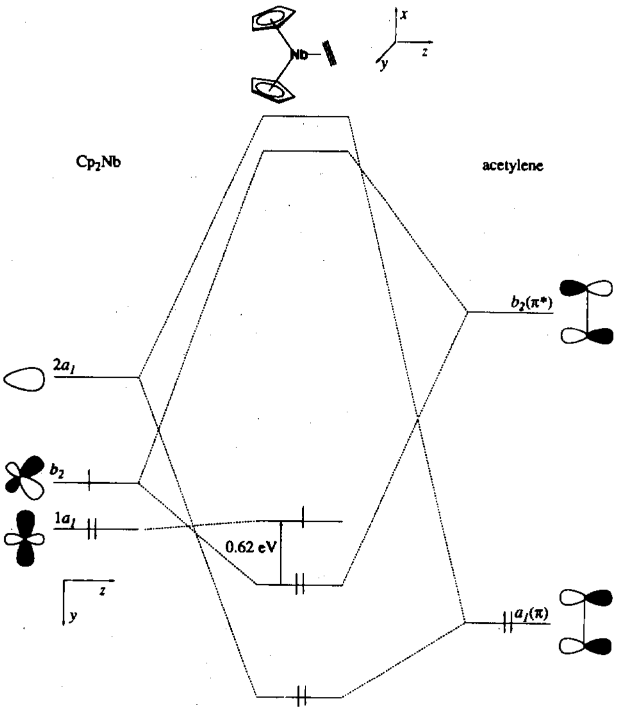

Fig. 2. Partial interaction diagram for $[Cp_2Nb(C_2H_2)]$.

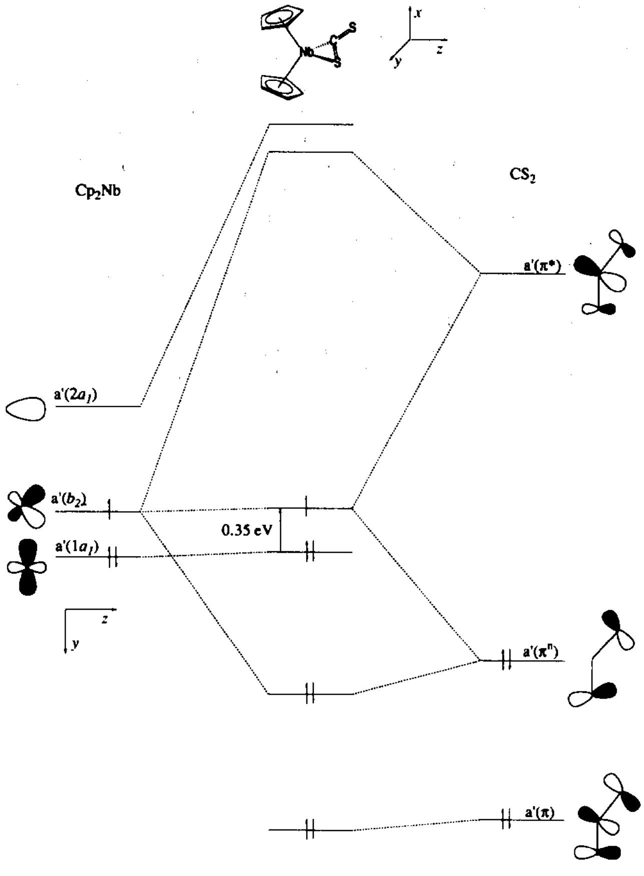

Fig. 3. Partial interaction diagram for complex $[Cp_2Nb(CS_2)]$.

TABLE 2. Contribution to the HOMO of the niobium, cyclopentadienyl, and orbitals in the complexes

Complex	Niobium (%)	Cyclopentadienyl (%)	L (%)
$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PhC{\equiv}CPh)]$	86	9	5
$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Ph_2C{=}C{=}O)]$	83	13	4
$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Ph_2C{=}C{=}NPh)]$	85	12	3
$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Ph_2CHCHO)]$	74	16	10
$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CS_2)]$	45	18	37

a'(b_2) metal orbital to the π^* orbital lies above the a'($1a_1$) metal orbital; this is the HOMO. This situation is quite different from that in the other complexes. This is because the π^* orbital is higher in energy in the CS_2 molecule so that it back-donates less efficiently than in the other cases, and because it is destabilized by interaction with the π^n orbital. Thus the unpaired electron in this complex is highly delocalized onto the ligand, in contrast to the other complexes where it has basically a metal character (see Table 2).

3. Conclusions

The extended Hückel calculations for our paramagnetic niobocene species are consistent with the ESR data and allow us to establish the delocalization of the unpaired spin density onto the different ligands. In the acetylene and ketene niobocene complexes, the unpaired spin density is mainly localized on the metal whereas in the carbon disulfide species, there is a high delocalization onto the ligand.

4. Experimental

The molecular orbital calculations were carried out by the extended Hückel method [14]. The basis set used for niobium consists of single Slater orbitals for the 5s ($H_{ii} = -10.10$ eV, $\xi = 1.89$) and 5p ($H_{ii} = -6.86$ ev, $\xi = 1.85$) functions, and a 4d ($H_{ii} = -12.10$ eV, $\xi_1 = 4.08$, $\xi_2 = 1.64$, $C_1 = 0.6401$, $C_2 = 0.5516$) function taken as a contracted linear combination of two Slater-type functions. The modified Wolfsberg–Helmoltz formula was used throughout this work [15]. For the calculations, the atomic parameters of the ligands to the Cp_2Nb fragment were taken from experimental data of related compounds. Further, the angles were adjusted to minimize the sum of one-electron energies (Fig. 4). We have used the data of the following crystal structures: $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(PhC{\equiv}CPh\text{-}C,C')]$ [16]; $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(Ph_2C{=}$

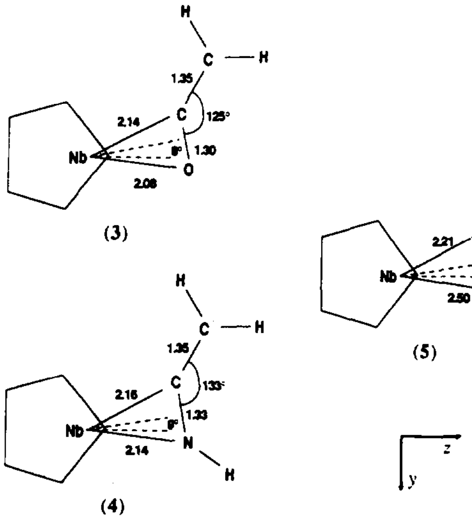

Fig. 4. Dimensions of the ligand bonded to the Cp_2Nb fragment used in calculations for some complexes.

C=O–*C*,*O*)] [2]; $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(Ph_2C{=}C{=}NPh\text{-}C,N)$] [3] and $[Nb(\eta^5\text{-}C_5H_5)_2Br(\mu\text{-}(CS_2))W(CO)_5]$ [17].

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