A new method to radical anions derived from *s*-Indacene organobimetallic complexes, their ESR characterization

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ABSTRACT

The following organobimetallic radical anions derived from 2,6-diethyl-4,8-dimethyl-*s*-indacene (*s*-Ic′): [CODRh(*s*-Ic′)RhCOD]$^{\cdot-}$ (**IIa**), [Cp*Ru(*s*-Ic′)RuCp*]$^{\cdot-}$ (**IIb**), [Cp*Ru(*s*-Ic′)RhCOD] $^{\cdot-}$ (**IIc**), [Cp*Ru(*s*-Ic′)NiCp*]$^{\cdot-}$ (**IId**) [(CO)$_3$Mn(*s*-Ic′)NiCp*]$^{\cdot-}$ (**IIe**) and [Cp*Fe(*s*-Ic′)NiCp*]$^{\cdot-}$ (**IIf**) (COD = 1,5-cyclooctadiene; Cp* = pentam-ethylcyclopentadienyl) were prepared by reduction of the parent complexes using a monoelectronic transfer from an electron rich olefin. The radical anions were fully characterized by ESR spectroscopy which usually gave a well resolved hyperfine coupling structure, indicating that the spin distribution in the symmetrical radical anions (**IIa**, **IIb**) affects mainly the organic spacer whereas in the unsymmet-rical ones (**IIc–f**) it is displaced towards the most electronegative metal center and its ligands. This effect is most pronounced in **IId**, **IIe** and **IIf**. The calculated *g* tensor values of the radical anions are in good agreement with the experimental values. In heterobimetallic radical anions, the dissymmetric spin dis-tribution shows that the two metals present different electrophile properties leading to potentially dif-ferent catalytic activities.

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1. Introduction

There is considerable interest in understanding intermetallic communication in mixed-valence bimetallic complexes in which the two metallic centers are linked through a π-spacer ligand [1–28]. This interest lies on the unusual behavior of mixed-valence molecules and their potential applications as advanced materials because they possess unique properties, such as charge transfer and conductivity [29–32] and non linear optical activity [33–35]. Intramolecular interaction between redox centers mediated by linking ligands is an important process in chemical and biological systems, in which the electron-transfer process plays a key role ranging from simple redox reactions to more complex enzymatic cycles. Recently there has been a growing interest about the cata-lytic behavior of several bimetallic complexes derived from various brigding ligands, such as polyalkyl-*s*-indacenes [5,6,14,26–27]. Their electron delocalization and electronic cooperative interac-tions were examined because electron transfer is a fundamental

process involved in the chemical reactivity of these molecules. Studies of several bimetallic complexes indicate that the 14 π elec-trons of the *s*-indacene (Ic) ligand allows a strong electronic inter-action between the metal centers [3,28,32,36–48], converting these complexes into very good candidates to study cooperative effects.

Knowledge of the electron distribution in the ionic mixed-va-lence species derived from these bimetallic complexes would be very useful for a better understanding of their catalytic properties. Actually, the radical anions are appropriate models for the species involved in the first step of some catalytic processes. Even though these electron distributions can be obtained by means of theoreti-cal calculations, we attempted to make these paramagnetic anionic species and establish their spin distributions through a combined theoretical and experimental ESR study.

In this article we describe the reduction of several symmetrical and dissymmetrical organobimetallic complexes derived from 2,6-diethyl-4,8-dimethyl-*s*-indacene (*s*-Ic′), in order to obtain the corresponding radical anions. The organometallic complexes employed as precursors for obtaining the radical anions are the following: **Ia** [CODRh(*s*-Ic′)RhCOD], **Ib** [Cp*Ru(*s*-Ic′)RuCp*], **Ic**
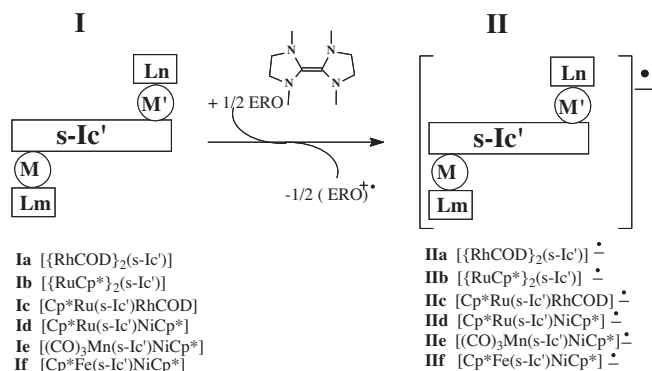
Scheme 1. Reduction of binuclear complexes **I** with ERO.

[Cp*Ru(s-Ic′)RhCOD], **Id** [Cp*Ru(s-Ic′)NiCp*], **Ie** [(CO)₃Mn(s-Ic′) NiCp*] and **If** [Cp*Fe(s-Ic′)NiCp*], (COD = 1,5-cyclooctadiene; Cp* = pentamethylcyclopentadienyl), see Scheme 1. These systems were chosen with the objective of gaining an insight into the first step of their catalytic mechanisms, some of which exhibit catalytic properties in dehydrogenative silylation reactions [14]. Although in several cases the reduction of binuclear complexes has been achieved using strong mono electronic electron donors, such as metals or sodium naphtalenide [39], or an electron rich organometallic arene complex [40,41], here, we decided to experiment the effect of a soft organic electron donor – *an electron rich olefin* (ERO) – already successfully employed for the reduction of the metallic moiety in an organometallic halide [42–44] and more recently in monolithio and 1,5-dilithio-polyalkyl-*s*-indacenes [45,46].

2. Experimental

All reactions were carried out under nitrogen using standard Schlenk tube techniques and dry solvents. NMR spectra were recorded on Bruker ARX400 (^{1}H, 400.13 MHZ); AC 200 (^{13}C, 50.32 MHz), ARX 400 (^{13}C, 100.62 MHz) and Avance II 500 (^{1}H: 500.13 MHz, ^{13}C: 125.77 MHz) spectrometers at 298 K. Chemical shifts are expressed in parts per million with residual solvent signals as internal reference (^{1}H and ^{13}C{^{1}H}). Infrared spectra were recorded on a Perkin Elmer 1600FT spectrometer, and ESR spectra in toluene/THF solutions at 243 K, on a Bruker EPR ELFXSYS E500, *g* values were calculated with Bruker Xepr software using the frequencemeter integrated to the ER049X microwave bridge. The magnetic field was controlled by the NMR teslameter Bruker and verified against dpph. Melting points of recrystallized compounds were measured with a standard Leitz microscope or a Stuart Melting Point SMP3 apparatus. Mass spectra were measured with a Hewlett–Packard 5989A in the electron impact mode (70 eV). HR-MS spectra were measured with a GCT Premier Waters in DCI mode (CH₄).

Theoretical calculations were made with the Amsterdam Density Functional package, ADF 2008.01 [47]. Structures were fully optimized (without any geometric constrain) by analytical energy gradient techniques employing the Local Density Approximation [48] (LDA), and the Generalized Gradient Approximation (GGA) method using Vosko, Wilk and Nusair's local exchange correlations [49], with non local exchange corrections by Becke [50], and non local electronic correlations by Perdew [51]. The uncontracted type IV basis set having Triple-ξ accuracy sets of Slater-Type Orbitals [52] (STO) with a single polarization function added for the main group elements (2p on H and 3d on C) were used. Frozen Core approximation [53] was applied to the inner orbitals of the constituent atoms: C core up to 1s; Mn, Fe and Ni up to 3p; Ru and Rh up

to 4p. The isotropic *g*-tensor value was obtained by the methods developed by van Lenthe et al. [54,55] in which a spin-nonpolarized wavefunction after incorporating the spin–orbit (SO) coupling by first-order perturbation theory from zeroth order regular approximation ZORA Hamiltonian in the presence of a time-independent magnetic field, which has been used before [56–60]. It must be noted that the relativistic atomic potentials or effective core potentials were calculated using the auxiliary code DIRAC [61] implemented in the ADF package. The figures shown here for spin densities were prepared using MOLEKEL [62], employing in all cases a isosurface cutoff value of 0.002 a.u.

2.1. Preparation of **Ia–e**

Homobimetallic complexes LmM(*s*-Ic′)MLn were synthesized as previously described [27] from the corresponding dilithium derivatives Li(*s*-Ic′)Li, while the heterobimetallic complexes LmM(*s*-Ic′)M′Ln were synthesized from the corresponding mononuclear lithium derivatives LmM(*s*-Ic′)Li (LmM = (CO)₃Mn, Cp*Ru, Cp*Fe reacting with [η⁵-Cp*-Ni(acac)] or[{η⁴-COD-Rh(μ-Cl)}₂]) according to the general process hereafter described [26,63].

One equivalent of *n*-Butyllithium was added dropwise to a solution of one equivalent of LnM(2,6-diethyl-4,8-dimethyl-1-hydro-*s*-indacene) in THF at −80 °C. To the resulting mixture was added at −80 °C a solution of one equivalent of Cp*Ni(acac). After 2 h stirring, the solvent was removed. **I** were extracted with Toluene and isolated after evaporation of the solvent. Recrystalization in toluene afforded crystals suitable for X-ray analysis, all of them display a trans geometry [26,64].

Id: ^{1}H NMR (500 MHz, C₆D₆): δ 1.12** (t, $^3J_{HH}$ = 7.5 Hz, 3H, **C**H₃—CH₂—C₍₆₎₍Ni₎); 1.27 (t, $^3J_{HH}$ = 7.4 Hz, **C**H₃—CH₂—C₂₍Ru₎); 1.54** (s, 15H, **C**H₃(Cp*)₍Ni₎); 1.63 (s, 15H, **C**H₃(Cp*)₍Ru₎); 1.82 (s, 6H, **C**H₃—C₍₄,₈₎); 2.19** (q, $^3J_{HH}$ = 7.7 Hz, 2H, CH₃—**C**H₂—C₍₆₎₍Ni₎); 2.69 (q, $^3J_{HH}$ = 7.3 Hz, 3H, CH₃—**C**H₂—C₂₍Ru₎); 3.93** (s, 2H, C₍₅,₇₎₍Ni₎**H**); 4.45 (s, 2H, C**H**₍₁,₃₎₍Ru₎).

^{13}C NMR (125.76 MHz, C₆D₆): δ 9.18** (**C**H₃(Cp*)₍Ni₎), 10.34 (**C**H₃(Cp*)₍Ru₎); 11.29** (**C**H₃—CH₂—C₍₆₎₍Ni₎); 14.99 (**C**H₃-CH₂—C₂₍Ru₎); 15.46 (**C**H₃—C₍₄,₈₎); 23.01** (CH₃—**C**H₂—C₍₆₎₍Ni₎), 25.75 (CH₃—**C**H₂—C₂₍Ru₎); 60.71** **C**₍₅,₇₎₍Ni₎H; 66.87 (**C**₍₁,₃₎₍Ru₎H); 83.22** (**C**q(Cp*)₍Ni₎); 95.65(**C**q(Cp*)₍Ru₎); 103.37** (**C**₍₆₎₍Ni₎); 108.43 (C₂₍Ru₎), 111.90(C₍₄ₐ,₇ₐ₎); 116.61(C ₍₃ₐ,₈ₐ₎); 137.42 (**C**q₍₄,₈₎).The chemical shifts of the Ru moiety are in good agreement with that of mono and di ruthenium tetraalkyl-*s*-indacene [26,27].

Mass HRMS C₃₈H₅₀NiRu: calc. 666.2314, Fd. 666.2311.

Ie: ^{1}H NMR (400 MHz, C₆D₆): δ 0.94** (t, $^3J_{HH}$ = 7.5 Hz, 3H, **C**H₃—CH₂—C₍₂₎₍Ni₎·); 1.06 (t, $^3J_{HH}$ = 7.5 Hz, 3H, **C**H₃—CH₂—C₍₆₎₍Mn₎·);1.30** (s, 15H, **C**H₃(Cp*)); 1.84 (s, 6H,**C**H₃—C₍₄,₈₎); 2.08** (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH₃—**C**H₂—C₍₂₎₍Ni₎·); 2.50 (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH₃—**C**H₂—C₍₆₎₍Mn₎·); 3.77** (s, 2H, C₍₅,₇₎₍Ni₎**H**); 4.49 (s, 2H, C₍₁,₃₎₍Mn₎**H**).

^{13}C NMR (100 MHz, C₆D₆): δ 9.18** (**C**H₃(Cp*)₍Ni₎); 11.99** (**C**H₃—CH₂—C₍₆₎₍Ni₎); 14.03 (**C**H₃-CH₂—C₍₂₎₍Mn₎); 14.34 (**C**H₃—C₍₄,₈₎); 21.82** (CH₃—**C**H₂—C₍₆₎₍Ni₎); 24.25 (CH₃—**C**H₂—C₍₂₎₍Mn₎); 60.13** (**C**₍₅,₇₎₍Ni₎H); 69.67 (**C**₍₁,₃₎₍Mn₎H); 99.55 (**C**q(Cp*)₍Ni₎); 103.37** (C₍₆₎₍Ni₎); 108.43 (C₍₂₎₍Mn₎); 108.79 (C₍₈ₐ,₃ₐ₎); 119.13 (C₍₄ₐ,₇ₐ₎); 140.27 (C₍₄,₈₎); 226.5 (**C**O).

IR (Nujol): ν (C≡O) 2003 (s), 1924 (s) cm⁻¹.

Mass HRMS C₃₁H₃₅NiMnO₃: calc. 568.1320, Fd. 568.1331.

If: ^{1}H NMR (400 MHz, C₆D₆): δ 1.13** (t, $^3J_{HH}$ = 7.5 Hz, 3H, **C**H₃—CH₂—C₍₆₎₍Ni₎); 1.31 (t, $^3J_{HH}$ = 7.4 Hz, 3H, **C**H₃—CH₂—C₂₍Fe₎); 1.50** (s, 15H, Cp*₍Ni₎); 1.59 (s, 15H, Cp*₍Fe₎); 1.92 (s, 6H, **C**H₃—C₍₄,₈₎); 2.25** (q, $^3J_{HH}$ = 7.4 Hz, 2H, CH₃—**C**H₂—C₍₆₎₍Ni₎); 2.73 (q, $^3J_{HH}$ = 7.7 Hz, 2H, CH₃—**C**H₂—C₂₍Fe₎); 3.85** (s, 2H, C₍₅,₇₎₍Ni₎**H**); 3.99 (s, 2H, C₍₁,₃₎₍Fe₎**H**).

^{13}C NMR (100 MHZ, C₆D₆): 9.43** (**C**H₃(Cp*₍Ni₎); 9.55 (**C**H₃(Cp*₍Fe₎); 14.05** (**C**H₃—CH₂—C₍₆₎₍Ni₎); 15.39 (**C**H₃—CH₂—C₂₍Fe₎);