A new heterobimetallic manganese–rhodium carbonyl complex derived from partially alkylated s-indacene

César Morales-Verdejo [a,*], Luciano Oehninger [b,d], Iván Martínez-Díaz [b], Desmond Mac-Leod Carey [c], Ramiro Arratia-Pérez [c], Ivonne Chávez [b], Juan Manuel Manríquez [b]

[a] Departamento de Química y Bioquímica, Facultad de Ciencias, Universidad de Valparaíso, Casilla 5030, Avda., Gran Bretaña 1111, Playa Ancha, Valparaíso, Chile
[b] Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Santiago, Casilla 306, Chile
[c] Universidad Andres Bello, Departamento de Ciencias Químicas, Relativistic Molecular Physics (ReMoPh) Group, Republica 275, Santiago, Chile
[d] Institut of Medicinal and Pharmaceutical Chemistry, Technische Universität Braunschweig, Beethovenstr. 55, 38106 Braunschweig, Germany

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ABSTRACT

This work describes the synthesis and characterization by means of ^1H, ^{13}C NMR and FT-IR spectroscopies of new heterobinuclear carbonylated complex derived from partially alkylated s-indacene. The heterobimetallic complex $[(CO)_3Mn(2,6-diethyl-4,8-dimethyl-s-indaceneiide)Rh(COD)]$ **1** was synthesized from the monometallic specie $[(CO)_3Mn(2,6-diethyl-4,8-dimethyl-1-hydroindacenide)]$ and $[Rh(\mu-Cl)(COD)]_2$. Secondly, its respective carbonylated complex $[(CO)_3Mn(2,6-diethyl-4,8-dimethyl-s-indaceneiide)Rh(CO)_2]$ **2** was obtained by under an atmosphere of carbon monoxide in hexanes. Theoretical calculations of these two compounds were carried out to gain further understanding of these novel molecular systems.

1. Introduction

The presence of two metal centers within the same molecule may have profound effects on both the physical properties and the reactivity of the compound as reported in the literature [1–5]. These effects may be observed as significant modifications of the individual properties of certain monometallic compounds or in the development of novel characteristics, which do not happen in them. Complexes in which two metals are connected by an organic π-spacer ligand [6–33] are interesting due to their potential applications in the development of original organometallic materials with conducting, ferromagnetic [34–37] and/or optical properties [38–40], which are finely tuned by the electronic interaction between the metal centers. Most of the studies concerning electronic interaction between two metals centers deal typically with homobimetallics systems, where the two active sites are equivalent. Conversely, to the extent of our knowledge, there is little information on heterobimetallic systems, hampering the elucidation the origin of the localization/delocalization in mixed valence systems and cooperative effects.

There are no reports in the literature about wholly carbonylated heterobinuclear indacenyl compounds. However, the synthesis and characterization of the mononuclear complexes $[(CO)_3Mn-s-Ic^*H]$ with s-Ic* = 1,5-dihydro-s-indacene and 1,2,3,4,5,6,7,8-octa-

methyl-1,5-dihydro-s-indacene have been previously reported [7,41]. Our interest has focused on the synthesis of binuclear complexes bridged by fused-ring systems and the study of their physical and chemical properties, in which we recently have developed a new, effective, and selective route to synthesize polyalkylated s-indacenes [42]. These polyalkylated s-indacene present a unique opportunity for the synthesis of heterobimetallic complexes by stepwise introduction of different metal fragments [31].

This contribution describes the general approach for the successful preparation of the first wholly carbonylated s-indacenedi-idederived heterobimetallic complex $[(CO)_3Mn(2,6-diethyl-4,8-dimethyl-s-indacenediide)Rh(CO)_2]$. This molecular species was fully characterized by methods such as FT-IR and (^1H–^{13}C) NMR spectroscopic analysis as well as mass spectrometry.

2. Experimental

2.1. General data

All manipulations were carried out under pure dinitrogen atmosphere using a Vacuum Atmospheres drybox equipped with a Model HE 493 Dri-Train purifier or a vacuum line using standard Schlenk-tube techniques. Reagent grade solvents were distilled under dinitrogen from sodium/benzophenone (tetrahydrofuran, hexanes, petroleum ether). The starting compounds $BrMn(CO)_3(py)_2$ [43], $[Rh(\mu-Cl)(COD)]_2$ [44], and 2,6-diethyl-4,8-dimethyl-1,5-dihydro-s-indacene ($Ic'H_2$) [42] were prepared according to published

* Corresponding author.
E-mail address: camoralv@uc.cl (C. Morales-Verdejo).
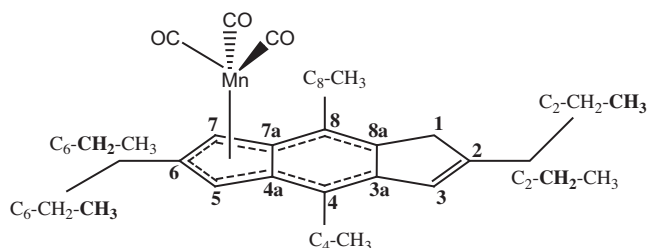
Scheme 1. NMR assignation of the tetraalkylated *s*-indacene ligand for the here reported complex.
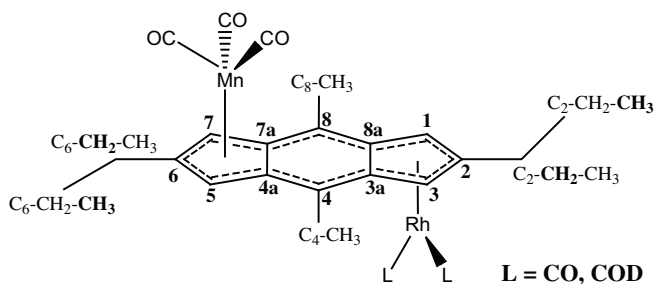
Scheme 2. NMR assignation of the tetraalkylated *s*-indacene ligand for the here reported complexes.

methods. *n*-Butyl-lithium (1.6 M in hexanes) and C_6D_6 (C_6D_6 was dried with Na prior use) were purchased from Aldrich. Elemental analyses (C and H) were made with a Fisons EA 1108 microanalyzer. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-400, Bruker AC-200P and Bruker AC 80 Spectrometers. Chemical shifts are reported in ppm relative to tetramethylsilane. All peaks reported are singlets, unless otherwise specified. Mass spectra (EI, 70 eV) were recorded on HP-5889A spectrometer. IR spectra on a Perkin-Elmer 1600 FT-IR spectrometer or Bruker Vector 22 in Nujol.

2.2. Computational details

Density functional theory (DFT) calculations were carried out by using the Amsterdam Density Functional (ADF) package [45]. Geometry optimizations were done via the analytical energy gradient method implemented by Verluis and Ziegler employing the Local Density Approximation (LDA) within the Vosko, Wilk and Nusair parametrization (VWN) for the local exchange correlation [46], and non-local corrections via the general gradient approximation (GGA) according to the proposed by Perdew–Wang [47] treated by a fully self-consistent method. For the calculations we used the standard slater type orbitals (STO) basis set [48], which is an uncontracted triple-ζ STO basis set for H 1s, C 2s, Mn 3d, Rh 4d; augmented with one 3d single polarization function for C atoms, a 2p single polarization function for H atoms and a 4p single polarization function for Mn atom and 5p single polarization function for Rh atom. The molecular structure described here have been characterized as the energy minima through calculations of normal mode vibrational frequencies, which were performed at the optimized geometry via second derivatives of the total energy with respect to the internal coordinates as implemented in the ADF code [49,50].

2.3. [(CO)₃Mn(2,6-diethyl-4,8dimethyl-5-hydroindacenide)] [(CO)₃Mn-s-Ic′H]

A *n*-Butyl-lithium solution (1.6 M in hexanes, 2.6 mL, 4.20 mmol) was slowly added to a solution of 2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene (1.0 g, 4.20 mmol) in THF (30 mL)

at −80 °C. The mixture was stirred for 1 h at room temperature to yield the monolithiated ligand. The solution was cooled to −80 °C, and a solution of $BrMn(CO)_3(py)_2$ (1.56 g, 4.20 mmol) in THF (30 mL) was added via syringe. The mixture was allowed reach room temperature and then stirred for 2 h. Then, the solvent was removed and the raw product was dissolved with pentane and filtered to remove the insoluble LiBr. After removal of the solvent via vacuum, bright yellow crystals unstable to air were obtained. Yield: 60% (0.95 g).

Anal. Calc. for $C_{21}H_{21}MnO_3$ (376.33 g mol^{-1}): C: 67.02; H: 5.62. Found: C: 66.72; H: 5.26%.

IR(Nujol): (C≡O) 2012 (s), 1926 (s) cm^{-1}.

^1H NMR (400 MHz, ppm in C_6D_6): 0.93 (t, 3H, CH_3–CH_2–$C_{(6)}$, $^3J_{H–H}$ = 7.66 Hz); 0.98 (t, 3H, CH_3–CH_2–$C_{(2)}$, $^3J_{H–H}$ = 7.44 Hz); 2.08 (q, 2H, CH_3–CH_2–$C_{(6)}$, $^3J_{H–H}$ = 7.66 Hz); 2.14 (s, 3H, CH_3–$C_{(8)}$); 2.27 (s, 3H, CH_3–$C_{(4)}$); 2.70 (q, 2H, CH_3–CH_2–$C_{(2)}$, $^3J_{H–H}$ = 7.44 Hz); 3.00 (s, 2H, $C_{(1)}H_2$); 4.64 (s, 2H, $C_{(5,7)}H$); 6.38 (s, 1H, $C_{(3)}H$).

^{13}C NMR (100 MHz, ppm in C_6D_6): δ = 13.11 (CH_3–CH_2–$C_{(6)}$); 14.14 (CH_3–$C_{(8)}$); 14.98 (CH_3–CH_2–$C_{(2)}$); 15.39 (CH_3–$C_{(4)}$); 22.69 (CH_3–CH_2–$C_{(6)}$); 25.19 (CH_3–CH_2–$C_{(2)}$); 39.93 ($C_{(1)}H_2$); 70.32 ($C_{(5,7)}H$); 106.30 ($C_{(8a)}$); 102.78 ($C_{(3a)}$); 152.11 ($C_{(2)}$); 111.96 ($C_{(4)}$); 118.06 ($C_{(8)}$); 124.40 ($C_{(3)}$); 140.12 ($C_{(4a)}$); 143.66 ($C_{(6)}$); 138.27 ($C_{(7a)}$); 226.7 (CO).

Mass spectroscopy results: MS (EI, *m/z*, %): M$^+$ 376 (100%), [M−(CH₃)]$^{·+}$ 361.

2.4. [(CO)₃Mn(2,6-diethyl-4,8-dimethyl-s-indaceneiide)Rh(COD)] [(CO)₃Mn-s-Ic′-Rh(COD)] [1]

A *n*-Butyl-lithium solution (1.6 M in hexanes, 0.797 mmol) was dropwise added to a solution of [(CO)₃Mn-*s*-Ic′H] (0.3 g, 0.797 mmol) in THF (30 mL) at −80 °C. The resulting mixture was vigorously stirred for 1 h at room temperature. Afterwards, a solution of [Rh(μ-Cl)(COD)]₂ (0.196 g, 0.399 mmol) in THF (20 mL) was added to the mixture of lithiated complex [(CO)₃Mn-*s*-Ic′][Li] at −80 °C and the mixture was vigorously stirred for 2 h at room temperature. After complete elimination of the solvent, the resulting product was dissolved with hexane and filtered to remove the insoluble LiCl. A yellow powder-like solid unstable to air was obtained. Yield 0.26 g (55.3%).

Anal. Calc. for $C_{29}H_{32}MnO_3Rh$ (586.41 g mol^{-1}): C: 59.40; H: 5.50. Found: C: 59.02; H: 5.14%.

IR (Nujol): (C≡O) 2008 (s), 1905 (s) cm^{-1}.

^1H NMR (400 MHz, ppm in C_6D_6): δ = 0.89 (t, 3H, CH_3–CH_2–$C_{(2)(Rh)}$, $^3J_{H–H}$ = 7.48 Hz); 1.15 (t, 3H, CH_3–CH_2–$C_{(6)(Mn)}$, $^3J_{H–H}$ = 7.45 Hz); 1.62 (m, 8H, CH_2–COD$_{(Rh)}$); 2.07 (q(d), 2H, CH_3–CH_2–$C_{(2)(Rh)}$, $^3J_{H–H}$ = 7.48 Hz, $^3J_{H–Rh}$ = 1.18 Hz); 2.28 (s, 6H, CH_3–$C_{(4,8)}$); 2.34 (q, 2H, CH_3–CH_2–$C_{(6)(Mn)}$, $^3J_{H–H}$ = 7.45 Hz); 4.16 (s, 4H, CH–COD$_{(Rh)}$); 4.80 (s, 4H, $C_{(1,3,5,7)(Mn,Rh)}H$).

^{13}C NMR (100 MHz, ppm in C_6D_6): δ = 13.57 (CH_3–CH_2-$C_{(2)(Rh)}$); 13.91 (CH_3–CH_2-$C_{(6)(Mn)}$); 14.99 (CH_3–$C_{(4,8)}$); 22.19 (CH_3–CH_2-$C_{(2)(Rh)}$); 23.09 (CH_3–CH_2-$C_{(6)(Mn)}$); 31.32 (CH_2–COD$_{(Rh)}$); 67.95 ($C_{(7,5)(Mn)}H$); 70.99 (d, CH–COD$_{(Rh)}$, $^1J_{C–Rh}$ = 13.49 Hz); 72.14 ($C_{(1,3)(Rh)}H$); 104.79 ($C_{(6)(Mn)}$); 112.34 ($C_{(4,8)}$); 114.76 ($C_{(4a,7a)(Mn)}$); 114.66 ($C_{(3a,8a)(Rh)}$); 118.34 ($C_{(2)(Rh)}$); 225.9 (CO).

The ^{103}Rh–^{13}C coupling constants were not observed due to the low concentration of the product.

Mass spectroscopy results: MS (EI, *m/z*, %): M$^+$ 586 (100%), [M−(CH₃)]$^+$ 571.

2.5. [(CO)₃Mn(2,6-diethyl-4,8-dimethyl-s-indaceneiide)Rh(CO)₂] [(CO)₃Mn-s-Ic′-Rh(CO)₂] [2]

A solution of complex [(CO)₃Mn-*s*-Ic′-Rh(COD)] (0.2 g, 0.34 mmol) in hexanes (20 mL) was exposed under a carbon monoxide atmosphere for 2 h with stirring. The resulting solution was