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Heterobimetallic Iron−Rhodium Complexes. Synthesis and Characteristics of CpFe(μ-η^5:η^5-*as*-indacenediide)RhL$_2$ (L$_2$ = COD, NBD, (ethylene)$_2$)

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The heterobimetallic CpFe(μ-η^5: η^5-*as*-indacenediide)RhL$_2$ complexes (L$_2$ = COD (**2**), NBD (**3**), (ethylene)$_2$ (**4**)) have been obtained from metalation of the mononuclear lithium CpFe(η^5-*as*-indacenediide) with [Rh(μ-Cl)L$_2$]$_2$. Mixtures of *syn* and *anti* heterobimetallic complexes were formed and fully characterized by 2D NMR spectroscopy. The reactivity at the rhodium center is greatly influenced by the presence of the ferrocenyl moiety. The voltammetric behavior and the optical spectra are in favor of the existence of significant electronic interactions between the two metals.

Introduction

The *s*- and *as*-indacenediide ligands, owing to the high delocalizability of their 14-π-electron system, have been identified as suitable bridging ligands in view of strong electronic interactions between two coordinated metal centers which may result in interesting chemical and physical properties.[1]

A number of homobimetallic sandwich and half-sandwich complexes of these ligands have been reported. In a study by Miller et al.,[2] the synthesis, the characterization, and the physical properties of (*s*-indacenediide)- and (*as*-indacenediide)(MCp*)$_2$ complexes (M = Fe, Co, Ni; Cp* = C$_5$Me$_5$) have been thoroughly investigated. In all complexes the two MCp* groups reside on opposite faces of the fused μ-bridging ring system (*anti* geometry), which is believed to be due to steric reasons. The structure of (*s*-indacenediide)-[Mn(CO)$_3$]$_2$ was reported by Smart et al.,[3a] and even in this half-sandwich complex the manganese atoms are located *anti* with respect to the bridging ligand. On the other hand, a 3/1 *anti*/*syn* isomeric mixture of the (2,7-dimethyl-*as*-indacenediide)[Mn(CO)$_3$]$_2$ has been obtained by the same authors.[3b]

The stereochemical control of the reaction between the indacenediide dilithium salts and metal reagents is still a vexing problem. Recently, we have prepared a number of bis-(RhL$_2$)$_2$ and bis-(IrL$_2$)$_2$ complexes of *s*- and *as*-indacenediides.[4] Under the same synthetic conditions, the ratio of the *syn* and *anti* isomers as measured in the crude reaction mixtures was shown to be strongly dependent on the nature of the metal ancillary ligands L. In fact, it was ascertained that mixtures with a very large preference (up to 90%) of the *syn* isomer are obtained if L$_2$ is COD or NBD, whereas the *anti* species was largely preferred (ca. 95%) if L is CO. An alternative synthetic route to indacenediide homobimetallics was offered by the availability of the 12-π-electron olefin 1,3,5,7-tetra-*tert*-butyl-*s*-indacene. Reaction of this olefin with Fe$_2$(CO)$_9$ or Co$_2$(CO)$_8$ afforded indacene bimetallic complexes with two metal fragments coordinated to the same face of the bridging ligand.[5] The *syn* coordination was probably favored by the bimetallic nature of the metalating reagents.

In comparison to these numerous reports on homobimetallic complexes of indacene, to the best of our knowledge no heterobimetallic complexes have been described up to now. In general, heterobimetallic compounds in which two metal atoms have the potential to interact with each other by direct means or through a suitable bridging ligand have been the target of many research groups. Thus, the characteristic properties of one metal may be changed substantially by the presence of the other metal center. Moreover, the effects can be modulated by changing the oxidation state of one of the

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two partners. In this respect the ferrocenyl group, Fc, an easily oxidable moiety, has been frequently coupled with metals such as chromium, molybdenum, tungsten,[6,7] and manganese.[8] In these complexes two cyclopentadienyl rings (or one Cp ring and one benzene ring) are directly linked through a σ bond or connected by a saturated or unsaturated hydrocarbon chain. In indacenyl complexes the two metals would instead participate with the whole 14-π-electron system of the bridge, so that the coordination mode of one metal is expected to influence the coordination of the second. The particular physical and chemical characteristics of the second metal would also be influenced to a great extent.

As part of our effort to add to our understanding of the chemistry of bimetallic complexes, we have started an investigation into the heterobimetallic iron−rhodium complexes. In a recent paper[9] we have described the characteristics of some [η^5-(1-ferrocenyl)indenyl]RhL_2 complexes. Here we report the synthesis and characterization of the monometallic CpFe(η^5-*s*-hydroindacenide) (***s*-1**) and CpFe(η^5-*as*-hydroindacenide) (***as*-1**) complexes and of the heterobimetallic CpFe(μ-η^5: η^5-*as*-indacenediide)RhL_2 compounds (L_2 = COD (**2**), NBD (**3**), $(ethylene)_2$ (**4**)). The chemical and electrochemical oxidation of some of these complexes has also been investigated.

Experimental Section

General Procedures. All reactions and manipulations of organometallic compounds were performed in an oxygen- and moisture-free atmosphere; all solvents were dried and distilled using standard procedures. Ferrocene and $Na[N(SiMe_3)_2]$ were Fluka products. [CpFe(η^6-fluorene)]PF_6 was prepared as described by Chung.[10] Melting points are uncorrected. Microanalyses were performed at the Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova. IR, near-IR, and visible spectra were recorded on a Bruker Equinox 55 spectrophotometer operating in the FT mode; a Greaseby-Specac temperature-controlled cell with CaF_2 windows (0.25 mm optical path) was used for the low-temperature measurements. ^1H and ^{13}C NMR spectra were obtained at 298 K as acetone-d_6 solutions on a Bruker Avance-400 spectrometer operating at 400.13 and 100.61 MHz, respectively. Relaxation delays of at least 10 s between the single 90° pulses have been used to ensure correct signal integration in the ^1H spectra. The chemical shift values are given as δ values having internal TMS as reference. The assignments of the proton resonances were performed by standard chemical shift correlations and NOESY experiments. The ^{13}C resonances were attributed through 2D-heterocorrelated COSY experiments (HMQC with *bird* sequence[11] and quadrature along F1 achieved using the TPPI method[12] for the H-bonded carbon atoms, HMBC[13] for the quaternary ones). Cyclic voltammetry experiments were performed in an airtight three-electrode cell connected to a vacuum/argon line. The reference electrode was an SCE (Tacussel ECS C10) separated from the solution by a bridge compartment filled with the same solvent/supporting electrolyte solution used in the cell. The counter electrode was a platinum spiral with ca. 1 cm^2 apparent surface area. The working electrodes were disks obtained from a cross section of gold wires of 0.5 mm diameter sealed in glass. Between each CV scan the working electrodes were polished on alumina according to standard procedures and sonicated before use. An EG&G PAR-175 signal generator was used. The currents and potentials were recorded on a Lecroy 9310L oscilloscope. The potentiostat was home-built with a positive feedback loop for compensation of ohmic drop.[14]

(η^5-Cyclopentadienyl)(η^5-1-hydro-*s*-indacenide)iron(II) (*s*-1). To a solution of 0.28 g (0.649 mmol) of [CpFe(η^6-fluorene)]-PF_6 in THF (20 mL) was added 0.68 mmol of $Na[N(SiMe_3)_2]$ at 0 °C, and the mixture (solution A) was kept for 1 h at this temperature. At the same time, 0.2 g (1.3 mmol) of dihydro-*s*-indacene (as a mixture of the 1,5- and 1,7-isomers) in THF (20 mL) was treated with 1.3 mmol of *n*-BuLi (1.1 mL of a 1.6 M solution in hexanes) at −78 °C (solution B). Solution B was then added to solution A (by cannula transfer) and the mixture warmed slowly to room temperature. Saturated aqueous NH_4-Cl (30 mL), petroleum ether (30 mL), and additional water (30 mL) were then added. The aqueous layer was washed twice with water (20 mL), and the organic layers were collected, dried over Na_2SO_4, and freed from solvent in vacuo. The ^1H NMR spectrum of the residue indicated a crude yield of ca. 60% (by signal integration). Purification by silica gel column chromatography (pentane as eluent) yielded 26 mg of the violet *product* (15%). Attempts to purify the crude mixture by sublimation of fluorene or chemical oxidation of the iron complex[15,16] were unsuccessful. ESY-MS: m/z 274 (M^+). Anal. Calcd for $C_{17}H_{14}Fe$: C, 74.44; H, 5.15. Found: C, 74.21; H, 5.02. ^1H NMR data (acetone-d_6): δ 7.52 (m, 1H, H_4), 7.40 (m, 1H, H_8), 6.75 (m, 1H, H_3), 6.42 (m, 1H, H_2), 4.91 (m, 1H, H_7), 4.89 (m, 1H, H_5), 4.03 (t, 1H, $^3J(H_5,H_6) = {}^3J(H_6,H_7)$ 2.4 Hz, H_6), 3.74 (s, 5H, C_5H_5), and 3.29 (m, 2H, $H_{1,1'}$). ^{13}C NMR data: δ 134.58 (C_2), 133.31 (C_3), 127.83 (C_{3a}), 126.41 (C_{8a}), 122.88 (C_8), 119.14 (C_4), 89.98 (C_{4a}), 88.75 (C_{7a}), 70.48 (C_6), 68.94 (C_5H_5), 62.26 (C_7), 62.10 (C_5), and 37.98 (C_1).

(η^5-Cyclopentadienyl)(η^5-1-hydro-*as*-indacenide)iron(II) ((1-hydro)-*as*-1) and (η^5-Cyclopentadienyl)(η^5-3-hydro-*as*-indacenide)iron(II) ((3-hydro)-*as*-1). By the same synthetic procedure as that used for ***s*-1**, 0.14 g (58%) of a 2/3 mixture (by NMR integration) of (1-hydro)-***as*-1** and (3-hydro)-***as*-1** was obtained as a violet powder. The mixture of isomers was used in the second metalation reaction. ESY-MS: m/z 274 (M^+). Anal. Calcd for $C_{17}H_{14}Fe$: C, 74.44; H, 5.15. Found: C, 74. 11; H, 5.26. (1-hydro)-***as*-1**: ^1H NMR data δ 7.50 and 7.15 (2H, AB quartet, $J_{AB} = 8.8$ Hz, H_5 and H_4, respectively), 7.21 (dt, 1H, $^3J(H_2,H_3) = 5.4$ Hz, $^4J(H_2,H_{1,1'}) = 1.9$ Hz, H_3), 6.84 (dt, 1H, $^3J(H_2,H_3) = 5.4$ Hz, $^4J(H_2,H_{1,1'}) = 1.9$ Hz, H_2), 5.04 (m, 1H, H_6), 5.00 (m, 1H, H_8), 4.41 (t, 1H, $^3J(H_6,H_7) = {}^3J(H_7,H_8) = 2.7$ Hz, H_7), 3.70 (s, 5H, C_5H_5), 3.68 and 3.31 (2H, AB quartet, $J_{AB} = 24$ Hz, $H_{1,1'}$); ^{13}C NMR data δ 143.69 (C_{3a}), 136.91 (C_{1a}), 133.54 (C_2), 131.38 (C_3), 128.25 (C_5), 120.31 (C_4), 85.17 (C_{5a}), 83.49 (C_{8a}), 70.48 (C_7), 68.84 (C_5H_5), 62.98 (C_8), 59.78 (C_6), and 39.66 (C_1). (3-hydro)-***as*-1**: ^1H NMR data δ 7.38 and 7.17 (2H, AB quartet, $J_{AB} = 8.8$ Hz, H_5 and H_4, respectively), 6.67 (dt, 1H, $^3J(H_1,H_2) = 5.4$ Hz, $^4J(H_2,H_{3,3'}) = 1.9$ Hz,

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H_2), 6.52 (dt, 1H, $^3J(H_1,H_2) = 5.4$ Hz, $^4J(H_1,H_{3,3'}) = 1.9$ Hz, H_1), 5.14 (m, 1H, H_8), 4.97 (m, 1H, H_6), 4.11 (t, 1H, $^3J(H_6,H_7) = {}^3J(H_7,H_8) = 2.7$ Hz, H_7), 3.68 (s, 5H, C_5H_5), 3.32 (m, 2H, $H_{3,3'}$); ^{13}C NMR data δ 141.23 (C_{3a}), 137.67 (C_{1a}), 134.50 (C_2), 131.73 (C_1), 125.74 (C_5), 121.75 (C_4), 86.79 (C_{8a}), 83.06 (C_{5a}), 70.48 (C_7), 68.91 (C_5H_5), 62.84 (C_6), 60.24 (C_8), and 41.33 (C_3).

***syn*- and *anti*-{(η^5-Cyclopentadienyl)iron(II)(μ-η^5:η^5-*as*-indacenediide)rhodium(I)(η^4-cycloocta-1,5-diene)} (*syn*-2 and *anti*-2).** A solution of 0.078 g (0.25 mmol) of ***as*-1** as a 2/3 1-hydro and 3-hydro mixture in THF (10 mL) was cooled to −78 °C, and 0.21 mL of 1.6 M *n*-BuLi in hexanes (0.36 mmol) was added. After 1 h a precooled solution of 0.063 mg (0.128 mmol) of $[Rh(\mu\text{-}Cl)(COD)]_2$[9] in THF was added, and the mixture was then warmed slowly to room temperature (ca. 3 h). The solvent was removed under vacuum, and the residue was treated with degassed cyclohexane (50 mL). Filtration under argon to remove LiCl and evaporation of the solvent in vacuo afforded 0.105 g (82%) of a 1/1.5 mixture of ***syn*-2** and ***anti*-2** (by NMR integration) as a dark red powder. ESY-MS: *m/z* 484 (M^+). Anal. Calcd for $C_{25}H_{25}FeRh$: C, 62.01; H, 5.20. Found: C, 59.95; H, 5.51. ***syn*-2**: ^1H NMR δ 7.18 and 6.77 (2H, AB quartet, $J_{AB} = 9.2$ Hz, H_4 and H_5, respectively), 5.96 (dt, 1H, $^3J(H_1,H_2) = {}^3J(H_2,H_3) = 2.6$ Hz, $J(^{103}Rh,H_2) = 1.6$ Hz, H_2), 5.12 (ddd, 1H, $^3J(H_1,H_2) = 2.6$ Hz, $^4J(H_1,H_3) = 1.6$ Hz, $^5J(H_1,H_5) = 0.7$ Hz, H_1), 5.12 (m, 1H, H_3), 4.84 (ddd, 1H, $^3J(H_6,H_7) = 2.4$ Hz, $^4J(H_6,H_8) = 1.1$ Hz, $^4J(H_5,H_6) = 0.8$ Hz, H_6), 4.70 (dd, 1H, $^3J(H_7,H_8) = 2.4$ Hz, $^4J(H_6,H_8) = 1.1$ Hz, H_8), 4.23 and 4.16 (2m, 2H each, olefin COD protons), 4.12 (s, 5H, C_5H_5), 4.07 (t, 1H, $^3J(H_6,H_7) = {}^3J(H_7,H_8) = 2.4$ Hz, H_7), 2.32 and 2.20 (2m, 4H each, methylene COD protons); ^{13}C NMR δ 126.07 (C_5), 118.39 (C_4), 113.13 (C_{3a}), 108.87 (C_{1a}), 87.86 (C_2), 83.16 (C_{8a}), 83.05 (C_{5a}), 80.60 (C_3), 78.75 (C_1), 70.35 (C_5H_5), 67.93 (C_7), 66.47 and 64.70 (olefin COD carbons), 62.79 (C_6), 61.10 (C_8), 29.34 and 29.25 (methylene COD carbons). ***anti*-2**: ^1H NMR δ 6.96 and 6.91 (2H, AB quartet, $J_{AB} = 9.2$ Hz, H_4 and H_5, respectively), 5.63 (m, 1H, H_3), 5.54 (dt, 1H, $^3J(H_1,H_2) = {}^3J(H_2,H_3) = 2.7$ Hz, $J(^{103}Rh,H_2) = 1.1$ Hz, H_2), 5.25 (ddd, 1H, $^3J(H_1,H_2) = 2.6$ Hz, $^4J(H_1,H_3) = 1.5$ Hz, $^5J(H_1,H_5) = 0.6$ Hz, H_1), 4.78 (ddd, 1H, $^3J(H_6,H_7) = 2.4$ Hz, $^4J(H_6,H_8) = 1.1$ Hz, $^4J(H_5,H_6) = 0.8$ Hz, H_6), 4.67 (dd, 1H, $^3J(H_7,H_8) = 2.4$ Hz, $^4J(H_6,H_8) = 1.1$ Hz, H_8), 4.06 (t, 1H, $^3J(H_6,H_7) = {}^3J(H_7,H_8) = 2.4$ Hz, H_7), 3.73 (s, 5H, C_5H_5), 3.72 and 3.22 (2m, 2H each, olefin COD protons), 1.91 and 1.69 (2m, 4H each, methylene COD protons); ^{13}C NMR δ 123.01 (C_5), 119.47 (C_4), 104.67 (C_{1a}), 103.99 (C_{3a}), 87.09 (C_2), 84.85 (C_{5a}), 83.21 (C_{8a}), 81.82 (C_1), 78.86 (C_3), 69.28 (C_5H_5), 68.21 and 65.64 (olefin COD carbons), 67.97 (C_7), 64.40 (C_6), 60.70 (C_8), 31.79 and 31.72 (methylene COD carbons).

***syn*- and *anti*-{(η^5-Cyclopentadienyl)iron(II)(μ-η^5:η^5-*as*-indacenediide)rhodium(I)(η^4-norbornadiene)} (*syn*-3 and *anti*-3).** These isomers were obtained as a red powder in a 1/1.5 ratio in a strictly similar way to that for the ***syn*-2** and ***anti*-2** analogues by using the $[Rh(\mu\text{-}Cl)(NBD)]_2$ dimer.[9] Yield: 91%. Purification by silica gel column chromatography using 2/1 pentane/diethyl ether as eluent results in the decomposition of ***syn*-3** and affords only a small quantity of pure ***anti*-3**. ESY-MS: *m/z* 468 (M^+). Anal. Calcd for $C_{24}H_{21}FeRh$: C, 61.57, H, 4.52. Found: C, 61.31; H, 4.74. ***syn*-3**: ^1H NMR δ 7.09 and 6.70 (2H, AB quartet, $J_{AB} = 9.2$ Hz, H_4 and H_5, respectively), 5.82 (dt, 1H, $^3J(H_1,H_2) = {}^3J(H_2,H_3) = 2.7$ Hz, $J(^{103}Rh,H_2) = 1.6$ Hz, H_2), 5.18 (ddd, 1H, $^3J(H_1,H_2) = 2.7$ Hz, $^4J(H_1,H_3) = 1.6$ Hz, $^5J(H_1,H_5) = 0.6$ Hz, H_1), 5.18 (m, 1H, H_3), 4.88 (ddd, 1H, $^3J(H_6,H_7) = 2.4$ Hz, $^4J(H_6,H_8) = 1.1$ Hz, $^4J(H_5,H_6) = 0.8$ Hz, H_6), 4.25 (m, 1H, H_8), 4.20 (s, 5H, C_5H_5), 4.05 (t, 1H, $^3J(H_6,H_7) = {}^3J(H_7,H_8) = 2.4$ Hz, H_7), 3.67 (m, 2H, bridgehead NBD protons), 3.37 and 3.29 (2m, 2H each, olefin NBD protons), 0.89 (m, 2H, methylene NBD protons); ^{13}C NMR δ 125.55 (C_4), 119.35 (C_5), 110.02 (C_{3a}), 105.04 (C_{1a}), 86.09 (C_2), 85.19 (C_{5a}), 82.82 (C_{8a}), 78.72 (C_1), 76.43 (C_3), 70.52 (C_5H_5), 70.51 (C_6), 67.48 (C_7), 61.19 (C_8), 56.04 (methylene NBD carbon), 48.29 (bridgehead NBD carbons), 38.29 and 30.40 (olefin NBD carbons). ***anti*-3**: ^1H NMR δ 6.93 and 6.90 (2H, AB quartet, $J_{AB} = 9.2$ Hz, H_4 and H_5, respectively), 5.66 (m, 1H, H_3), 5.52 (dt, 1H, $^3J(H_1,H_2) = {}^3J(H_2,H_3) = 2.7$ Hz, $J(^{103}Rh,H_2) = 1.6$ Hz, H_2), 5.26 (ddd, 1H, $^3J(H_1,H_2) = 2.7$ Hz, $^4J(H_1,H_3) = 1.5$ Hz, $^5J(H_1,H_5) = 0.6$ Hz, H_1), 4.78 (ddd, 1H, $^3J(H_6,H_7) = 2.4$ Hz, $^4J(H_6,H_8) = 1.1$ Hz, $^4J(H_5,H_6) = 0.8$ Hz, H_6), 4.65 (dd, 1H, $^3J(H_7,H_8) = 2.3$ Hz, $^4J(H_6,H_8) = 1.1$ Hz, H_8), 4.03 (t, 1H, $^3J(H_6,H_7) = {}^3J(H_7,H_8) = 2.4$ Hz, H_7), 3.69 (s, 5H, C_5H_5), 3.05 (m, 2H, bridgehead NBD protons), 2.97 and 2.66 (2m, 2H each, olefin NBD protons), 0.72 (m, 2H, methylene NBD protons); ^{13}C NMR δ 122.75 (C_4), 120.15 (C_5), 103.05 (C_{3a}), 105.95 (C_{1a}), 85.29 (C_2), 82.99 (C_{5a}), 80.51 (C_{8a}), 79.41 (C_1), 76.37 (C_3), 69.11 (C_5H_5), 68.31 (C_6), 70.27 (C_7), 64.15 (C_8), 56.17 (methylene NBD carbon), 46.43 (bridgehead NBD carbons), 33.33 and 32.27 (olefin NBD carbons).

***syn*- and *anti*-{(η^5-Cyclopentadienyl)iron(II)(μ-η^5:η^5-*as*-indacenediide)rhodium(I)(η^2-ethylene)$_2$} (*syn*-4 and *anti*-4).** These isomers were obtained as a red powder in a 1/1.4 ratio in a way strictly similar to that for the ***syn*-2** and ***anti*-2** analogues by using the $[Rh(\mu\text{-}Cl)(ethylene)_2]_2$ dimer.[4] The yield is 40%, the rest being unreacted iron complexes whose signals do not interfere with the NMR analysis. Attempted purification of the bimetallic complexes (crystallization, column chromatography, etc.) resulted in their decomposition. MS: *m/z* 430 (M^+). ***syn*-4**: ^1H NMR δ 7.34 and 6.72 (2H, AB quartet, $J_{AB} = 9.3$ Hz, H_4 and H_5, respectively), 5.89 (dt, 1H, $^3J(H_1,H_2) = {}^3J(H_2,H_3) = 2.7$ Hz, $J(^{103}Rh,H_2) = 1.5$ Hz, H_2), 5.44 (ddd, 1H, $^3J(H_1,H_2) = 2.9$ Hz, $^4J(H_1,H_3) = 1.6$ Hz, $^5J(H_1,H_4) = 0.5$ Hz, H_1), 5.08 (ddd, 1H, $^3J(H_2,H_3) = 2.9$ Hz, $^4J(H_1,H_3) = 1.6$ Hz, $^5J(H_3,H_4) = 0.5$ Hz, H_3), 5.02 (ddd, 1H, $^3J(H_6,H_7) = 2.4$ Hz, $^4J(H_6,H_8) = 1.1$ Hz, $^4J(H_5,H_6) = 0.8$ Hz, H_6), 4.72 (dd, 1H, $^3J(H_7,H_8) = 2.5$ Hz, $^4J(H_6,H_8) = 1.1$ Hz, H_8), 4.13 (s, 5H, C_5H_5), 4.10 (t, 1H, $^3J(H_6,H_7) = {}^3J(H_7,H_8) = 2.5$ Hz, H_7), 3.75 and 3.67 (2m, 4H each, ethylene protons); ^{13}C NMR δ 128.09 (C_4), 117.19 (C_5), 110.41 (C_{3a}), 106.63 (C_{1a}), 87.83 (C_2), 85.30 (C_{5a}), 83.60 (C_1), 82.78 (C_{8a}), 80.56 (C_3), 70.83 (C_5H_5), 70.16 (C_7), 63.08 (C_8), 61.97 (C_6), 28.06 and 27.99 (ethylene carbons). ***anti*-4**: ^1H NMR δ 7.03 and 6.90 (2H, AB quartet, $J_{AB} = 9.2$ Hz, H_4 and H_5, respectively), 5.73 (m, 1H, H_3), 5.54 (dt, 1H, $^3J(H_1,H_2) = {}^3J(H_2,H_3) = 2.7$ Hz, $J(^{103}Rh,H_2) = 1.1$ Hz, H_2), 5.32 (ddd, 1H, $^3J(H_1,H_2) = 2.7$ Hz, $^4J(H_1,H_3) = 1.5$ Hz, $^5J(H_1,H_5) = 0.5$ Hz, H_1), 4.87 (ddd, 1H, $^3J(H_7,H_8) = 2.5$ Hz, $^4J(H_6,H_8) = 1.2$ Hz, $^4J(H_5,H_5) = 0.9$ Hz, H_8), 4.69 (dd, 1H, $^3J(H_6,H_7) = 2.5$ Hz, $^4J(H_6,H_8) = 1.1$ Hz, H_6), 4.12 (t, 1H, $^3J(H_6,H_7) = {}^3J(H_7,H_8) = 2.6$ Hz, H_7), 3.75 (s, 5H, C_5H_5), 3.31 and 3.21 (2m, 4H each, ethylene protons); ^{13}C NMR δ 124.26 (C_4), 118.86 (C_5), 104.39 (C_{1a}), 104.27 (C_{3a}), 87.09 (C_2), 83.18 (C_{8a}), 83.10 (C_{5a}), 83.27 (C_1), 80.04 (C_3), 70.83 (C_5H_5), 70.16 (C_7), 63.08 (C_8), 61.97 (C_6), 28.18 and 28.12 (ethylene carbons).

Results and Discussion

Ligand Synthesis. We have slightly modified the reported[17] route to unsubstituted 1,5- and 1,7-dihydro-*s*-indacene isomers, which consists of a sequence of many steps starting from 1,2,4,5-tetrakis(bromomethyl)-benzene and ethyl acetate so that better final yields have been obtained. On the other hand, different reaction pathways have been suggested for the preparation of 1,6-, 1,8-, and 3,6-dihydro-*as*-indacenes with modest or very low final yields. The scheme, originally proposed by Wasserman and Doumaux,[18] and then improved by Katz,[19] consists of the synthesis of an oxy-diketone followed by its photolysis to the 1,8-dioxo-2,3,6,7-tetrahydro-*as*-indacene which was then reduced

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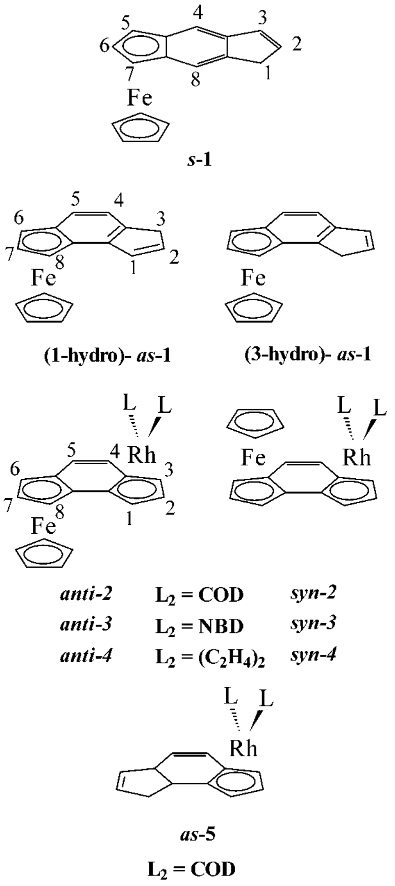
to the 1,8-diol and finally dehydrated to dihydro-*as*-indacene. A different pathway consists of the preparation of the tricyclic hexahydro-*as*-indacene, whose dehydrogenation with 2,3-dichloro-5,6-dicyanobenzoquinone gave the expected final product.[20] A different route was proposed by Prinzbach, who originally obtained dihydro-*as*-indacene in 3−5% yield from the condensation of glyoxal sulfate with cyclopentadienylsodium.[21] This procedure represents the classical approach to the preparation of fulvenes, and it was recently resumed by Erden, who claimed a 55% yield of dihydro-*as*-indacene by treating aqueous glyoxal with methanolic cyclopentadiene in the presence of pyrrolidine.[22] This method seemed to us the most efficient; however, in at least 14 experiments we were unable to reproduce the reported yield. Variation of reagent concentrations, temperature, and reaction time did not afford any appreciable increase of the yield, which fluctuated within 5 and 7%. Even the use of ammonium chloride in the workup did not influence the total yield, whereas in the presence of anhydrous $CaCl_2$ we got the highest yield, i.e., 9%. Even the experiments carried out in the absence of light and by refluxing the ligroin extracts for several hours in an attempt to convert the reaction intermediate into the final product were fruitless. The mixture of the three isomers 1,6-, 1,8-, and 3,6-dihydro-*as*-indacene obtained from several trials was then used for the preparation of mononuclear ferrocenyl complexes.

Cyclopentadienyliron(η^5-hydro-*s*-indacenide) and Cyclopentadienyliron(η^5-hydro-*as*-indacenide). The most commonly utilized synthesis of homobimetallic indacenediide complexes consists of the double deprotonation of the dihydroindacene ligands with lithium alkyls and subsequent quenching of the dilithium salts with the appropriate $[M(\mu\text{-Cl})L_2]_2$ metal dimer (M = Rh, Ir). For rhodium and iridium bimetallic complexes overall yields between 80 and 50%, respectively, were obtained.[4] This one-step pathway involving the simultaneous coordination of two metal units could not be pursued to obtain heterobimetallic complexes; a two-step pathway consisting of metalating one of the two Cp rings, leaving the other available for the second metalation, was then necessary.

Many synthetic approaches to the synthesis of ferrocenes having unsymmetrically substituted Cp rings (mixed ferrocenes) were checked by different authors. Our first attempt was the use of Cp*Fe(acac) as Cp*Fe transfer reagent to prepare Cp*Fe(η^5-hydroindacenide) analogously to the synthesis of Cp*Fe(η^5-hydropentalene).[2] In many experiments[23] the only reaction observed was the isomerization of the dihydroindacenes to the statistic mixture of the three isomers probably arising from an ionization−protonation process of the ligand. Reaction of $FeCl_2(THF)_2$[24] or anhydrous $FeCl_2$[25] with sodium cyclopentadienyl and 2,7-dimethyl-*as*-hydroindacenide salts, besides the aforementioned isomerization of the ligand, gave a small yield of the homobimetallic complex *anti*-[CpFe(μ-η^5:η^5-2,7-dimethyl-*as*-indacenediide)FeCp][23] without any trace of the monometallic CpFe(η^5-2,7-dimethyl-*as*-hydroindacenide) complex.

Chart 1



A successful route to the synthesis of mixed ferrocenes was recently suggested by Chung et al.[13] and consists of the use of [CpFe(η^6-fluorene)]PF_6 as an FeCp transfer reagent. Thus, the lithium salt of *s*- (or *as*-) hydroindacenide was reacted with CpFe(η^5-fluorenide) to obtain the complexes ***s*-1** and ***as*-1** (see Chart 1) in 55−65% yield (by NMR integration of the crude mixture). Purification by column chromatography on silica or alumina gave different results for the two complexes. In fact, we have been able to obtain pure ***as*-1** (as a 2/3 mixture of the 1-hydro- and 3-hydro isomers) in good yield (ca. 58%) with little decomposition. On the contrary, ***s*-1** was obtained pure in a very small amount owing to its high instability under the chromatographic conditions.

For ***s*-1** only one isomer exists, owing to the molecular symmetry. All the nuclei are nonequivalent, so that the ^1H and ^{13}C NMR spectra are characterized by a distinct absorbance for each proton and carbon atom. The resonances of the H4−H8 protons (*see* Chart 1) and

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[23] Casarotto, A. Thesis, University of Padova, 1999. The complex *anti*-[CpFe(μ-η^5:η^5-2,7-dimethyl-*as*-indacenediide)FeCp] was characterized by X-ray diffractometric analysis.

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those of the C_5H_5 ring appear at values very close to those reported many years ago for CpFe(η^5-indenide) by King.[26] We observe that the resonances of the H5−H7 nuclei resonate at markedly higher field than the corresponding protons in the analogous monometallic rhodium complex.[27] In particular, H6 resonates at δ 4.03, and it appears as a sharp triplet. In contrast, in the ^{13}C spectrum the signal of C6 appears at a lower field (δ 70.48) with respect to those of C5 (δ 62.10) and C7 (δ 62.26).

For the hydro-*as*-indacenide complexes 1-hydro-***as*-1** and 3-hydro-***as*-1** (see Chart 1), the spectrum of the mixture is quite complex, due to the presence of numerous signals with slight chemical shift differences. Despite this, the assignment of the proton and carbon resonances has been accomplished by 2D measurements, viz., homonuclear $^1H-^1H$ COSY and NOESY, and by heteronuclear $^1H-^{13}C$ COSY. The trend of the ^1H and ^{13}C values of the chemical shifts is comparable with that observed for ***s*-1**, minor differences being likely due to local anisotropy effects.

Cyclopentadienyliron(μ-η^5:η^5-*as*-indacenediide)-RhL$_2$ (L$_2$ = COD (2), NBD (3), (ethylene)$_2$ (4)). The synthesis of heterobimetallic iron−rhodium complexes has been carried out by deprotonation of cyclopentadienyliron(η^5-hydro-*as*-indacenide) with *n*-BuLi in THF at −78 °C and reaction of the [cyclopentadienyliron(η^5-*as*-indacenediide)]Li salt with a THF solution of the appropriate rhodium dimer $[Rh(\mu\text{-}Cl)_2L_2]_2$ (L_2 = COD, NBD, (ethylene)$_2$). The transfer of the RhL_2 unit was highly effective, and the yields were in the range of 80−85%. Unfortunately, attempts to obtain crystals suitable for X-ray analysis were unsuccessful, so that the characterization of the products was obtained by spectroscopic methods.

The NMR spectra demonstrated that the metalation with rhodium afforded mixtures of heterobimetallic species. In fact, the resonances typical of the protons of the cyclopentadiene ring of ***as*-1** were replaced by signals due to an ABCX spin system in the range of 5.1−6.0 ppm, as already reported for comparable RhL_2 complexes.[4,27,28] The benzene protons H4 and H5 are nonequivalent, and they appear as an AB quartet ($^3J_{AB}$ = ca. 9 Hz), the proton nearest to the Fe-coordinated Cp ring, viz., H5, resonating always at higher field. Similar behavior is shown by the ^{13}C chemical shift values; in particular, the nuclei of the Rh-coordinated Cp rings resonate at noticeably lower field than that of the corresponding nuclei of the Fe-coordinated Cp's. The low solubility of these heterobimetallic complexes as well as their poor stability in solution did not allow the detection of all the ^{13}C NMR signals in the monodimensional spectra. Complete sets of the δ values for the carbons bonded to hydrogen atoms were instead obtained by 2D HMQC measurements[11,12] and, for the quaternary carbon atoms, by means of heterocorrelated HMBC spectra optimized for the long-range proton−carbon coupling constants.[13] In all the recorded ^1H spectra, two sets of signals are observed with very similar multiplicities, suggesting that two isomeric species are formed in the metalation reaction. The structural rigidity of the indacenyl bridging ligand allows, in fact, two stereoisomers (*syn* and *anti*) to be formed, as was found for the homobimetallic complexes of several *s*- and *as*-indacenediides.[4,29] A confident structural assignment of the heterobimetallic species was made possible by comparing their spectral pattern with those of the homobimetallic complexes. In the structurally characterized *syn*- and *anti*-{2,7-dimethyl-*as*-indacenediide[Rh(COD)]$_2$} stereoisomers[29] the main feature of the ^1H NMR spectra is the chemical shift difference, $\Delta\delta$, between the resonances of the olefin protons of COD, which in the *anti* isomer (0.56 ppm) is markedly higher than that found for the corresponding nuclei in the *syn* isomer (0.14 ppm). A quite similar trend was shown as well by the corresponding complexes having NBD as ancillary ligand.[4] We observe quite similar features in the FeCp(indacenediide)RhL$_2$ complexes presented here. For the COD derivative **2**, the $\Delta\delta$ values are 0.50 and 0.13 ppm; therefore, we have confidently assigned the *anti* and *syn* structures to the corresponding isomers, respectively.

Integration of the NMR signals due to the ancillary ligand protons afforded the *syn*/*anti* ratio of the isomers, which was confirmed by the integral values of the other signals and in particular of H4 and H5 obtained by means of fully relaxed spectral measurements. The chemical shift values of the bis complexes are reported in the Experimental Section.

The *syn*/*anti* ratio is temperature dependent. Metalation at −78 °C affords a *syn*/*anti* ratio of 1/1.5 unaffected by the nature of the olefin ancillary ligands, while the *syn* isomer is the preferred product (*syn*/*anti* ratio 3/1 with L$_2$ = COD) when the reaction is accomplished at −10 °C. These findings suggest that an isomerization process takes place at higher temperature; i.e., the *anti* isomer, which prevails at lower temperature, is the kinetic product and it is transformed into the *syn* derivative after its production. The available data do not allow the establishment of a mechanism for the isomerization process; however, we must recall that a comparable isomerization in the same *anti*−*syn* direction was observed for the heterobimetallic Cr(CO)$_3$-(indenyl)Rh(NBD) complex.[30]

It appeared worthwhile to compare the reactivity of homo- and heterobimetallic indacenediide complexes in the substitution of the ancillary NBD or COD ligands with carbon monoxide. For the homobimetallic *syn*- and *anti*-{(2,7-dimethyl-*as*-indacenediide)[Rh(COD)]$_2$} this substitution occurs very easily by bubbling CO even at −50 °C into a CH_2Cl_2 solution with retention of the stereochemistry of the starting complexes.[4] This huge reactivity is similar to that of the (indenyl)Rh(COD) analogue and contrasts with the inertness of the (cyclopentadienyl)Rh(olefin)$_2$ complexes, and it is attributed to the so-called *indenyl effect*.[31] Surprisingly, no substitution product was obtained when CO was bubbled even at room temperature through CH_2Cl_2 solutions of

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heterobimetallic **2** and **3**. We believe that this large difference in the reactivity of the rhodium center between homo- and heterobimetallic complexes must be ascribed to the lack of the indenyl effect due to the very strong η^5 coordination of iron to the Cp ring of the bridging ligand. This causes the quenching of the π-electron delocalization typical of the *as*-indacenediide[32] so that RhL_2 is forced to coordinate in a strict η^5 fashion as well. In other words, in the heterobimetallic iron–rhodium complexes the indacenyl bridge is no longer a flexible 14-π-electron system and it behaves—at least in the L ligand exchange reaction for CO—as two electronically isolated σ-bonded cyclopentadienyl rings connected by an additional olefin bridge. This reduced aromatic character of the central six-membered ring is confirmed by the remarkable downfield shift observed for C4 and C5 (δ 118.39 and 126.07, respectively) in comparison with the same carbon atoms in the homobimetallic species (δ 116.7)[4] indicating a more "olefin" character for these nuclei.

Electrochemistry. Cyclic voltammetry has been widely used to investigate metal–metal interactions. In homobimetallic systems which contain two equivalent redox centers ($M_1 = M_2$),[1c,33] the ΔE separation between the two reversible (in the chemical and electrochemical sense) redox events is indicative of an interaction between the two sites. Larger values correspond to a stabilization of the mixed-valence intermediates involving totally delocalized systems (class III) and to a very large comproportionation constant K for the equilibrium (eq 1).

$$M_1{\sim\!\sim}M_2 + M_1^+{\sim\!\sim}M_2^+ \rightleftharpoons 2M_1^{+1/2}{\sim\!\sim}M_2^{+1/2} \qquad (1)$$

On the other hand, much smaller ΔE separations correspond to weaker interaction between the metals and to a smaller K for equilibrium 2. The valences are described by a mixed-valence state involving trapped-valence systems (class II).

$$M_1{\sim\!\sim}M_2 + M_1^+{\sim\!\sim}M_2^+ \rightleftharpoons M_1^+{\sim\!\sim}M_2 + M_1{\sim\!\sim}M_2^+ \qquad (2)$$

Finally, ΔE values close to zero are characteristic of noninteracting metal sites (class I).

In the case of heterobimetallic complexes ($M_1 \neq M_2$) the ΔE which is indicative of the metal–metal interactions is no longer that between the two subsequent reversible redox waves. It is now the difference between the redox potential of the reversible second wave and the redox potential of the reversible wave of the corresponding monometallic species, except eventually the substituent effect due to the presence of the other metal.[34]

For either *syn*- (***syn*-2**) or *anti*-CpFe(*as*-indacenediide)Rh(COD) (***anti*-2**) (Chart 1), the reference monometallic species is the 1-hydro-*as*-indacenide-Rh(COD)[27b] (***as*-5**), provided its oxidation be Nernstian and chemically reversible. In Figure 1a, we report the voltammetric oxidation of the mononuclear complexes ***as*-1** and ***as*-5** in THF/0.2 M *n*-Bu_4NBF_4 (see Table 1 for data). For the mixed ferrocene ***as*-1** the electron transfer is almost electrochemically and chemically reversible, as expected for substituted ferrocenes, and its oxidation potential ($E_p = 0.44$ V) is lower than that of ferrocene, owing to π-electron delocalization within the metal, similar to what is found in CpFe(η^5-indenide) ($E_p = 0.52$ V).[35] Conversely, the oxidation of ***as*-5** is not chemically reversible at low scan rate and occurs at higher potential than that of the iron derivative. The peak current of the wave is proportional to $v^{1/2}$, as would be expected for a simple Nernstian process,[36] so that the current function $i_p v^{-1/2}$ is constant by varying the potential scan

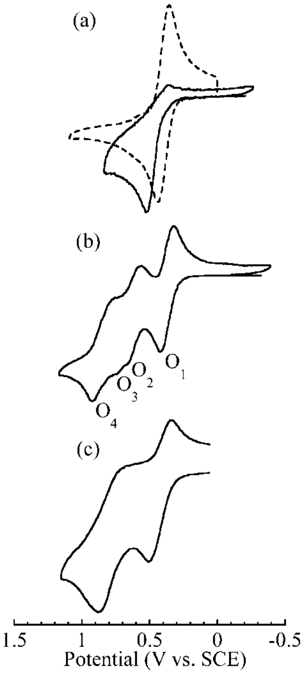

Figure 1. Cyclic voltammetric scan at a 0.5 mm diameter gold-disk electrode ($T = 20$ °C, solvent THF/0.2 M *n*-Bu_4NBF_4, scan rate $v = 0.5$ V s^{-1}): (a, dashed line) 3 mM CpFe(η^5-hydro-*as*-indacenide) (***as*-1**); (a, solid line) 3 mM hydro-*as*-indacenide-Rh(COD) (***as*-5**); (b) 3 mM mixture (1/1.5) of *syn*-[CpFe(*as*-indacenediide)Rh(COD)] (***syn*-2**) and *anti*-[CpFe(*as*-indacenediide)Rh(COD)] (***anti*-2**); (c) 1 mM *anti*-[CpFe(*as*-indacenediide)Rh(NBD)] (***anti*-3**).

Table 1. Cyclic Voltammetric Data[a]

complex	$E_p{}^{1\,b}$	$\Delta E_p{}^{1\,b}$	$E_p{}^{2\,b}$	$\Delta E_p{}^{2\,b}$
Cp_2Fe	0.65	0.085		
as-**1**	0.44	0.085		
as-**5**	0.57[c]	0.07[c]		
syn-**2**	0.66	0.100	0.75	*d*
anti-**2**	0.42	0.100	0.92	0.15
anti-**3**	0.50	0.150	0.87	0.20

[a] Conditions: solvent THF/0.2 M *n*-Bu_4NBF_4; potential vs SCE at a 0.5 mm diameter gold-disk electrode; $T = 20$ °C; potential scan rate 0.5 V s^{-1}. [b] In volts. [c] Estimated at high scan rate; see Figure 2. [d] Not measured due to the overlapping of the cathodic waves.

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rate. In the range 0.05−10 V s^{-1} the plot of E_p vs the potential scan rate displays the slope $d(E_p)/d(\log v) =$ 28 mV and it tends to a constant value (0.57 V) at higher scan rate, typical behavior for a Nernstian electron transfer followed by a chemical reaction (EC mechanism).

The ***syn*-2** and ***anti*-2** isomers are available in an unresolved mixture in which the *syn* isomer, the minor product, decomposes in solution within few hours. The CV of this mixture (Figure 1b) shows two well-defined waves, O_1 and O_4, and two superposed waves, O_2 and O_3. The assignment of the waves to the corresponding isomers was made possible by comparison with the CV measured in a low-volume cell containing 0.5 mL of the analogous complex *anti*-CpFe(indacenediide)Rh(NBD) (***anti*-3**) (Figure 1c) obtained pure in a very small quantity (see Experimental Section). In fact, the potential peak values of the two oxidation waves of ***anti*-3** are very close to those of O_1 and O_4, which we have assigned to the *anti* isomer. Therefore, in the CV of Figure 1b we have assigned the waves O_1 and O_4 to ***anti*-2**, and they correspond to two successive chemically reversible oxidations, yielding the monocation and the dication, respectively. The oxidation potential of the first wave, O_1, and its ΔE_p value are close to those of the monometallic iron complex ***as*-1**, indicating that the presence of the second metal does not change the electron density and the kinetics of the first electron transfer at the iron center (low substituent effect). On the other hand, the comparison of the E_p value of the second wave O_4 with the Nernstian but chemically irreversible wave of the monometallic rhodium complex ***as*-5** is not properly correct. However, since at higher scan rate (50 V s^{-1}) this wave begins to be chemically reversible, as described above, the estimated limit value of the potential peak ($E_p = 0.57$) of ***as*-5** can be compared with that of the second wave of ***anti*-2** ($E_p = 0.92$). The resulting ΔE value is ca. 350 mV, a value between trapped (class II) and detrapped (class III) mixed-valence systems.[37] Another interesting feature of ***anti*-2** is the chemical reversibility of the second wave, corresponding to the oxidation of the rhodium site, whereas in ***as*-5** the process is almost chemically irreversible at low scan rates. This is clear evidence that the presence of the CpFe group stabilizes the positive charge at the rhodium site.

The oxidation of the ***syn*-2** isomer occurs as two one-electron transfers at very close potentials. The wave O_2, which corresponds to the oxidation of iron, is Nernstian as well as in the ferrocene derivatives, but its potential is more positive (200 mV) than that measured for the same oxidation of the *anti* isomer. Conversely, the wave O_3, that is, the oxidation of rhodium, is chemically irreversible and occurs at lower potential than that of ***anti*-2**. The values of the potentials of the two waves O_2 and O_3 are very close to those of mononuclear ferrocene and CpRh(COD)[38] derivatives, respectively, indicating that the *syn* isomer can be figured by the sum of two isolated metal systems (class I). This is likely due to the folding of the indacenyl skeleton induced by steric requirements determining a minor delocalization of the π-electron system of the indacenediide ligand. As can be demonstrated by using suitable molecular models, the steric interaction between the two metal groups forces a distortion of the bridging ligand so that the ring centroid to metal vector cannot be parallel.

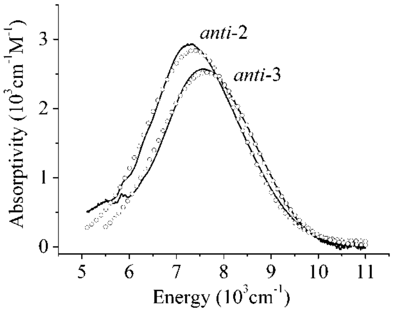
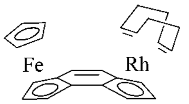


Figure 2. Near-IR spectra of 1 mM ***anti*-2** and ***anti*-3** (solid line, experimental curves; open circles, Gaussian fitting) in THF ($T = -78$ °C).

Table 2. Near-IR Data[a]

complex	ν_{max}[b]	ϵ[c]	$\Delta\nu_{1/2}$[b] found	$\Delta\nu_{1/2}$[b] theory[d]
anti-$\mathbf{2}^+$	7580	2570	2020	3800
anti-$\mathbf{3}^+$	7310	2760	1980	3900

[a] Conditions: solvent THF; $T = -78$ °C. [b] In cm^{-1}. [c] In cm^{-1} M^{-1}. [d] From eq 3.



We found similar distortions in the structure of the complex *syn*-{2,7-dimethyl-*as*-indacenediide[Rh(COD)]$_2$}.[4]

Electronic Spectra.[39] The mixed-valence radical cation ***anti*-3**$^+$ was generated at −78 °C in THF by chemical oxidation of the neutral red complex with 1 equiv of ferrocenium tetrafluoroborate, $FeCp_2BF_4$. The near-IR spectrum of the resulting deep green solution shown in Figure 2 (the neutral ***anti*-3** does not absorb in this spectral region) displays a strong absorption at 7600 cm^{-1} ($\epsilon = 2600$ cm^{-1} M^{-1}; Table 2). This spectral region is often diagnostic for a charge-transfer process,[40] and in this case the strong absorption can be assigned to an intervalence transition (IT). The bandwidth, $\Delta\nu_{1/2} \approx 2000$ cm^{-1}, is much lower than the theoretical value (3800 cm^{-1}) expected for a trapped mixed-valence (class 2) asymmetric complex in which the two metal centers are weakly interacting (eq 3),[41a] where ν_c is the frequency at the center of the peak and E_0 (0.13 V, i.e. 1050 cm^{-1}) is the energy difference between the initial and the final states evaluated from the oxidation potentials

$$\Delta\nu_{1/2} = (2310\ \nu_c - E_0)^{1/2}\ \mathrm{cm}^{-1} \qquad (3)$$

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[37] Winter, R.; Pierce D. T.; Geiger, W. E.; Lynch, T. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1949 and references therein.

[38] For instance, we found that the oxidation of (indenyl)Rh(COD) shows a chemically irreversible wave with $E_p = 0.72$ V at 0.5 V s^{-1} and a chemically and electrochemically reversible wave with $E° = 0.71$ V at 4000 V s^{-1}.

[39] All the cationic species generated at −78 °C by chemical oxidation are frangible intermediates, and further analytical characterization was not possible.

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of the model compounds ***as*-1** and ***as*-5** (Table 1). The spectrum in CH_3NO_2, whose dielectric constant (39.4) is much higher than that of THF (7.5), shows no variation of the band energy. Furthermore, there is no dependence of the band energy on ionic strength up to an electrolyte concentration of 0.2 M in [*n*-Bu_4N]-[BF_4].[40a,41] These data allow the assignment of the class III (detrapped mixed valence) to the radical cation ***anti*-3**$^+$.

The dication ***anti*-3**$^{2+}$, generated by chemical oxidation of the neutral complex with 2 equiv of $AgBF_4$ at −78 °C, shows an absorption at 670 nm that can be likely assigned to a ligand-to-metal charge transfer (LMCT) transition.

The near-IR spectrum of the solution generated by oxidation of the ***syn*-2** and ***anti*-2** mixture under the same conditions (Figure 2) shows an analogous absorption at lower energy (7300 cm^{-1}) as well as similar absorptivity (2800 cm^{-1} M^{-1}) and bandwidth (1980 cm^{-1}, see Table 2). This band can be assigned to the monocation ***anti*-2**$^+$. Ferrocenium does not oxidize the isomer ***syn*-2**, as expected on the basis of the redox potentials, which result in the order ***syn*-2** ≈ $FeCp_2$ > ***anti*-2**.

Conclusions

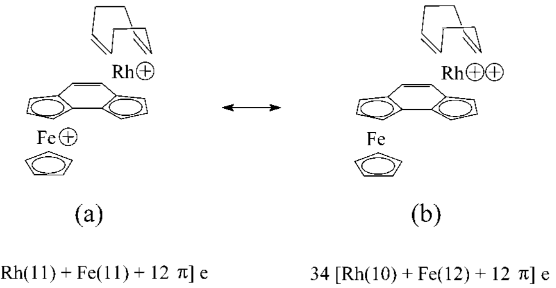
The heterobimetallic *syn*- and *anti*-CpFe(*as*-indacenediide)RhL_2 have been prepared by reaction of lithium CpFe(*as*-indacenediide) with rhodium $[Rh(\mu\text{-}Cl)L_2]_2$ dimers (L = ethylene, L_2 = COD, NBD). Due to the instability of the isomer CpFe(*s*-hydroindacenide), it was not possible to form the analogous heterobimetallic *s* complexes.

The chemical behavior of the heterobimetallic CpFe-(*as*-indacenediide)RhL_2 (L_2 = COD, NBD) complexes was shown to be quite different from that of the homobimetallic RhL_2−RhL_2 complex. Their inertness toward the substitution of COD by CO is interpreted by assuming an η^5 coordination of Rh to the Cp ring arising from a localization of the π electron density by CpFe.

The voltammetric oxidation of *anti*-CpFe(*as*-indacenediide)RhCOD occurs in two successive waves, yielding the monocation and the dication. The ΔE value of 350 mV for ***anti*-2** (and a similar value for ***anti*-3**) does not allow a clear-cut assignment between trapped (class II) and detrapped (class III) interactions. In the near-IR time scale (ca. 10^{-13} s) the results indicate that the radical cation is valence detrapped (class III). At the most, the systems could have a borderline behavior between class II and class III, having almost delocalized valence.[42]

In contrast, the oxidation of the *syn* isomer indicates that the two metal units behave as two noninteracting centers (class I like) because of the folding of the bridging ligand induced by the steric hindrance between Cp and COD.

The chemical reversibility of the second wave, corresponding to the oxidation of the rhodium site, and the absorption in the visible spectrum suggest that the dication is stabilized by a metal−bridge−metal delocalization described mostly by a resonance structure with the two positive charges localized on the rhodium center. Therefore, we describe the dication by the limit structures



In structure a the positive charges are localized on the two metals (Rh(II)−Fe(III)), while in structure b they both reside on the rhodium center (Rh(III)−Fe(II)). It is worth noting that the electrochemical and chemical oxidation of the complex [η^5-(1-ferrocenyl)indenyl]Rh-$(CO)_2$, which similarly contains CpFe and RhL_2 units linked through a fulvalenyl bridge, yielded a dication with the positive charges on the rhodium site,[9] as in structure b.

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