

[Rh₂(μ-CO)(CO)₂(η-indenyl)₂] from solid state decarbonylation of the monomer (η-indenyl)-Rh(CO)₂

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Abstract

The complex [Rh₂(μ-CO)(CO)₂(η-indenyl)₂] was obtained as pure crystals by warming the solid monomer (η-indenyl)-Rh(CO)₂ in vacuo at 50°C. The characterization of the dimer by spectroscopic and X-ray analysis is described. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Complex; Dimer; Spectroscopic and X-ray analysis

1. Introduction

The synthesis of CO-bridged unsaturated bi- or trimetallic complexes of the triad Co, Rh, Ir can be accomplished either photochemically or thermally starting from the mononuclear complex η⁵-LM(CO)₂ (L = Cp, Cp*, and similar ligands) [1] or chemically by reaction between the monomer and another reagent containing very labile ligands, e.g., η⁵-LM(ethylene)₂ [2,3]. For example, by photolysis at low temperature of CpCo(CO)₂ the trimer Cp₃Co₃(CO)₃ was isolated which is likely produced from an intermediate dimer of formula [Co₂(μ-CO)(CO)₂Cp₂] [4]. Moreover, the dinuclear complex [Rh₂(μ-CO)(CO)₂(η⁵-Cp)₂] was prepared since the 1960s by photolysis of the monomer CpRh(CO)₂, and its structure showed an anti disposition for the two Cp rings with respect to the plane (Rh(1), μ-CO, Rh(2)) [5]. A comprehensive kinetic analysis of the photochemical data obtained in the

presence and in the absence of C–H and Si–H bond activation reactions has been published [6].

The analogous complex [Rh₂(μ-CO)(CO)₂(η⁵-Cp*)₂] could not be obtained either photochemically or thermally. Instead, it was synthetically accessible through a pathway consisting in protonation–decarbonylation of the monomer Cp*Rh(CO)₂ followed by a reaction with an alkoxy base [7]. Conversely, pyrolysis at 200°C of the same mononuclear complex afforded the trirhodium species [Rh₃(μ-CO)₃(η⁵-Cp*)₃] [8a] probably via the dirhodium species [Rh₂(μ-CO)₂(η⁵-Cp*)₂] which was isolated by warming at 80–85 °C and 10–20 mmHg [8]; this dimer was also obtained from the monomer by decarbonylation with Me₃NO [8a].

Finally, the indenyl green trimer [Rh₃(μ-CO)₃(η-indenyl)₃] was characterized as the final product obtained by refluxing heptane solutions of the monomer (η-indenyl)-Rh(CO)₂, **A** [2]. The existence of the bimetallic species, viz., [Rh₂(μ-CO)(CO)₂(η-indenyl)₂], **B**, was inferred by the observation of the building up and of the gradual disappearance of CO stretching bands attributable to this species when the reaction was monitored by IR, its isolation and characterization being elusive [9]. The trimer [Ir₃(μ-CO)₃Ind₃] was similarly

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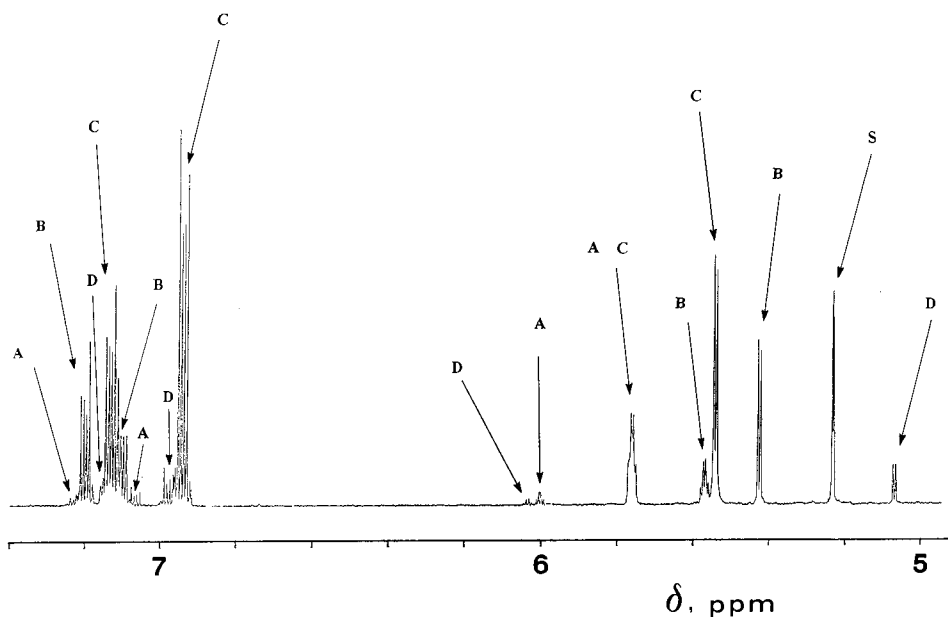


Fig. 1. $^1\text{H-NMR}$ spectrum of the reaction products obtained by warming (η -indenyl)- $\text{Rh}(\text{CO})_2$, **A**, in CD_2Cl_2 at 50°C for several days. Chemical shifts are given in δ from internal Me_4Si . **S** indicates the residual proton signal of the solvent. For the identification of the species **B**, **C**, and **D**, see the text.

obtained by refluxing hexane solutions of the monomer $\text{IndIr}(\text{CO})_2$ [10].

In the course of our investigation of the chemical and electrochemical reactivity of the monomer **A** we obtained the dimer **B** as a crystalline solid by warming **A** in vacuo at 50°C . We report here its characterization by spectroscopic and X-ray crystallographic analyses as well as some preliminary results of its thermal reactivity in solution.

2. Results and discussion

Complex **A** was obtained by bubbling CO through a solution of indenyl- $\text{Rh}(\text{COD})$ in CH_2Cl_2 and its physical and spectroscopic characteristics agree with those already reported [11,12]. We have observed in the $^1\text{H-NMR}$ spectrum that **A** is not stable in CD_2Cl_2 solution even if kept at -30°C in the dark, and new resonances appear within few days. To hasten the reaction, a carefully tightened NMR tube was warmed at 50°C and every hour checked by recording its $^1\text{H-NMR}$ spectrum. After 3 days (with occasional flushing to remove excess CO), a new spectrum (shown in Fig. 1) was recorded containing at least three new species, **B**, **C**, and **D**, together with a small amount of unreacted **A**. All the new species exhibit an $\text{AA}'\text{BB}'$ pattern between δ 7.2 and 6.9 and an $\text{AA}'\text{BX}$ pattern between δ 6.1 and 5.0, i.e. the NMR pattern typical of an indenyl ligand η -coordinated to a RhL_2 unit. Since no other proton signals appear in the spectrum, taking into account the nature of the

reagent **A**, the new species appear to be carbonylated indenyl-rhodium complexes. This hypothesis is confirmed by (i) the presence of the coupling constant between ^{103}Rh and the H-2 proton amounting to ca. 2.4 Hz [12], and (ii) by a complex system of IR bands in the rhodium-bonded CO stretching region ($2000\text{--}1800\text{ cm}^{-1}$). The relative percentages of the various compounds and the proton chemical shift values (obtained by a first-order analysis) are reported in Table 1.

In order to identify the new species, we synthesized the trimer $[\text{Rh}_3(\mu\text{-CO})_3(\eta\text{-indenyl})_3]$ according to the method reported [2]. After a one night reflux of a solution of **A** in oxygen-free heptane, a dark green solid was obtained in quantitative yield. The product gave a satisfactory elemental analysis and the m/z 738 peak in the mass spectrum. The IR spectrum showed two bands at 1860.8 and 1816.5 cm^{-1} in THF and at 1855.2 and 1809.4 cm^{-1} in CH_2Cl_2 , i.e. in the region typical of the rhodium-bridging carbonyl groups. The IR data in CH_2Cl_2 are in good agreement with those previously reported [2]. The $^1\text{H-NMR}$ spectral parameters of the trimer are identical to those shown by the complex **C**, the nature of which is then stated. In the $^{13}\text{C-NMR}$ spectrum (see Section 3) we did not observe any ^{13}C resonance in the carbonyl region of $220\text{--}225\text{ ppm}$ [9] probably because of a fast carbonyl scrambling occurring at room temperature. The very low solubility of the trimer at low temperatures did not allow us to obtain natural-abundance ^{13}C spectra in the slow-motion region. Bubbling CO through solutions of **C** restore the monomer **A**.

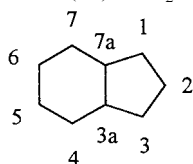
Table 1
Yields, $^1\text{H-NMR}$ chemical shift values^a and $\Delta(\text{M-C})$ values^b for the species **A**, **B**, **C** and **D**

Compound	Relative %	$\delta\text{H}_{4,7}$	$\delta\text{H}_{5,6}$	$\delta\text{H}_{1,3}$	δH_2	$\Delta\delta(^1\text{H})^c$	$\Delta(\text{M-C})$
A	4.5	7.303	7.142	6.116	5.850	0.266	0.200
B	27.8	7.276	7.177	5.682	5.510	0.142	0.205
C	58.5	7.208	7.017	5.845	5.625	0.220	–
D	9.2	7.226	7.057	6.085	5.156	0.929	–

^a Chemical shift values in ppm (δ) from internal Me_4Si , T 298 K, ν , 400.13 MHz.

^b $\Delta(\text{M-C}) = [d(\text{Rh-C}_{7a}) + d(\text{Rh-C}_{3a})]/2 - [d(\text{Rh-C}_1) - d(\text{Rh-C}_3)]/2$, values in Å.

^c $\Delta\delta(^1\text{H}) = \delta\text{H}_2 - \delta\text{H}_{1,3}$.



In another experiment, solid **A** was warmed in vacuo at 50°C for 2 h and a red-brown solid was obtained as a stable microcrystalline powder. Its $^1\text{H-NMR}$ spectrum indicates that this species is pure **B**. It exhibits a $m/z = 520$ in the MS spectrum and two bands at 1980 and 1834 cm^{-1} (solvent, CH_2Cl_2) in the $\nu(\text{CO})$ region of the IR spectrum, suggesting the presence of both terminal and bridging CO ligands, respectively. This result was confirmed by the low-temperature ^{13}C spectrum described below where resonances have been detected at δ 191 and δ 223 for bridged and terminal CO's, respectively.

From suitable crystals obtained by crystallization at low temperature, the molecular structure shown in Fig. 2 was obtained, so that **B** was demonstrated to be the dimeric $[\text{Rh}_2(\mu\text{-CO})(\text{CO})_2(\eta\text{-indenyl})_2]$ species. Some relevant geometrical parameters are reported in Table 2

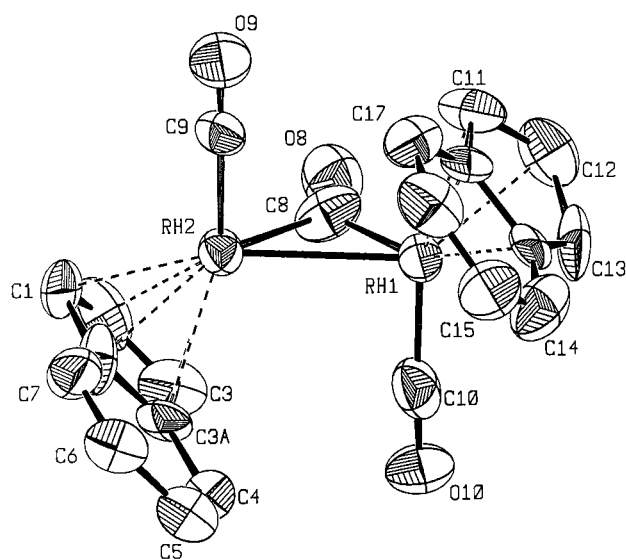


Fig. 2. ORTEP view of the $[\text{Rh}_2(\mu\text{-CO})(\text{CO})_2(\eta\text{-indenyl})_2]$.

as well as the ring slip distortion ($\Delta(\text{M-C})$) and hinge angle (HA) parameters [13]. In the molecule two centers of stereoisomery are present located on the Rh atoms. The virtual C_2 symmetry which characterizes the molecule is consistent with a *racemic* configuration of the compound; the *pseudo* binary axis passes through the bridging CO group and the middle point of the Rh–Rh bond. The terminal C=O groups are almost orthogonal to the central three-membered ring and show usual Rh–C distances of ca. $1.80\text{--}1.82\text{ \AA}$, in contrast with the largely lengthened Rh–C bonds ($1.98\text{--}2.00\text{ \AA}$) with the bridged C=O group, which is due to intra-annular constraints and to the bridging character of C=O as well. This feature is usually present in many similar cases [14]. The conformations of the two indenyl groups are quite in the norm and their orientation with respect to each other and to the central three-membered ring seems to be controlled on one side by the maintenance of the C_2 symmetry and on the other side by the chance to produce a sort of stacking structure with interlocked molecules as actually found in the crystallographic b direction, with ring to ring graphite-like contact distances of $3.5\text{--}3.6\text{ \AA}$ (see Fig. 3). It can be noted that the alternative molecular *meso* configuration which could form during the same reaction would exhibit conformations only slightly more constrained (as can be estimated qualitatively by using suitable molecular models) but it would likely produce a quite more intriguing mode of packing, so preventing or hindering the crystallization.

The C_2 molecular symmetry with the corresponding arrangement of the two indenyl moieties in **B** could justify the temperature dependence of its NMR spectra. In fact, lowering the temperature from 298 to 178 K , the doublet due to $\text{H}_{1,3}$ broadens, disappears at 228 K and reappears as two signals centered at δ 6.24 and 4.86 with a $\Delta\nu = 552\text{ Hz}$ at 178 K . At the same time,

Table 2
Selected bond lengths, bond angles and geometrical parameters for the complex $[\text{Rh}_2(\mu\text{-CO})(\text{CO})_2(\eta\text{-indenyl})_2]$, **B**

Bond lengths (Å)			
Rh(1)–C(17a)	2.45(1)	Rh(2)–C(7a)	2.41(1)
Rh(1)–C(11)	2.24(1)	Rh(2)–C(1)	2.21(1)
Rh(1)–C(12)	2.23(1)	Rh(2)–C(2)	2.19(1)
Rh(1)–C(13)	2.19(1)	Rh(2)–C(3)	2.22(1)
Rh(1)–C(13a)	2.39(1)	Rh(2)–C(3a)	2.43(1)
Rh(1)–C(8)	1.98(1)	Rh(2)–C(8)	2.00(1)
Rh(1)–C(10)	1.82(1)	Rh(2)–C(9)	1.80(1)
Rh(1)–Rh(2)	2.698(2)		
Bond angles (°)			
C(10)–Rh(1)–C(8)	94.8(6)	C(9)–Rh(2)–C(8)	94.8(6)
C(10)–Rh(1)–Rh(2)	89.7(4)	C(9)–Rh(2)–Rh(1)	90.2(4)
C(8)–Rh(1)–Rh(2)	47.6(4)	C(8)–Rh(2)–Rh(1)	47.1(4)
Rh(2)–C(8)–Rh(1)	85.3(5)		
HA parameter (°)			
[C(11a)C(11),C(12),C(13),C(13a)]	8.3	[C(1a),C(1),C(2),C(3),C(3a)]	12.3

the AA'BB' pattern due to $H_{4,7}$ and $H_{5,6}$ changes into two apparent doublets at δ 7.22 and 7.04 ($H_{4,7}$) and two apparent triplets at δ 7.00 and 6.88 ($H_{5,6}$). In contrast, the shape of the resonance attributed to the H_2 proton does not change in the same temperature range. From the above mentioned values, an activation ΔG^\ddagger value of $41.8 \pm 6 \text{ kJ mol}^{-1}$ is calculated for the process. A quite similar behaviour is exhibited by the ^{13}C spectrum

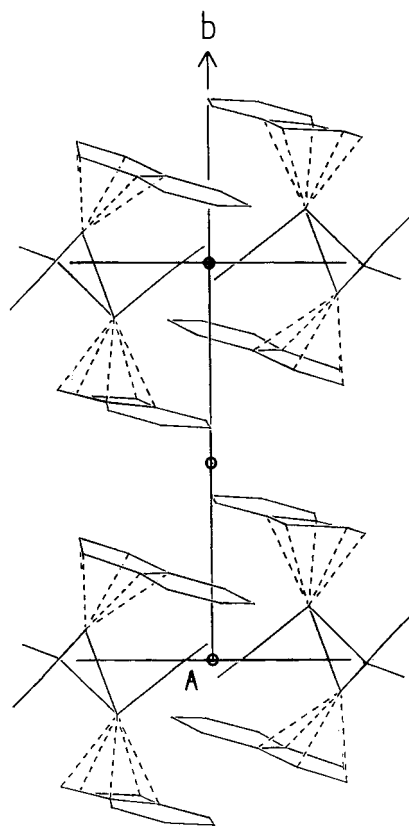


Fig. 3. Packing of molecules of **B** along the b axis as viewed down (001). The stacking disposition of the indenyl groups is shown.

as shown in Fig. 4: at 298 K resonances have been detected at δ 125.066 ($C_{5,6}$), 119.121 ($C_{4,7}$), 115.571 ($C_{3a,7a}$), 95.257 (C_2) and 79.285 ($C_{1,3}$). No resonances for the CO carbons are visible probably because of a carbonyl fast scrambling process. At 178 K, the shape of the resonance of C_2 did not change and was detected at δ 95.327. On the contrary, the resonances attributed to the other indenyl carbons are doubled and appear at δ 125.159 and 124.873 ($C_{5,6}$), 119.173 and 118.816 ($C_{4,7}$), 116.666 and 112.901 ($C_{3a,7a}$), 80.010 and 77.708 ($C_{1,3}$). In addition, resonances have been observed at δ 191 (bridging CO) and δ 223 (terminal CO). These features are in accord with a fast rotation (at room temperature) of the two indenyl moieties around their coordinative bond with the rhodium atoms. If at low temperature the indenyls adopt a geometrical arrangement likely similar to that observed in the solid state by X-ray measurements, the C_1 , C_4 and C_5 carbon atoms are no longer equivalent to the C_2 , C_6 and C_7 ones, as observed.

B is not stable in solution and at room temperature slowly transforms into **A** and **C**, as shown by NMR measurements. Bubbling CO through solutions of **B** quickly restores the monomer **A**.

We are not able, at present, to give a definitive structural assignment for the fourth species, **D**. No IR and ^{13}C -NMR data have been obtained because of its low yield, and purification by chromatography was unsuccessful. However, a working hypothesis can be proposed on the basis of the $\Delta\delta(^1\text{H}) = \delta(H_2) - \delta(H_{1,3})$ parameter proposed by us [15] as an alternative of the pure geometric parameter $\Delta(\text{M}-\text{C})$ [13,16] to connect the variations of selected spectroscopic properties with the hapticity changes of the rhodium–indenyl bond. The values of this parameter for the complexes **A–D** reported in the last column of Table 1 indicate for **D** a strong increase of $\Delta\delta(^1\text{H})$ with respect to **A**, **B** and **C**,

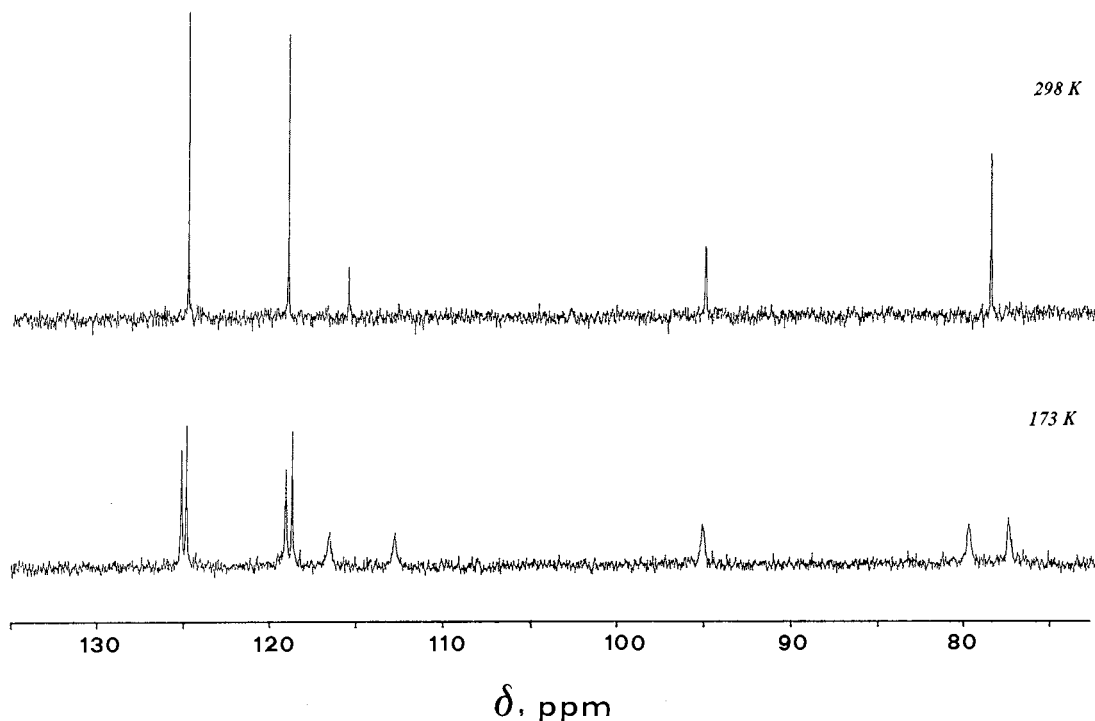


Fig. 4. ^{13}C -NMR spectrum (ν_c 100.61 MHz) of **B** in CD_2Cl_2 at 298 and 173 K. Chemical shifts are given in δ from internal Me_4Si .

suggesting a noticeable shift of the metal hapticity from η^5 towards η^3 . This hypothesis is in accord, on the basis of the electron counting, with a substantial lowering of the rhodium–indenyl bond order, which should be counterbalanced by an increase of the metal–metal bond order. The lack of crystallographic data for **D** does not allow this hypothesis to be further substantiated.

3. Experimental

3.1. General

All reactions and complex manipulations were performed in an oxygen-free atmosphere. The solvents were carefully dried and deoxygenated before use. The complexes appear as microcrystalline air-stable powders, which gave satisfactory elemental analysis. Melting point are uncorrected. Microanalyses were performed at the Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova. The IR spectra were recorded as THF solutions with a Perkin-Elmer 1600 FT-IR spectrometer, and the 70 eV electron impact mass spectra were measured with a VG 16 Micromass spectrometer. The ^1H - and ^{13}C -NMR spectra were obtained as CD_2Cl_2 solutions on a Bruker AM400 spectrometer operating at 400.13 and 100.61 MHz, respectively.

3.2. $\text{Rh}(\text{CO})_2$ -(η -indenyl), **A**

The complex was obtained from indenyl– $\text{Rh}(\text{COD})$ and CO as reported [13]. M.p. 114°C (decomp.); $\nu_{\text{max}}(\text{THF})$ (cm^{-1}): 2041, 1981 ($\text{C}\equiv\text{O}$). m/z 274 (M^+). ^1H -NMR (CD_2Cl_2 , ppm from internal TMS): δ 7.303 (m, 2H, $\text{H}_{4,7}$), 7.142 (m, 2H, $\text{H}_{5,6}$), 6.116 (m, 1H, H_2), 5.850 (m, 2H, $\text{H}_{1,3}$). ^{13}C -NMR (CD_2Cl_2 , ppm from internal TMS, T 298 K): δ 190.49 ($\text{C}\equiv\text{O}$), 125.322 ($\text{C}_{4,7}$), 119.407 ($\text{C}_{5,6}$), 117.873 ($\text{C}_{3a,7a}$), 98.167 (C_2), 76.016 ($\text{C}_{1,3}$).

3.3. $[\text{Rh}_2(\text{CO})_2(\mu\text{-CO})(\eta\text{-indenyl})_2]$, **B**

The complex was obtained by warming $\text{Rh}(\text{CO})_2$ -(η -indenyl) (50 mg) in a Schlenk tube in vacuo for 2 h at 50°C . A dark-red powder was obtained in quantitative yield. M.p. 130°C (decomp.); $\nu_{\text{max}}(\text{THF})$ (cm^{-1}): 1980, 1834 ($\text{C}\equiv\text{O}$). m/z 520 (M^+). ^1H -NMR (CD_2Cl_2 , ppm from internal TMS): T 298 K, δ 7.208 (m, 2H, $\text{H}_{4,7}$), 7.017 (m, 2H, $\text{H}_{5,6}$), 5.845 (m, 1H, H_2), 5.625 (m, 2H, $\text{H}_{1,3}$). T 178 K, δ 7.22 and 7.04 (2m, 1H each, H_4 and H_7), 7.00 and 6.88 (2m, 1H each, H_5 and H_6), 5.81 (m, 1H, H_2), 6.24 and 4.86 (2 broad m, 1H each, H_1 and H_3). ^{13}C -NMR (CD_2Cl_2 , ppm from internal TMS) T 298 K, δ 125.066 ($\text{C}_{4,7}$), 119.121 ($\text{C}_{5,6}$), 115.571 ($\text{C}_{3a,7a}$), 95.257 (C_2), 79.825 ($\text{C}_{1,3}$). T 178 K, δ 223 (broad, terminal $\text{C}\equiv\text{O}$), 191 (broad, bridging $\text{C}\equiv\text{O}$), 125.159 and 124.873 (C_4 and C_7), 119.173 and 118.816 (C_5 and C_6),

116.666 and 112.901 (C_{3a} and C_{7a}), 95.327 (C_2), 80.010 and 77.708 (C_1 and C_3).

3.4. $[Rh_3(\mu-CO)_3(\eta-indenyl)_3]$, **C**

The complex was obtained by refluxing overnight $Rh(CO)_2(\eta-indenyl)$ (40 mg) in *n*-heptane (10 ml). A dark-green precipitate separates on cooling in quantitative yield. M.p. 170°C (decomp.); $\nu_{max}(THF)$ (cm^{-1}): 1860.8, 1816.5 ($C=O$); $\nu_{max}(CH_2Cl_2)$ (cm^{-1}): 1855.2, 1809.4 ($C=O$). m/z 738 (M^+). ^1H-NMR (CD_2Cl_2 , ppm from internal TMS): δ 7.276 (m, 2H, $H_{4,7}$), 7.177 (m, 2H, $H_{5,6}$), 5.652 (m, 1H, H_2), 5.510 (m, 2H, $H_{1,3}$). $^{13}C-NMR$ (CD_2Cl_2 , ppm from internal TMS, T 298 K): δ 125.221 ($C_{4,7}$), 120.763 ($C_{5,6}$), 116.572 ($C_{3a,7a}$), 95.669 (C_2), 84.714 ($C_{1,3}$). No carbonyl resonances have been observed.

3.5. Isomerization reactions

3.5.1. Thermal reaction of $Rh(CO)_2(\eta-indenyl)$, **A**

A 10^{-2} M solution of **A** in CD_2Cl_2 in a 5 mm NMR sample tube was deoxygenated carefully, saturated with purified argon and the tube tightly closed. The sample was then warmed at 50°C (external bath) and checked at different times (at room temperature) by ^1H-NMR spectroscopy. The relative percentage of the present species was obtained by signal integration. After 2 days, the spectrum of the solution did not change further, and it is shown in Fig. 1. When the tube was opened and CO bubbled in, the spectrum of pure **A** was obtained within few minutes.

3.5.2. Thermal reaction of

$[Rh_2(CO)_2(\mu-CO)(\eta-indenyl)_2]$, **B**

By using the same procedure described above, after 5 h a 1:1 mixture of the monomer **A** and the trimer $[Rh_3(\mu-CO)_3(\eta-indenyl)_3]$, **C**, was obtained. Bubbling CO restored pure **A**.

3.6. Crystallography

Crystals suitable for diffractometric analysis were obtained by slow precipitation at low temperature from saturated solutions of **B** in methylene chloride. Crystal data, intensity data collection and processing details are presented in Table 3. The data were obtained with a Philips PW-100 four-circle automated diffractometer with a graphite monochromator. Standard centering and autoindexing procedures indicated a monoclinic lattice, space group $P2_1/c$ (no. 14). The orientation matrix and accurate unit cell dimensions were determined from angular settings of 25-high angle reflections. Intensity data were collected at 25°C using the 2θ scan method. Two reference reflections, monitored periodically, showed no significant variation in intensity.

Table 3

Data collection and structure refinement parameters for the complex $[Rh_2(\mu-CO)(CO)_2(\eta-indenyl)_2]$, **B**

Formula	$C_{21}H_{14}O_3Rh_2$
M	520.15
Space group	$P2_1/c$
a (Å)	13.160(2)
b (Å)	9.494(1)
c (Å)	14.812(2)
α (°)	90
β (°)	99.1(1)
γ (°)	90
V (Å ³)	1828.44(66)
Z	4
Crystal dimensions (mm)	$0.2 \times 0.2 \times 0.3$
D_{calc} ($g\ cm^{-3}$)	1.89
μ (cm^{-1})	142.36
T (K)	298
Radiation ($\lambda/\text{Å}$)	Cu-K $_{\alpha}$ (1.5418)
Take off angle (°)	3
Scan speed (deg min ⁻¹)	2.0 in 2θ scan mode
Scan width (°)	1.2
2θ range (°)	$2.0 \leq 2\theta \leq 45$
Unique reflections ($F_o^2 > 2\sigma(F_o^2)$)	1840
R (on F_o)	0.062
R_w	0.064
Goodness-of-fit	0.694

Data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied to the intensities (Ψ scan). Rh atoms were determined from the three-dimensional Patterson function. All the remaining atoms, including hydrogens, were located from successive Fourier maps using SHELX-76 [17]. Anisotropic thermal parameters were used for all the non-hydrogen atoms. Blocked-cascade least-square refinements converged to R 0.062. The positional parameters of the non-hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, the positional parameters of the hydrogen atoms, full lists of bond lengths and angles, and a list of the calculated and observed structure factors are available as supplementary material.

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