Synthesis and Characterization of η^6-Cr(CO)$_3$-Indenyl-η^3-rhodium-η^4-C$_8$H$_{12}$: an η^3 : η^6 Co-ordination for the Indenyl Ligand

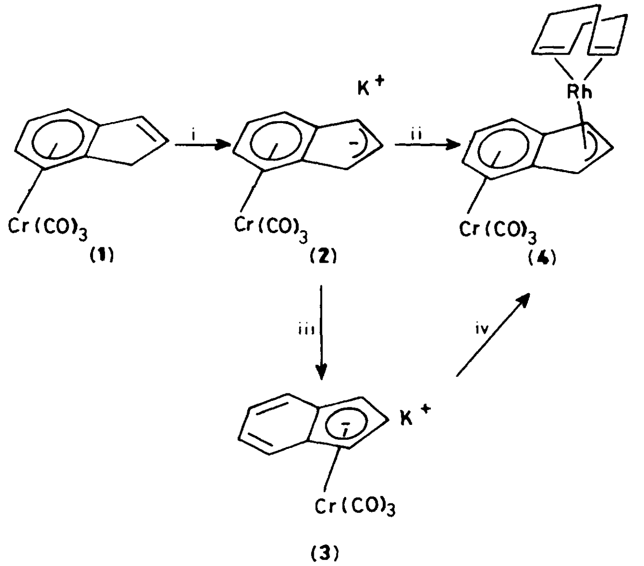
Alberto Ceccon,[a] Alessandro Gambaro,[a] Saverio Santi,[a] Giovanni Valle,[b] and Alfonso Venzo[a]

[a] Department of Physical Chemistry and [b] Department of Organic Chemistry, University of Padova, Via Loredan, 2 - 35131 Padova, Italy

Deprotonation of indene–tricarbonylchromium with KH in tetrahydrofuran at −40 °C gives the η^6-tricarbonylchromium–indenyl anion which reacts with [Rh(Cl)COD]$_2$ (COD = cyclo-octa-1,5-diene) to form [η^6-Cr(CO)$_3$-indenyl-η^3-rhodium-η^4-COD]; the same bimetallic complex is obtained by reaction of the rhodium dimer with the isomeric η^5-indenyl-tricarbonylchromium anion.

In recent years, much attention has been devoted to the chemistry of indenyl–metal complexes.[1] The huge rate enhancement for carbonyl substitution by triphenylphosphine in the indenyl complexes of rhodium and manganese over the corresponding cyclopentadienyl compounds has been attributed to the re-aromatisation of benzene in the transition state and stabilization of an allyl-ene intermediate.[2] The slippage from an η^5- to an η^3-bonding mode has been supported by *X*-ray crystallographic data[3] and by barriers to hindered indenyl rotation which correlate with the degree of slip–fold distortion.[4,3b] Finally, the recent isolation of η^3-indenyl complexes of iridium[3b] has provided clear evidence of the 'indenyl effect.'

Here we describe the isolation and properties of a bi-



Scheme 1. *Reagents and conditions:* i, KH/THF, −40 °C; ii, $[Rh(Cl)COD]_2$; iii, heat; iv, $[Rh(Cl)COD]_2$.

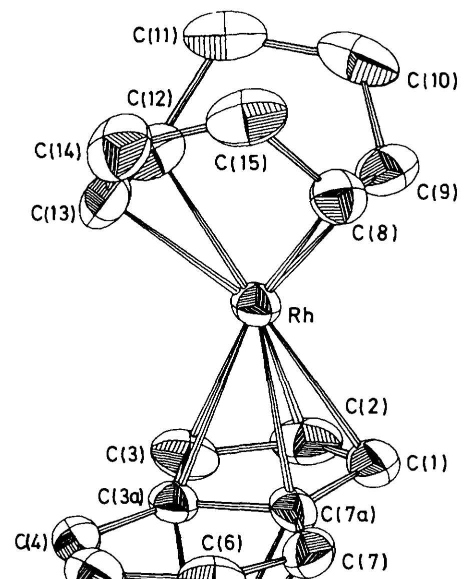


Figure 1. ORTEP view of (**4**). Selected bond lengths (Å): Rh–C(1) 2.231(8), Rh–C(2) 2.248(8), Rh–C(3) 2.236(8), Rh–C(3a) 2.378(7), Rh–C(7a) 2.392(6), Cr–C(7a) 2.331(7), Cr–C(7) 2.237(7), Cr–C(6) 2.211(8), Cr–C(5) 2.221(8), Cr–C(4) 2.245(8), and Cr–C(3a) 2.331(6).

metallic complex in which the indenyl ligand is co-ordinated to tricarbonylchromium at the *benzo* ring, and to rhodium–COD (COD = cyclo-octa-1,5-diene) at the cyclopentadienyl one. As far as we are aware, the only other example of an indenyl ligand co-ordinated at both rings is the rhodium–rhenium complex recently reported by Green *et al.*[5]

Metallation of indene–$Cr(CO)_3$, (**1**),† with potassium hydride under argon at −40 °C produced the η^6-indenyl anion, (**2**) (Scheme 1). Support for the formulation of (**2**) was provided by i.r. and ^1H n.m.r. spectra recorded in $[^2H_8]$tetrahydrofuran (THF) at −20 °C.‡

Treatment of (**2**) with $[Rh(Cl)COD]_2$ gave, after removal of THF, a solid residue which was crystallised from cyclohexane–THF yielding bright orange crystals, soluble in benzene and CH_2Cl_2, of $Cr(CO)_3$-(η^6:η^3-indenyl)Rh-η^4-COD, (**4**). If the solution of (**2**) is warmed to room temperature, the $Cr(CO)_3$ unit migrates to produce the more stable η^5-isomer, (**3**).§¶ Treatment of this species with rhodium dimer gave complex (**4**) again, in which the chromium group had shifted back to the initial η^6-co-ordination, indicating the preference of Rh^I for the allyl site with respect to the diene system. Physical and spectroscopic data for (**4**) agree with the proposed formula.‖

The results of an *X*-ray diffraction study on (**4**) are illustrated in Figure 1.** The $Cr(CO)_3$ and Rh(COD) units

---

† Complex (**1**) was prepared by heating indene with $(NH_3)_3Cr(CO)_3$ in dioxane at reflux under argon. It was characterized by ^1H n.m.r., i.r., and mass spectra and elemental analysis.[6]

‡ *Spectroscopic data* for complex (**2**): i.r., $\nu_{max.}$(THF) 1922, 1828, and 1807 cm^{-1} (C≡O); ^1H n.m.r. ($[^2H_8]$THF, 253 K, 80.13 MHz) δ 5.72 (2H, d, $J(H_1–H_2) = J(H_2–H_3) = 3.6$ Hz, $H_{1,3}$], 6.87 [1H, t, $J(H_1–H_2)$ 3.6 Hz, H_2], 6.39 and 4.86 [2H each, AA′BB′, m, $J(H_4–H_5) = J(H_6–H_7) = 6.9$, $J(H_5–H_6)$ 5.5 Hz, $H_{4,7}$ and $H_{5,6}$, respectively].

§ Quenching of both (**2**) and (**3**) with H_2O regenerates $Cr(CO)_3$–indene. *Spectroscopic data* for complex (**3**): i.r. data, $\nu_{max.}$(THF) 1896, 1793, and 1751 cm^{-1} (C≡O); ^1H n.m.r. ($[^2H_8]$THF, 298 K, 80.13 MHz) 4.85 [2H, d, $J(H_1–H_2) = J(H_2–H_3) = 2.9$ Hz, $H_{1,3}$], 4.76 [1H, t, $J(H_1–H_2)$ 2.9 Hz, H_2], 7.24 and 6.56 [2H each, AA′BB′, m, $J(H_4–H_5) = J(H_6–H_7) = 8.6$, $J(H_5–H_6)$ 6.47 Hz, $H_{4,7}$ and $H_{5,6}$, respectively].

¶ The activation parameters for the $\eta^6 \rightleftharpoons \eta^5$ haptotropic rearrangement have been measured and will be published elsewhere.

‖ Complex (**4**): yield 51%; m.p. 168—172 °C (decomp.); satisfactory elemental analyses were obtained; *m/z* 462. *Spectroscopic data*: u.v., $\lambda_{max.}$ (log ε) (CH_2Cl_2) 251(4.44), 321sh(4.10), 346(4.16), and 432(3.80) nm; i.r., $\nu_{max.}$(CH_2Cl_2) 1949, 1877, and 1854 cm^{-1} (C≡O); ^1H n.m.r. ($[^2H_6]C_6H_6$, 298 K, 80.13 MHz) δ 4.31 [2H, d, $J(H_1–H_2) = J(H_2–H_3) = 3.0$ Hz, $H_{1,3}$], 5.74 [1H, dt, $J(H_1–H_2) = J(H_2–H_3) = 3.0$, $J(^{103}Rh–H_2)$ 2.1 Hz, H_2), 4.56 and 5.26 [2H each, AA′BB′, m, $J(H_4–H_5) = J(H_6–H_7) = 6.6$ Hz, $H_{5,6}$ and $H_{4,7}$, respectively], no hyperfine coupling between the $H_{1,3}$ and ^{103}Rh nuclei was detected; ^{13}C n.m.r. (100.62 MHz) 234.87 (C≡O), 104.19 ($^1J_{C–H}$ 177, $^1J_{Rh–C}$ 5.4 Hz, C_2), 90.49 ($^1J_{C–H}$ 176 Hz, $C_{5,6}$), 87.52 ($^1J_{Rh–C}$ 2.2 Hz, $C_{3a,7a}$), 85.97 ($^1J_{C–H}$ 176 Hz, $C_{4,7}$), 75.19 ($^1J_{C–H}$ 180, $^1J_{Rh–C}$ 4.5 Hz, $C_{1,3}$), 71.33 ($^1J_{C–H}$ 155, $^1J_{Rh–C}$ 13.0 Hz, =*C*–H in C_8H_{12}), and 31.44 ($^1J_{C–H}$ 129 Hz, –CH_2 in C_8H_{12}).

** *Crystal data* for (**4**): $C_{20}H_{19}CrO_3Rh$, $M = 462.3$, triclinic, space group $P\bar{1}$, $a = 12.074(2)$, $b = 11.651(1)$, $c = 6.533(1)$ Å; $\alpha = 96.4(1)$, $\beta = 97.9(1)$, $\gamma = 96.7(1)°$, $U = 896.6$ Å^3, $Z = 2$, $D_c = 1.712$ g cm^{-3}. A total of 4329 unique reflections were read on a Philips PW 110 four circle diffractometer in the θ–2θ scan mode to 2θ = 50° using Mo-K_α radiation (λ = 0.71069 Å), $w = 1$. No corrections for absorption were made. The structure was resolved with Patterson and Fourier synthesis. The refinement was carried out by anisotropic full-matrix least-squares methods for all the non-hydrogen atoms. The hydrogen atoms were located on a Δ*F* map and refined with the thermal parameter '*U*' isotropic. The final conventional *R* factor for the 2991 considered observed reflections with $I > 3\sigma(I)$ was 0.0478. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

are situated *trans* to the indenyl ligand. The dihedral 'fold' angle between the C(1)–C(2)–C(3) plane and the C(3)–C(3a)–C(7a)–C(1) least-squares plane in the five membered ring is 8.2° with the phenylene frame folded away from the Rh atom. The Rh–C distances to the quaternary carbons C(3a) and C(7a) are slightly longer than those to the allylic carbons C(1), C(2), and C(3), the difference between the average of the two sets of metal–carbon bond distances being $\overline{\Delta M\text{–}C} = 0.15$ Å.[1c] Similar distortions have been observed in other rhodium complexes where the indenyl ligand exhibits a pronounced η^3 hapticity.[1c,3b] The pattern of the Cr–arene distances is very similar to that observed for other neutral bicyclic η^6-$Cr(CO)_3$–benzenoid complexes, and the $Cr(CO)_3$ group adopts an *exo* conformation.[7]

The extent of allyl-ene distortion in indenyl transition metal complexes can also be evaluated by taking into account the $\Delta\delta_{^{13}C} = \delta_{C(1,3)} - \delta_{C(2)}$ value, which ranges from −7.9 p.p.m. for the (bis-η^5-indenyl)Fe^{II} to −39.0 p.p.m. for the (bis-η^3-indenyl)Ni^{II}:[8] *i.e.*, a more negative value of $\Delta\delta_{^{13}C}$ corresponds to a higher degree of η^3-allyl character of the co-ordination bond. Therefore, a well advanced degree of η^3-allyl bonding of rhodium to the indenyl frame in **(4)** is strongly supported by the value of $\Delta\delta_{^{13}C} = -29.0$ p.p.m. Analogous conclusions can be drawn for the rhodium–rhenium complex described by Green *et al.*[5] for which a value of $\Delta\delta_{^{13}C} = -26.4$ p.p.m. can be calculated. In addition, the more negative $\Delta\delta_{^{13}C}$ value in **(4)** with respect to that found for the mono-metallic indenyl-rhodium-COD complex, $\Delta\delta_{^{13}C} = -16.4$ p.p.m.,[††] clearly indicates that the rhodium unit is forced towards η^3-hapticity when the benzo ring is engaged in co-ordination with the $Cr(CO)_3$ group. This trend is induced by the strong co-ordination ability of the tricarbonylchromium unit *versus* π-electron sextets.[10]

We thank the C.N.R. (Rome) for financial support.

Received, 20th June 1988; Com. 8/02436G

References

1 (a) J. W. Faller, R. H. Crabtree, and A. Habib, *Organometallics*, 1985, **4**, 929; (b) C. P. Casey and J. M. O'Connor, *ibid.*, 1985, **4**, 384; (c) R. T. Baker and T. H. Tulip, *ibid.*, 1986, **5**, 839; (d) J. M. O'Connor and C. P. Casey, *Chem. Rev.*, 1987, **87**, 307.

2 M. E. Rerek, Liang-Nian Ji, and F. Basolo, *J. Chem. Soc., Chem. Commun.*, 1983, 1208.

3 (a) J. S. Merola, R. T. Kacmarcik, and D. Van Engen, *J. Am. Chem. Soc.*, 1986, **108**, 329; (b) T. B. Marder, J. C. Calabrese, D. C. Roe, and T. H. Tulip, *Organometallics*, 1987, **6**, 2012; (c) M. Mlekuz, P. Bougeard, B. G. Sayer, M. J. McGlinchey, C. A. Rodgers, M. R. Churchill, J. W. Ziller, Sung-Kwon Kong, and T. A. Albright, *ibid.*, 1986, **5**, 1656.

4 R. D. Barr, M. Green, T. B. Marder, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1261.

5 M. L. H. Green, N. D. Lowe, and D. O'Hare, *J. Chem. Soc., Chem. Commun.*, 1986, 1547.

6 A. N. Nesmeyanov, N. A. Ustynyuk, L. G. Makarova, S. Andre, Y. A. Ustynyuk, L. N. Novikova and Y. N. Luzikov, *J. Organomet. Chem.*, 1978, **154**, 45.

7 T. A. Albright, P. Hoffmann, R. Hoffman, G. P. Lillya, and P. A. Dobosh, *J. Am. Chem. Soc.*, 1983, **105**, 3396.

8 F. H. Köhler, *Chem. Ber.*, 1974, **107**, 570.

9 D. T. Clark, M. Mlekuz, B. G. Sayer, B. E. McCarry, and M. J. McGlinchey, *Organometallics*, 1987, **6**, 2201.

10 A. Ceccon, A. Gambaro, and A. Venzo, *J. Organomet. Chem.*, 1985, **281**, 221; A. Ceccon, A. Gambaro, A. Romanin, and A. Venzo, *ibid.*, 1982, **239**, 345; A. Ceccon, A. Gambaro, L. Pizzato, A. Romanin, and A. Venzo, *J. Chem. Soc., Chem. Commun.*, 1982, 907.

[††] The ^1H n.m.r. data for the indenyl-rhodium-COD complex agree with the literature.[9] ^{13}C N.m.r. data ($[^2H_2]CH_2Cl_2$, 100.62 MHz): 119.66 ($^1J_{C\text{–}H}$ 170 Hz, $C_{5,6}$), 113.61 ($^1J_{Rh\text{–}C}$ 2.4 Hz, $C_{3a,7a}$), 112.71 ($^1J_{C\text{–}H}$ 170 Hz, $C_{4,7}$), 92.90 ($^1J_{C\text{–}H}$ 173, $^1J_{Rh\text{–}C}$ 4.9 Hz, C_2), 76.52 ($^1J_{C\text{–}H}$ 173, $^1J_{Rh\text{–}C}$ 4.6 Hz, $C_{1,3}$, 67.87 ($^1J_{C\text{–}H}$ 155, $^1J_{Rh\text{–}C}$ 13.4 Hz, =*C*–H in C_8H_{12}), and 31.70 ($^1J_{C\text{–}H}$ 127 Hz, –*C*H_2 in C_8H_{12}).