The Hapticity of η-Indenyl Complexes: Molecular Structures of [(η^5-C_9R_7)Rh(η^4-cod)] (R = H, Me) (cod = Cyclo-octa-5-diene)

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The molecular structures of [(η^5-C_9R_7)Rh(η^4-cod)] [R = H (**2**); R = Me (**3**); cod = cyclo-octa-1,5-diene] are reported along with a discussion of the distinction between η^5- and η^3-indenyl co-ordination modes; a recent assertion that co-ordination of $Cr(CO)_3$ to the benzo ring of (**2**) induces enhanced ground-state slippage of the Rh(η^4-cod) moiety is not borne out by the structures of (**2**) and (**3**).

It has been demonstrated that [(η-indenyl)ML_2] complexes (M = Co, Rh; L = alkene) display significantly enhanced catalytic activity in inter-molecular hydroacylation reactions,[1] cyclo-trimerisation of alkynes to benzenes,[2] and cyclo-co-trimerisation of alkynes and nitriles to pyridines[3] compared with their cyclopentadienyl analogues. It is also known that [(η-indenyl)ML_n] complexes show enhanced reactivity in both S_N1[4] and S_N2[4—7] substitution reactions. Recent kinetic studies[4,6] and the isolation and structural characterisation[8—10] of several [(η^3-C_9H_7)ML_n] complexes point to the relative ease

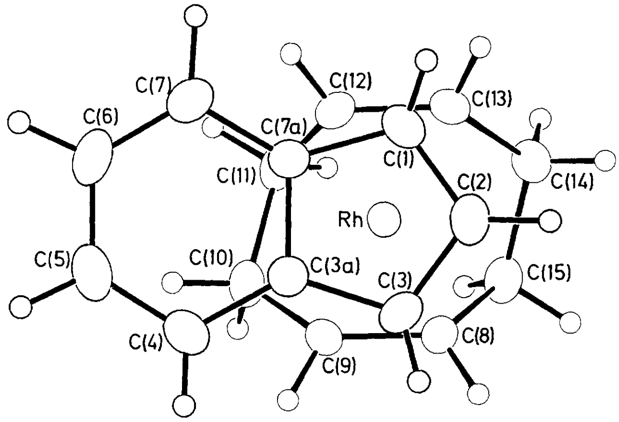

Figure 1. Molecular structure of (**2**). Selected distances (Å) and angles (°): Rh–C(1) 2.221(2), Rh–C(2) 2.245(2), Rh–C(3) 2.211(3), Rh–C(3a) 2.362(2), Rh–C(7a) 2.373(2), Rh–C(8) 2.137(2), Rh–C(9) 2.120(2), Rh–C(12) 2.133(2), Rh–C(13) 2.117(3), C(1)–C(2) 1.406(4), C(1)–C(7a) 1.448(3), C(2)–C(3) 1.409(3), C(3)–C(3a) 1.444(4), C(3a)–C(7a) 1.429(3), C(8)–C(9) 1.408(3), C(12)–C(13) 1.405(4), Δ = 0.152(3) Å {[average of Rh–C(3a),C(7a)]–[average of Rh–C(1), C(3)]}, hinge angle = 8.90° between planes C(1), C(2), C(3), and C(1), C(3), C(3a), C(7a), fold angle = 7.38° between planes C(1), C(2), C(3) and C(3a), C(4), C(5), C(6), C(7), C(7a), L–M–L angle = 87.6(1)° = mid [C(8)–C(9)]–Rh–mid [C(12)–C(13)].

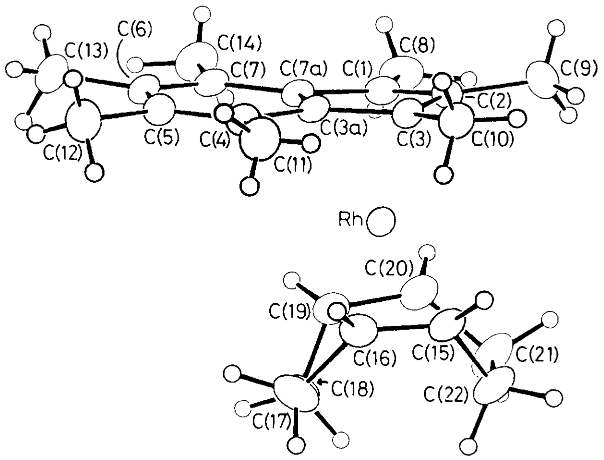

Figure 2. Molecular structure of (**3**). Selected distances (Å) and angles (°): Rh–C(1) 2.215(3), Rh–C(2) 2.231(3), Rh–C(3) 2.206(3), Rh–C(3a) 2.347(3), Rh–C(7a) 2.381(3), Rh–C(15) 2.121(3), Rh–C(16) 2.119(3), Rh–C(19) 2.121(3), Rh–C(20) 2.106(3), C(1)–C(2) 1.422(4), C(1)–C(7a) 1.461(4), C(2)–C(3) 1.418(4), C(3)–C(3a) 1.456(4), C(3a)–C(7a) 1.438(4), C(15)–C(16) 1.388(5), C(19)–C(20) 1.393(5), Δ = 0.153(3) Å, hinge angle = 9.50°, fold angle = 9.95°, L–M–L angle = 87.6(1)°; Δ, hinge angle, and fold angle as defined in Figure 1; L–M–L angle = mid [C(15)–C(16)]–Rh–mid [C(19)–C(20)].

of slippage of the indenyl ring from η^5 to η^3 during S_N2 substitutions. We[11] and others[5,12—15] have found significant slip-distortions from η^5 towards η^3 co-ordination in the ground state of all d^8-[(η-C_9H_7)RhL_2] complexes. It should be emphasized, however, that none of the RhL_2 species is actually an η^3 complex in the ground-state. A recent publication,[16] claiming '$\eta^3:\eta^6$ co-ordination' for an indenyl ligand highlights such a misconception of hapticity which is more than semantic. In addition, this paper[16] suggests that co-ordination of $Cr(CO)_3$ to the 'benzo ring' is responsible for an increased slip-fold distortion in [$Cr(CO)_3$(μ-η^6:η^n-C_9H_7)Rh(η^4-cod)] (**1**) with respect to [(η^5-C_9H_7)Rh(η^4-cod)] (**2**) (cod = cyclo-octa-1,5-diene).[17] We report herein the molecular structures of (**2**) and [(η^5-C_9Me_7)Rh(η^4-cod)] (**3**) which demonstrate unambiguously that neither the $Cr(CO)_3$ moiety in (**1**) nor permethylation of the indenyl ring affect the degree of ground-state slip distortion in [(η^5-indenyl)Rh(η^4-cod)] complexes. In addition, we demonstrate that there is a clear distinction between η^5- and η^3-indenyl complexes. Complex (**3**) is the first structurally characterized compound containing an η-C_9Me_7 ligand.

[$Cr(CO)_3$(μ-η^6:η^n-C_9H_7)Rh(η^4-cod)]
(**1**)

[(η^5-C_9R_7)Rh(η^4-cod)]
(**2**) R = H
(**3**) R = Me

[(η^3-C_9H_7)Ir(PMe_2Ph_3)]
(**4**)

[(η^3-C_9H_7)$Fe(CO)_3$]$^-$
(**5**)

[(η^3-C_9H_7)(η^5-C_9H_7)$W(CO)_2$]
(**6**)

[(η-C_9H_7)$_2V(CO)_2$]
(**7**)

[(η-C_9H_7)$_2$Ni]
(**8**)

The molecular structures† of (**2**) and (**3**) are presented in Figures 1 and 2 respectively. Relevant data for (**1**)[16] are: 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) Å. None of these Rh–C(indenyl) distances is significantly different from those in (**2**), and the values for (**3**) are also similar. The values of the slip parameter Δ (see Figure 1) for (**1**)—(**3**) are 0.151(8), 0.152(3), and 0.154(3) Å, and the hinge angles[11,13] are 8.2,‡ 8.9, and 9.5° respectively. Thus, co-ordination of Rh to the indenyl ring is essentially invariant in (**1**), (**2**), and (**3**).

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† *Crystal data*, collection and refinement for (**2**): $RhC_{17}H_{19}$, M = 326.246, monoclinic, space group $C2/c$, a = 15.625(2), b = 6.430(1), c = 26.882(5) Å, β = 100.681(1)°, U = 2654.0(7) Å^3, Z = 8, D_c = 1.633 g cm^{-3}, F(000) = 1328, T = 294 ± 1 K, λ = 0.71073 Å, μ(Mo-K_α) = 12.31 cm^{-1}. Data were collected from an epoxy-coated crystal of dimensions 0.27 × 0.28 × 0.31 mm on a Syntex P2$_1$ diffractometer by the ω scan method ($2\theta \leqslant 60°$). From 3857 unique measured reflections corrected for Lorentz and polarisation effects but not for absorption, 3048 with $I \geqslant 3\sigma(I)$ were used in the structure solution (Patterson and Fourier methods) and refinement which converged at R and R_w values of 0.023 and 0.027 respectively.

For (**3**): $RhC_{24}H_{33}$, M = 424.436, monoclinic, space group $P2_1/n$, a = 11.867(1), b = 14.244(1), c = 12.333(1) Å, β = 109.60(1)°, U = 1963.9(3) Å^3, Z = 4, D_c = 1.435 g cm^{-3}, F(000) = 888, T = 294 ± 1 K, λ = 0.71073 Å, μ(Mo-K_α) = 8.52 cm^{-1}. Data were collected from a crystal of dimensions 0.24 × 0.30 × 0.33 mm on a Syntex P2$_1$ diffractometer by the ω scan method ($\theta \leqslant 60°$). From 5725 unique measured reflections corrected for Lorentz and polarisation effects but not for absorption, 3934 with $I \geqslant 3\sigma(I)$ were used in the structure solution (Patterson and Fourier methods) and refinement which converged at R and R_w values of 0.028 and 0.032 respectively. 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.

‡ This angle is referred to as the 'fold angle' in ref. 16.

The results of *ca.* 20 crystal structure determinations[11] in our laboratory on $[(\eta^5\text{-}C_9H_{7-n}\,Me_n)RhL_2]$ complexes combined with those in refs. 5,12—14 demonstrate, for a wide variety of ligands L, a range of Δ values of 0.112(2)—0.227(3) Å.§ Clearly these are all formally η^5-complexes in that there is significant bonding of Rh to C(3a) and C(7a). For comparison, consider the values of Δ = 0.79(1), 0.689(7), and 0.72(2) Å respectively for complexes (**4**),[8] (**5**),[9] and (**6**).[10] Although hinge angles were not reported for (**4**—**6**), the fold angles are 28, 22, and 26° for the η^3-indenyl ligands. Thus, both the slip and fold distortions are extremely large for (**4**—**6**) and there is clearly no bonding between the metal atom and C(3a) or C(7a), as required to attain an 18e configuration at the metal. Interestingly, in $[(C_9H_7)_2\,V(CO)_2]$ (**7**),[18] Δ = 0.493(3) and 0.120(3) Å for the two different indenyl rings. The intermediate value of 0.493(3) Å presumably reflects the 17 or 19e configurations which would be attained by η^3- or η^5-coordination of this ring system.

Finally, until structural evidence¶ is in hand for $[(\eta\text{-}C_9H_7)_2Ni]$ (**8**), it is premature to utilize ^{13}C n.m.r. data for this complex as indicative of η^3-bonding. It is highly likely that (**8**) contains either one η^5- and one η^3-ring undergoing rapid exchange in solution [*cf.* (**6**)] or two rings exhibiting intermediate degrees of distortion.

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References

1 T. B. Marder, D. C. Roe, and D. Milstein, *Organometallics*, 1988, **7**, 1451.

2 P. Caddy, M. Green, L. E. Smart, and N. White, *J. Chem. Soc., Chem. Commun.*, 1978, 839; A. Borrini, P. Diversi, G. Ingrosso, A. Lucherini, and G. Serra, *J. Mol. Catal.*, 1985, **30**, 181.

3 H. Bonneman, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 248; H. Bonneman and W. Brijoux, in 'Aspects of Homogeneous Catalysis, Vol. 5,' ed. R. Ugo, D. Reidel, Dordrecht, 1984, p. 75.

4 C. White and R. J. Mawby, *Inorg. Chim. Acta*, 1970, **4**, 261; C. White, R. J. Mawby, and A. J. Hart-Davis, *ibid.*, 1970, **4**, 441; D. J. Jones and R. J. Mawby, *ibid.*, 1972, **6**, 157; N. N. Turaki, J. M. Huggins, and L. Lebioda, *Inorg. Chem.*, 1988, **27**, 424.

5 P. Caddy, M. Green, E. O'Brien, L. E. Smart, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1980, 962; *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 648.

6 M. E. Rerek and F. Basolo, *J. Am. Chem. Soc.*, 1984, **106**, 5908; L.-N. Ji, M. E. Rerek, and F. Basolo, *Organometallics*, 1984, **3**, 740; M. E. Rerek, L.-N. Ji, and F. Basolo, *J. Chem. Soc., Chem. Commun.*, 1983, 1208; A. J. Hart-Davis and R. Mawby, *J. Chem. Soc. A*, 1969, 2403.

7 T. B. Marder and I. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1987, 1478; A. K. Kakkar, N. J. Taylor, and T. B. Marder, *Organometallics*, 1989, **8**, 1765.

8 J. S. Merola, R.-T. Kacmarcik, and D. Van Engen, *J. Am. Chem. Soc.*, 1986, **108**, 329.

9 T. C. Forschner, A. R. Cutler, and R. K. Kullnig, *Organometallics*, 1987, **6**, 889.

10 A. W. Nesmeyanov, N. A. Ustynyuk, L. G. Makarova, V. G. Andrianov, Yu. T. Struchkov, S. Andrae, Yu. A. Ustynyuk, and S. G. Malyugina, *J. Organomet. Chem.*, 1978, **159**, 189.

11 T. B. Marder, J. C. Calabrese, D. C. Roe, and T. H. Tulip, *Organometallics*, 1987, **6**, 2012; R. T. Carl, R. P. Hughes, A. L. Rheingold, T. B. Marder, and N. J. Taylor, *ibid.*, 1988, **7**, 1613; A. K. Kakkar, N. J. Taylor, J. C. Calabrese, W. A. Nugent, D. C. Roe, E. A. Connaway, and T. B. Marder, *J. Chem. Soc., Chem. Commun.*, 1989, 990; A. K. Kakkar, S. Westcott, N. J. Taylor, and T. B. Marder, unpublished results; A. K. Kakkar, T. B. Marder, T. M. Frankcon, A. Nagy, and J. C. Green, unpublished results.

12 M. Mlekuz, P. Bougeard, B. G. Sayer, M. J. McGlinchey, C. A. Rodger, M. R. Churchill, J. W. Ziller, S.-W. Kanz, and T. A. Albright, *Organometallics*, 1986, **5**, 1656.

13 R. T. Baker and T. H. Tulip, *Organometallics*, 1986, **5**, 839.

14 Y. N. Al-Obaidi, P. K. Baker, M. Green, N. D. White, and G. E. Taylor, *J. Chem. Soc., Dalton Trans.*, 1981, 2321.

15 (M = Ir) J. S. Merola, personal communication to T.B.M.; see also: J. S. Merola and R. T. Kacmarcik, *Organometallics*, 1989, **8**, 778.

16 A. Ceccon, A. Gambaro, S. Santi, G. Valle, and A. Venzo, *J. Chem. Soc., Chem. Commun.*, 1989, 51.

17 H. Eshtiagh-Hosseni and J. F. Nixon, *J. Less Common Metals*, 1978, **61**, 107.

18 R. M. Kowaleski, A. L. Rheingold, W. C. Trogler, and F. Basolo, *J. Am. Chem. Soc.*, 1986, **108**, 2460.

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§ Detailed experimental and theoretical analysis of the relationship between Δ and L (*cf.* ref. 11) and reactivity, i.r., and photoelectron spectroscopic studies of the relative donor abilities of a series of $[C_9H_{7-n}Me_n]^-$ ligands will form the basis for subsequent full papers. The value of Δ = 0.112(2) Å is the result of our redetermination of the structure of $[(\eta^5\text{-}C_9H_7)Rh(\eta\text{-duroquinone})]$; a value of *ca.* 0.05 Å had been obtained previously from film data ($R \approx 9\%$): G. G. Aleksandrov and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 1971, **12**, 120. The value [13] of Δ = 0.227(3) Å is for $[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}PPh_2)_2Rh(\eta^5\text{-}C_9H_7)]$. Others have discussed distortions in earlier transition metal complexes, *e.g.* J. W. Faller, R. H. Crabtree, and A. Habib, *Organometallics*, 1985, **4**, 929; J. M. O'Connor and C. P. Casey, *Chem. Rev.*, 1987, **87**, 307, and references cited therein.

¶ Complex (**8**) was originally reported in F. H. Köhler, *Chem. Ber.*, 1974, **107**, 570. We find that the $^{13}C\{^1H\}$ n.m.r. spectrum of (**8**) is invariant from −100 to +25 °C. Our attempts to obtain a crystal structure of (**8**) at room temperature have been hampered by rapid decomposition of the single crystal. We are currently recollecting diffraction data at −123 °C: S. A. Westcott, N. J. Taylor, and T. B. Marder, unpublished results.