Notes

Synthesis and *X*-Ray Crystal Structure of a Naphthalene Complex of Ruthenium, [Ru(η^6-$C_{10}H_8$)(η^4-cod)] (cod = cyclo-octa-1,5-diene)†

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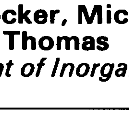
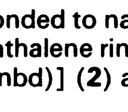
The naphthaleneruthenium complex [Ru(η^6-$C_{10}H_8$)(η^4-cod)] (**1**) (cod = cyclo-octa-1,5-diene) has been synthesised and characterised by *X*-ray crystallography. Compound (**1**) contains a ruthenium atom η^6-bonded to naphthalene and η^4-bonded to a cyclo-octa-1,5-diene ligand. Slip distortions in the naphthalene ring are discussed. Spectroscopic data for the norbornadiene complex [Ru(η^6-$C_{10}H_8$)(η^4-nbd)] (**2**) are also presented.

The chemistry and structural characterisation of transition-metal complexes containing π-bound naphthalene ligands is less well established in comparison with compounds containing the isoelectronic indenyl ligand. The latter class of complexes often show considerably enhanced reactivities with respect to cyclopentadienyl analogues, often termed 'the indenyl effect,' associated with an η^5—η^3 ring slippage which generates a vacant co-ordination site at the metal centre. Evidence for this slippage is provided by the ground-state slip distortions often observed in indenyl complexes,[1] and the origin of the effect is usually discussed in terms of a resonance stabilisation of the unco-ordinated double bond: (**A**) *vs.* (**B**). Although this is probably an oversimplification, a similar situation can be envisaged for naphthalene complexes involving η^6 and η^4 bonding modes, (**C**) and (**D**). Chemical evidence for this process is scarce but the structural data available for naphthalene complexes illustrate the presence of ground-state slip distortions similar to those observed in indenyl complexes. Herein we report the synthesis and structural characterisation of [Ru(η^6-$C_{10}H_8$)(η^4-cod)] (cod = cyclo-octa-1,5-diene).

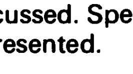


(**A**), η^5

(**B**), η^3



(**C**), η^6



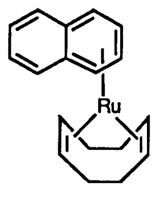
(**D**), η^4

Results and Discussion

The complex [Ru(η^6-$C_{10}H_8$)(η^4-cod)], (**1**) (cod = cyclo-octa-1,5-diene), was synthesised from [{$RuCl_2$(η^4-cod)}$_n$] and 2 equivalents of lithium dihydronaphthylide (Li[$C_{10}H_8$]), in formal accordance with equation (1), and was isolated after

$$\tfrac{1}{n}[\{RuCl_2(\eta^4\text{-cod})\}_n] + 2\,Li[C_{10}H_8] \longrightarrow [Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-cod})] + C_{10}H_8 + 2\,LiCl \quad (1)$$

work up as air-sensitive yellow crystals. Spectroscopic and analytical data were consistent with the anticipated structure and this was confirmed by *X*-ray diffraction, the results of which are shown in the Figure and presented in Tables 1 and 2. The ruthenium atom is η^4-bonded to a cyclo-octa-1,5-diene ligand and η^6-bonded to naphthalene.



(**1**)

The cod adopts a twist-boat or tub conformation, similar to that found in other complexes, *e.g.* [$RuCl_2(py)_2$(η^4-cod)][2] (py = pyridine), [RuH(Cl)(pip)$_2$(η^4-cod)][3] (pip = piperidine), and [$RuCl_2$(CO)(MeCN)(η^4-cod)],[4] which can be defined by two dihedral angles. Thus the angle between the planes defined by C(18), C(11), C(12) and C(11)—C(13) is 3.6° and that between the planes defined by C(15)—C(17) and C(14)—C(16) is 2.3°, both of which would be zero if no twist were present.

The naphthalene ligand is η^6-bonded to the ruthenium centre but shows a slip distortion towards an η^4 mode as indicated by the Ru–C distances; carbons C(1)—C(4) are significantly closer to the ruthenium [2.221(2), 2.276(3), 2.262(3), and 2.205(3), average 2.241 Å] than the ring-junction carbons C(5) and C(10) [2.346(3) and 2.338(2), average 2.342 Å]. A convenient measure of slip distortions in indenyl complexes is the Δ or slip parameter across the bonded face,[5] which for (**1**) is 0.07 Å. Also apparent is a non-planarity associated with the bonded ring which can be described as a bending along the vector defined by C(1) and C(4). This results in an angle of 8.4° between the planes defined by C(1)—C(4) and C(1), C(4), C(5), C(10). Distortions of a similar type and magnitude have also been observed for [$Cr(CO)_3$(η^6-$C_{10}H_8$)],[6] [$Cr(CO)_3$(η^6-$C_{10}H_7NH_2$)],[7] [$Cr(CO)_2${$P(OPh)_3$}(η^6-$C_{10}H_8$)],[8] [$Cr(CO)_3$(η^6-$C_{10}Me_8$)],[9] and [$Fe(Et_2C_2B_4H_4)$(η^6-

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† (η-Cyclo-octa-1,5-diene)[(1,2,3,4,4a,8a-η)-naphthalene]ruthenium(0).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

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$C_{10}H_8)]$.[10] Other structurally characterised naphthalene complexes include $[Cr(\eta^6\text{-}C_{10}H_8)_2]$,[11] where any distortions are masked by disorder, and the η^4-bonded compounds $[TaCl(Me_2PCH_2CH_2PMe_2)_2(\eta^4\text{-}C_{10}H_8)]$[12] and $[Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_{10}Me_8)]$.[13] In the latter two examples complete slippage to an η^4 geometry has occurred with correspondingly large deviations from planarity of the naphthalene ring. The angles of deformation [defined as for complex (**1**)] are 43.0, and 41.5, 43.3° for the tantalum and ruthenium complexes respectively (the latter having two crystallographically independent molecules per asymmetric unit).

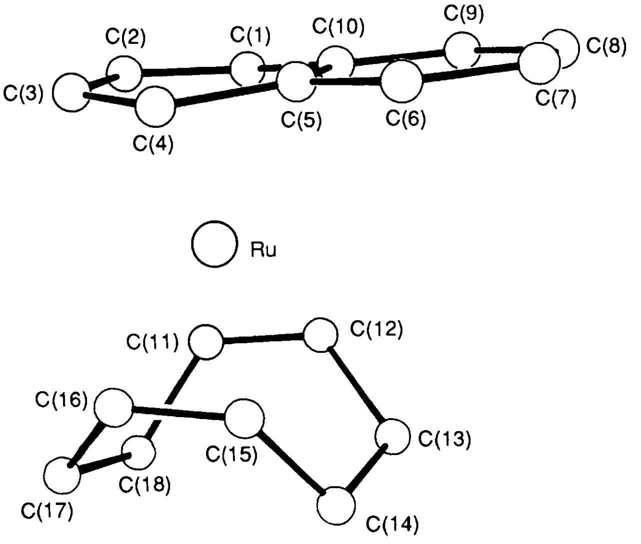
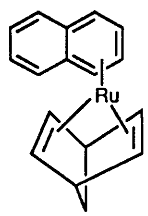


Figure. A view of the molecular structure of complex (**1**) showing the atom numbering scheme. Hydrogen atoms are omitted for clarity



(**2**)

Table 2. Atomic positional (fractional co-ordinates) parameters with e.s.d.s in parentheses for complex (**1**)

Atom	*x*	*y*	*z*
Ru	0.793 03(2)	−0.038 36(2)	0.707 66(2)
C(1)	0.647 9(4)	−0.224 4(3)	0.501 9(3)
C(2)	0.848 7(5)	−0.174 2(3)	0.509 4(3)
C(3)	0.980 2(4)	−0.169 8(4)	0.612 2(3)
C(4)	0.910 5(4)	−0.217 8(3)	0.706 7(3)
C(5)	0.706 0(4)	−0.290 3(3)	0.689 7(3)
C(6)	0.630 5(6)	−0.352 7(4)	0.775 9(3)
C(7)	0.432 1(7)	−0.411 7(4)	0.758 5(5)
C(8)	0.302 8(6)	−0.410 6(4)	0.657 7(5)
C(9)	0.368 6(5)	−0.352 7(3)	0.573 7(4)
C(10)	0.572 3(4)	−0.291 9(3)	0.586 2(3)
C(11)	0.759 9(4)	0.152 9(3)	0.679 7(3)
C(12)	0.593 2(4)	0.078 6(3)	0.712 2(3)
C(13)	0.550 5(5)	0.141 1(5)	0.848 4(4)
C(14)	0.719 4(5)	0.182 6(4)	0.963 4(3)
C(15)	0.853 4(4)	0.092 9(3)	0.919 4(3)
C(16)	1.017 6(4)	0.147 2(3)	0.875 3(3)
C(17)	1.076 4(5)	0.298 1(4)	0.861 5(4)
C(18)	0.911 4(5)	0.311 9(3)	0.778 2(3)

Table 1. Bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex (**1**)

Ru–C(1)	2.221(2)	Ru–C(2)	2.276(3)	C(5)–C(10)	1.423(4)	C(5)–C(6)	1.425(5)
Ru–C(3)	2.262(3)	Ru–C(4)	2.205(3)	C(7)–C(8)	1.395(7)	C(6)–C(7)	1.379(6)
Ru–C(5)	2.346(3)	Ru–C(10)	2.338(2)	C(10)–C(9)	1.426(4)	C(8)–C(9)	1.352(7)
Ru–C(11)	2.132(3)	Ru–C(12)	2.126(3)	C(11)–C(18)	1.539(3)	C(11)–C(12)	1.418(4)
Ru–C(15)	2.141(2)	Ru–C(16)	2.142(2)	C(13)–C(14)	1.518(5)	C(12)–C(13)	1.523(5)
C(1)–C(2)	1.410(4)	C(1)–C(10)	1.438(4)	C(15)–C(16)	1.413(4)	C(15)–C(14)	1.523(5)
C(2)–C(3)	1.394(5)	C(3)–C(4)	1.414(5)	C(18)–C(17)	1.517(5)	C(16)–C(17)	1.526(5)
C(4)–C(5)	1.437(4)						

C(1)–Ru–C(2)	36.5(1)	C(1)–Ru–C(3)	65.5(1)	Ru–C(1)–C(10)	76.1(1)	Ru–C(1)–C(2)	73.9(1)
C(2)–Ru–C(3)	35.8(1)	C(1)–Ru–C(4)	78.1(1)	Ru–C(2)–C(1)	69.6(2)	C(2)–C(1)–C(10)	121.4(3)
C(2)–Ru–C(4)	65.5(1)	C(3)–Ru–C(4)	36.9(1)	C(1)–C(2)–C(3)	119.6(3)	Ru–C(2)–C(3)	71.6(2)
C(1)–Ru–C(5)	65.1(1)	C(2)–Ru–C(5)	76.4(1)	Ru–C(3)–C(4)	69.4(2)	Ru–C(3)–C(2)	72.7(2)
C(3)–Ru–C(5)	65.3(1)	C(4)–Ru–C(5)	36.6(1)	Ru–C(4)–C(3)	73.7(2)	C(2)–C(3)–C(4)	119.6(3)
C(1)–Ru–C(10)	36.6(1)	C(2)–Ru–C(10)	65.1(1)	C(3)–C(4)–C(5)	121.5(3)	Ru–C(4)–C(5)	77.0(2)
C(3)–Ru–C(10)	76.7(1)	C(4)–Ru–C(10)	65.3(1)	Ru–C(5)–C(6)	130.7(2)	Ru–C(5)–C(4)	66.3(2)
C(5)–Ru–C(10)	35.4(1)	C(1)–Ru–C(11)	99.5(1)	Ru–C(5)–C(10)	72.0(1)	C(4)–C(5)–C(6)	123.3(3)
C(2)–Ru–C(11)	100.9(1)	C(3)–Ru–C(11)	124.5(1)	C(6)–C(5)–C(10)	118.4(3)	C(4)–C(5)–C(10)	118.2(3)
C(4)–Ru–C(11)	160.5(1)	C(5)–Ru–C(11)	158.0(1)	C(6)–C(7)–C(8)	120.9(4)	C(5)–C(6)–C(7)	120.0(4)
C(10)–Ru–C(11)	123.5(1)	C(1)–Ru–C(12)	95.8(1)	C(8)–C(9)–C(10)	120.5(3)	C(7)–C(8)–C(9)	120.9(4)
C(2)–Ru–C(12)	119.8(1)	C(3)–Ru–C(12)	155.0(1)	Ru–C(10)–C(5)	72.6(1)	Ru–C(10)–C(1)	67.2(1)
C(4)–Ru–C(12)	159.9(1)	C(5)–Ru–C(12)	123.5(1)	Ru–C(10)–C(9)	129.4(2)	C(1)–C(10)–C(5)	118.6(2)
C(10)–Ru–C(12)	98.4(1)	C(11)–Ru–C(12)	38.9(1)	C(5)–C(10)–C(9)	119.3(3)	C(1)–C(10)–C(9)	122.0(3)
C(1)–Ru–C(15)	160.6(1)	C(2)–Ru–C(15)	157.5(1)	Ru–C(11)–C(18)	115.2(2)	Ru–C(11)–C(12)	70.3(2)
C(3)–Ru–C(15)	122.6(1)	C(4)–Ru–C(15)	98.7(1)	Ru–C(12)–C(11)	70.8(2)	C(12)–C(11)–C(18)	122.6(2)
C(5)–Ru–C(15)	100.9(1)	C(10)–Ru–C(15)	124.7(1)	C(11)–C(12)–C(13)	124.4(2)	Ru–C(12)–C(13)	112.3(2)
C(11)–Ru–C(15)	89.7(1)	C(12)–Ru–C(15)	80.7(1)	C(13)–C(14)–C(15)	112.2(2)	C(12)–C(13)–C(14)	113.2(3)
C(1)–Ru–C(16)	159.8(1)	C(2)–Ru–C(16)	123.4(1)	Ru–C(15)–C(16)	70.8(1)	Ru–C(15)–C(14)	114.6(2)
C(3)–Ru–C(16)	97.8(1)	C(4)–Ru–C(16)	95.2(1)	Ru–C(16)–C(15)	70.7(1)	C(14)–C(15)–C(16)	123.3(3)
C(5)–Ru–C(16)	119.7(1)	C(10)–Ru–C(16)	154.5(1)	C(15)–C(16)–C(17)	124.2(3)	Ru–C(16)–C(17)	112.8(2)
C(11)–Ru–C(16)	80.3(1)	C(12)–Ru–C(16)	96.4(1)	C(11)–C(18)–C(17)	112.0(3)	C(16)–C(17)–C(18)	112.9(2)
C(15)–Ru–C(16)	38.5(1)						

The only other ruthenium–naphthalene complex of which we are aware is $[\mathrm{Ru}(\eta^6\text{-}C_{10}H_8)_2]^{2+}$ prepared by Fischer *et al.*[14] although no structural data have been reported. We have, however, also prepared the norbornadiene complex (**2**) although this is formed in lower yields and is more air- and thermally-sensitive than (**1**). More detailed studies on naphthalene complexes, particularly with regard to reactivity, are in progress and will be reported in a future publication.

Experimental

All experiments were performed using standard Schlenk techniques under an atmosphere of dry, oxygen-free dinitrogen. All solvents were distilled over appropriate drying agents immediately prior to use. Hydrogen-1 and ^{13}C n.m.r. data were recorded on JEOL FX90Q and FX200 spectrometers and were referenced to $SiMe_4$, positive values to high frequency. All materials were procured commercially and used without further purification except for $[\{\mathrm{RuCl}_2(\eta^4\text{-cod})\}_n]$ and $[\{\mathrm{RuCl}_2(\eta^4\text{-nbd})\}_n]$ (nbd = norbornadiene) which were prepared by literature methods.[15]

Preparation of $[\mathrm{Ru}(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-cod})]$, (**1**).—A sample of $[\{\mathrm{RuCl}_2(\eta^4\text{-cod})\}_n]$ (1 g, 3.57 mmol) was suspended in tetrahydrofuran (thf) (20 cm^3) and stirred at room temperature. To this a solution of lithium dihydronaphthylide (7.14 mmol of naphthalene, slight excess of Li) in thf (20 cm^3) was added and the resulting dark green-black mixture was stirred overnight. Most of the solvent was removed by vacuum and a small amount of alumina was then added followed by removal of all the remaining solvent. The resulting black solid was then transferred to an alumina–hexane column and eluted with hexane. A single yellow band moved slowly in hexane but continued elution with hexane was sufficient to remove most of the excess of naphthalene. The yellow product was then brought off the column rapidly with hexane–Et_2O (20:1). Removal of all solvent gave a dark yellow solid from which remaining traces of naphthalene were removed by sublimation. Crystallisation was effected from cooled (−20 °C) saturated solutions in hexane. Typical yields range from 10 to 20%.

On *some* occasions a dark red compound (**1a**) was also observed. This was formed in low yield and could be removed from the column with Et_2O. N.m.r. data are presented but the nature of the compound is unknown and further characterisation was hampered by its unrepeatable formation.

The norbornadiene analogue, $[\mathrm{Ru}(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-nbd})]$, (**2**), was synthesised in an analogous manner to the cod complex using $[\{\mathrm{RuCl}_2(\eta^4\text{-nbd})\}_n]$. However yields were lower ($\simeq 5\%$) and the complex is less stable (both to air and thermally) than the cod analogue, (**1**).

Spectroscopic Data.—Complex (**1**). N.m.r. (C_6D_6): ^1H, δ 7.10 (s, 4 H, unco-ordinated naphthalene), 5.62 and 4.32 (m, 2 H, co-ordinated naphthalene, AA′XX′ spin system), 3.58 (s br, 4 H, cod, CH), and 2.00 (s br, 8 H, cod, CH_2); $^{13}C\text{-}\{^1H\}$, δ 127.2, 126.3 (unco-ordinated naphthalene), 106.1 (ring junction C_2), 91.3, 74.6 (co-ordinated naphthalene), 63.6 (cod, CH), and 33.2 p.p.m. (cod, CH_2) (Found: C, 63.5; H, 6.2. $C_{18}H_{20}Ru$ requires C, 64.1; H, 5.9%).

Complex (**1a**). N.m.r. (C_6D_6): ^1H, δ 4.57 (m, 1 H), 4.27 (m, 1 H), 4.03 (m, 1 H), 3.75 (m, 2 H), 3.34 (s, 1 H), 2.8—2.4 (m br ≈ 9 H), 2.10 (m, 2 H), 1.67 (m, 2 H), and −1.78 (s, 1 H); $^{13}C\text{-}\{^1H\}$, δ 83.0, 82.0, 77.7, 76.2, 74.8, 74.1 (olefinic CH), 34.1, 33.6, 31.6, 31.1, and 30.5 p.p.m. (aliphatic CH).

Complex (**2**). N.m.r. (C_6D_6): ^1H, δ 5.82 and 5.53 (m, 2 H, unco-ordinated naphthalene, AA′XX′ spin system), 4.64 and 2.74 (m, 2 H, co-ordinated naphthalene, AA′XX′ spin system), 3.26 (m, 4 H, nbd, CH), 1.75 and 1.34 (m, 2 H, nbd, CH and CH_2). Incomplete resolution was obtained for complete analysis of the various spin systems in these compounds.

X-*Ray Structure Determination of Complex* (**1**).—Yellow blocks were grown from hexane. Diffracted intensities were collected on a Nicolet $P2_1$ diffractometer at 293 K. Of the 2 862 unique data collected (ω—2θ scans, $3.0 \leqslant 2\theta \leqslant 50.0°$), 2 802 with $I > 3.0\,\sigma(I)$ were used for structure solution and refinement. Data were corrected for Lorentz, polarisation, and crystal decay, but not for absorption.

Crystal data. $C_{18}H_{20}Ru$, M = 337.4, space group $P\bar{1}$ (no. 2), triclinic, a = 7.409(1), b = 10.027(2), c = 11.200(2) Å, α = 112.46(1), β = 96.96(1), γ = 106.35(1)°, U = 713.0(2) $Å^3$, Z = 2, D_c = 1.57 g cm^{-3}, $F(000)$ = 344, Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-K_α) = 10.62 cm^{-1}.

The structure was solved by conventional heavy-atom and Fourier difference methods. All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions 0.96 Å from their respective carbon atoms and allowed to refine with the C–H distance fixed and fixed isotropic thermal parameters. Refinement by blocked-cascade least-squares methods converged smoothly and led to $R = 0.023$ ($R' = 0.024$). A weighting scheme of the form $1/w = (\sigma_F)^2 + 0.000\,42\,|F_o|^2$ (in which σ_F was derived from counting statistics) was introduced in the final stages of refinement. A final electron-density difference map showed no features >0.45 or < −0.33 e $Å^{-3}$. Anomalous dispersion corrections were applied for all atoms and scattering factors were obtained from ref. 16. All computations were performed with the SHELXTL[17] program package.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

We are grateful to the S.E.R.C. for quota studentships (to M. C. and N. C. N.).

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Received 18*th December* 1989; *Paper* 9/05365D