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RHODIUM(I) AND IRIDIUM(I) π-ARENE COMPLEXES OF INDOLE AND OF *N*-INDOLYLGOLD(I) DERIVATIVES. X-RAY STRUCTURE OF [$(Me_3TFB)Rh(\eta^6\text{-HIn})]ClO_4$ (TFB = tetrafluorobenzobarrelene)

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Summary

The preparations of mononuclear rhodium(I) or iridium(I) η^6-indole (HIn) complexes of the type $[(\text{diolefin})M(\eta^6\text{-HIn})]^+$ and heterodinuclear rhodium(I)-gold(I) or iridium(I)-gold(I) indolyl-bridged complexes of the type $[(\text{diolefin})M(\eta\text{-In})AuPR_3]^+$ (M = Rh; diolefin = COD, TFB or Me_3TFB; M = Ir; diolefin = COD) are described. The mononuclear arene derivatives $[(\text{diolefin})Rh(\eta^6\text{-HIn})]ClO_4$ react with methanolic KOH to give the methoxy-bridged dinuclear complexes $[Rh(\mu\text{-OMe})(\text{diolefin})]_2$.

The structure of $[(Me_3TFB)Rh(\eta^6\text{-HIn})]ClO_4$ has been established by X-ray diffraction. In spite of the structural disorder, a $P2_1/m$ space group with lattice constants of 18.0342(26), 8.3061(6), 7.7546(10) Å, β 102.28(2)° could be established. The rhodium atom is η^6-bonded to the puckered six-membered ring of the indole ligand.

Introduction

In recent years the chemistry of arene complexes of transition metals has undergone considerable development. This has mainly been due to interest in the nature of the arene–metal bond [1] and the potential use of these complexes as catalysts for hydrogenation of aromatic substrates under mild conditions [2–5]. Although the chemistry of rhodium [6–8] and iridium [7–9] arene derivatives has been extensively studied, in only few cases were heterocyclic arenes involved [7–8]. We recently reported the structure of rhodium(I) arene complexes [10–13], which exhibit significant non-planarity of the arene ring, and the preparations of heterometallic rhodium(I)-gold(I) complexes containing anionic derivatives of pyrazole [14], imidazole [15], and 2,2′-bibenziimidazole [16] as bridging ligands.

In transition-metal complexes the indole group can act as an *N*-donor ligand [17],

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as η^5-indolyl via its five-membered ring [7,18] or as a η^6-arene via its six-membered ring [7,19,20]. We have now synthesised heterodinuclear rhodium(I)- or iridium(I)-gold(I) complexes in which the rhodium or iridium atoms are π-bonded to the arene ring and the gold atom is σ-bonded to the nitrogen atom. We also describe the preparation of some mononuclear rhodium(I) or iridium(I) indole complexes and present the results of a X-ray diffraction study of the complex $[(Me_3TFB)Rh(\eta^6\text{-}HIn)]ClO_4$.

Part of this work was the subject of a Preliminary Communication [21].

Experimental

The C, H, N analyses were carried out with a Perkin–Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer, using Nujol mulls between polyethylene sheets or KBr pellets, and calibrated with polystyrene. ^1H NMR spectra were recorded on a 80 MHz Varian FT-80A or a 90 MHz Bruker HX-90E spectrometer. Conductivities were measured with a Philips 9501/01 conductimeter in ca. 4×10^{-4} M acetone solutions.

$[RhCl(COD)]_2$ [22], $[RhCl(TFB)]_2$ [23], $[RhCl(Me_3TFB)]_2$ [23], $[IrCl(COD)]_2$ [24] and $Au(In)PR_3$ [21] were prepared as described previously. Solvents were dried and distilled before use. Reactions involving iridium compounds were performed under argon and in the absence of light using deoxygenated solvents. All the reactions were carried out at room temperature.

Preparation of $[(diolefin)Rh(\eta^6\text{-}HIn)]ClO_4$ (diolefin = COD, TFB, Me_3TFB) (I–III)

$[RhCl(diolefin)]_2$ (0.4 mmol), HIn (0.8 mmol) and $AgClO_4$ (0.8 mmol) in 20 ml of acetone were stirred for 30 min. After removal of the precipitated AgCl the filtrate was evaporated to leave a yellow oil, which was dissolved in ca. 2 ml of dichloromethane. Addition of ether (10 ml) to the stirred solution led to precipitation of a yellow solid, which was washed with ether and vacuum-dried.

Preparation of $[(COD)Ir(\eta^6\text{-}HIn)]BF_4$ (IV)

To a solution of $[IrCl(COD)]_2$ (200 mg, 0.298 mmol) and HIn (69.8 mg, 0.596 mmol) in 15 ml of dichloromethane was added $AgBF_4$ (116 mg, 0.596 mmol) in 5 ml of acetone. The mixture was stirred for 30 min, then evaporated. The residue was extracted with 20 ml of dichloromethane, and the solution was filtered, and concentrated to ca. 1 ml under vacuum. Addition of ether gave a tan-coloured solid, which was filtered off, washed with ether, and vacuum-dried.

Preparation of $[(diolefin)Rh(\mu\text{-}In)AuPR_3]ClO_4$ (diolefin = COD, TFB, Me_3TFB; R = C_6H_5, 2-MeC_6H_4, 4-MeC_6H_4) (V–XIII)

A mixture of $[RhCl(diolefin)]_2$ (0.15 mmol), $Au(In)PR_3$ (0.3 mmol) and $AgClO_4$ (0.3 mmol) in dichloromethane/acetone (3/1) was stirred for 30 min. The AgCl was filtered off and the filtrate was evaporated to dryness. The residue was extracted with 10 ml of dichloromethane, and the solution was filtered then evaporated. The residual oil was stirred with 10 ml of ether until a green solid separated out. The solid was filtered off, washed with ether, and vacuum-dried.

Preparation of [(COD)Ir(μ-In)AuPR$_3$]BF$_4$ (R = C$_6$H$_5$, 2-MeC$_6$H$_4$, 4-MeC$_6$H$_4$) (XIV–XVI)

To a solution of [IrCl(COD)]$_2$ (0.1 mmol) and Au(In)PR$_3$ (0.2 mmol) in 15 ml of dichloromethane was added AgBF$_4$ (0.2 mmol). After 30 min stirring the suspension was evaporated to dryness and the residue was extracted with 10 ml of dichloromethane. The solution was filtered and evaporated, leave a dense oil. Addition of ether and vigorous stirring led to precipitation of a deep-red solid, which was filtered off, washed with ether, and vacuum-dried.

Reaction of [(diolefin)Rh(η^6-HIn)]ClO$_4$ with methanolic KOH (diolefin = COD, TFB, Me$_3$TFB)

To a solution of [(diolefin)Rh(η^6-HIn)]ClO$_4$ (0.2 mmol) in 20 ml of methanol was

TABLE 1

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

Crystal data	
Formula	[(Me$_3$TFB)Rh(HIn)]ClO$_4$
Crystal habit	Yellow.Transparent.Prismatic
Size	0.10×0.18×0.33 mm
Symmetry	$2/m$ Monoclinic $P2_1/m$ (See text)
Unit cell determination least-squares fit	35°(θ_{Mx} (Mo) ≤ 20°)
Unit cell dimensions	18.0342(26), 8.3061(6), 7.7546(10) Å, β 102.28(2)°
Packing: V(Å^3), Z	1135.0(2), 2
D(g cm^{-3}), M, (F000)	1.72, 587.76, 588
Experimental data	
Radiation and technique	Cu-K_α; 4-Circle PW 1100 Philips diffactometer; Bisecting geometry
Monochromator	Graphite oriented
Orientation	$0k0$, $\chi \sim 12°$, $\phi \sim 276°$, $h0h$, $\chi \sim 25°$, $\phi \sim 131°$
Collection mode	$\theta \le 65°$
($\omega/2\theta$, 1° × 1°det.apertures)	1.4°scan width, 1 min/ reflex.
Total independent data	2084
Observed data: $2\sigma_c$(I)	1948
Stability	Two reflexions every 90 min; no variation detected
Absorption faces	±(100), ±(120), ±($\bar{1}$12)
μ -Min. and Mx. transmission	0.176–0.503
Solution and refinement	
Solution mode	Patterson
Refinement mode	Least-squares on F's. Observed reflexions only
Final shift/error	0.11
Parameters: no. variables	181
Degrees of freedom	1767
w -scheme	Empirical as to give no trends in $\langle w\Delta^2 \rangle$ vs. $\langle F_0 \rangle$ or $\langle \sin\theta/\lambda \rangle$
Δ F final	0.80
Max. thermal values (Å^2)	$U_{22}(F1) = 0.63(3)$
R, R_w	0.047, 0.055
Atomic factors	[25], International Tables for X-ray Crystallography; Neutral atoms;Anomalous dispersion applied for Rh and Cl

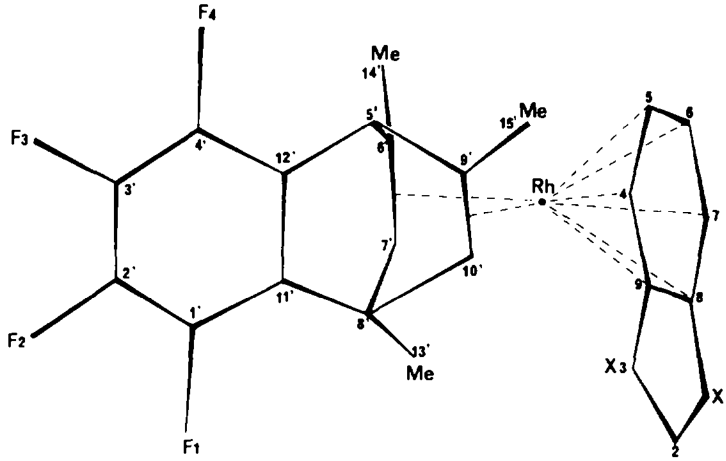


Fig. 1. A view of the studied complex with the atomic numbering (X = C or N, see text).

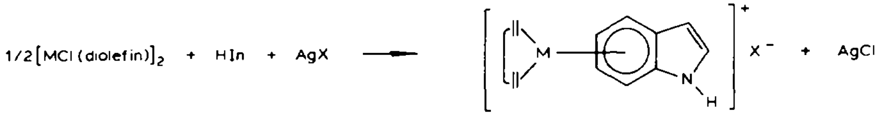
added KOH (0.23 mmol) in 5 ml of methanol. After 30 min stirring the yellow suspension was concentrated to ca. 2 ml. Addition of 10 ml of water led to precipitation of a yellow solid, which was filtered off, washed with water, dried over P_2O_5, and recrystallized from dichloromethane/hexane. Yield 40–60%. The isolated complexes, of the general formula $[Rh(\mu\text{-OMe})(\text{diolefin})]_2$, were characterized by elemental analysis and IR spectroscopy, and shown to be identical with samples obtained by conventional methods [22,23].

X-Ray analysis

Initially the intensities were collected for a structure with a unit cell with the *c* axis twice that shown in Table 1 and space group $P2_1/c$, the other parameters being the same. This model resulted in reflexions for **1** odd with much weaker intensities than those for **1** even (18% of the total scattering power versus 82% for **1** even, based on the structure factors $\Sigma_{\mathbf{1}\,\mathrm{odd}} F_{\mathrm{rel}}/\Sigma_{\mathbf{1}\,\mathrm{all}} F_{\mathrm{rel}} = 0.18$). A structure was derived on this basis and refined up to conventional *R* factors of *R* (**1** even) = 0.05 versus *R* (**1** odd) = 0.47, and the interatomic distances were unrealistic [11–13]. Thus we decided to reduce the cell, cutting the *c* axis by half, to give the parameters shown in Table 1, and assuming that some sort of unresolved disorder from cell to cell, accounted for the previous reflexions with **1** odd, which were thus no longer used. In this new cell two space groups were possible, either $P2_1$ or the corresponding centrosymmetric $P2_1/m$. Refinements were carried out for both, but the $P2_1$ space group again gave unrealistic values for the bond distances, while for $P2_1/m$ these values were as expected for arene-Rh(I) complexes [11–13]. Thus we decided that this group was appropriate for describing the structure, with the complex lying on a crystallographic mirror plane along the C_6F_4 ring of the TFB moiety. This plane is produced by the disorder; the description gives thermal factors with the highest values in the U_{22} components and assumes interchange of N and C between positions 1 and 3 of the five membered ring (see Fig. 1).

Results and discussion

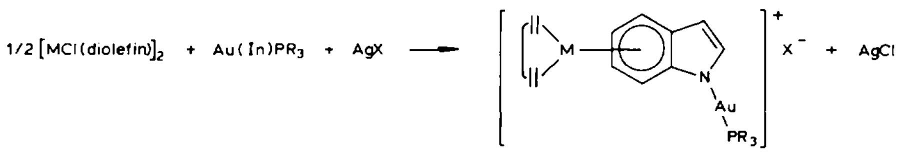
Rhodium(I) and iridium(I) η^6-arene complexes of indole (HIn) can be obtained in high yields by reacting the dimeric complexes $[RhCl(diolefin)]_2$ (diolefin = 1,5-cyclooctadiene (COD), tetrafluorobenzobarrelene (TFB) or trimethyltetrafluorobenzobarrelene (Me_3TFB)) or $[IrCl(COD)]_2$ with indole in the presence of silver salts ($AgClO_4$, M = Rh; $AgBF_4$, M = Ir) (eq. 1).



(1)

They are yellow (M = Rh) or tan-coloured (M = Ir) air-stable solids. Attempts to deprotonate the coordinated indole with potassium hydroxide in methanol led either to decomposition (M = Ir) or to formation of the previously described binuclear methoxy-bridged complexes $[Rh(\mu\text{-}OMe)(diolefin)]_2$ [22,23].

When reaction 1 is carried out with the *N*-indolyl gold(I) complexes $Au(In)PR_3$ ($R = C_6H_5$, $2\text{-}MeC_6H_4$ or $4\text{-}MeC_6H_4$) [21] instead of indole, heterobinuclear complexes in which the rhodium or iridium atoms are linked to the six-membered ring of the indolyl group are obtained in high yields (eq. 2).



(2)

The resulting green (M = Rh) or deep-red (M = Ir) complexes are air-stable.

The proposed type of bonding is supported by the analytical and spectroscopic data as well as the conductivities of the complexes, and was confirmed by the X-ray diffraction study of complex III. In acetone they behave as 1/1 electrolytes [26] (Table 2). Their IR spectra show, along with the bands arising from the other coordinated ligands and the uncoordinated anion, a decrease on coordination of the indole-ring stretching vibration [1] relative to that of HIn or $Au(In)PR_3$, as well a decrease of the stretching vibration ν(N–H) (for the mononuclear complexes) relative to that of HIn. The ^{1}H NMR spectra of the complexes of the type $[(diolefin)M(\eta^6\text{-}HIn)]ClO_4$ show a substantial downfield displacement for H(1) on coordination (from 7.57 for HIn to 10.3–10.9 ppm for the mononuclear complexes). In the case of the heterobinuclear complexes of the type $[(diolefin)Rh(\mu\text{-}In)AuPR_3]ClO_4$, the signals corresponding to the protons of the six-membered ring of the indolyl group move upfield on coordination relative to those observed for $Au(In)PR_3$. These displacements are consistent with a balance between the upfield shift experienced by the arene protons on complexation and a downfield shift arising from the increasing positive charge in the complexes [8]. Thus, the chemical shifts of the protons of the six-membered indole ring found for the described complexes (δ 6.43–7.36 ppm) are at a lower field than those for the neutral complex $Cr(CO)_3(HIn)$ (δ 5.27–6.55 ppm) [19], and at a higher field than those for the dicationic complex $[Rh(C_5Me_5)(\eta^6\text{-}HIn)](PF_6)_2$ (δ 7.16–7.96 ppm) [7]. On coordination the protons of the used diolefins are in each case shifted towards higher fields, the shifts being

TABLE 2

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES AND YIELDS OF THE COMPLEXES

Compound		Found (calcd.) (%)			Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)
		C	H	N		
$[(COD)Rh(\eta^6\text{-}HIn)]ClO_4$	(I)	45.50 (44.93)	4.60 (4.48)	3.34 (3.27)	146	88
$[(TFB)Rh(\eta^6\text{-}HIn)]ClO_4$	(II)	44.30 (44.02)	2.78 (2.40)	2.30 (2.57)	138	89
$[(Me_3TFB)Rh(\eta^6\text{-}HIn)]ClO_4$	(III)	47.25 (47.00)	3.48 (3.26)	2.40 (2.38)	139	88
$[(COD)Ir(\eta^6\text{-}HIn)]BF_4$	(IV)	38.23 (38.10)	3.72 (3.79)	2.86 (2.78)	134	81
$[(COD)Rh(\mu\text{-}In)AuP(C_6H_5)_3]ClO_4$	(V)	45.79 (46.10)	3.76 (3.76)	1.60 (1.58)	132	94
$[(TFB)Rh(\mu\text{-}In)AuP(C_6H_5)_3]ClO_4$	(VI)	44.60 (45.47)	2.83 (2.71)	1.42 (1.39)	124	96
$[(Me_3TFB)Rh(\mu\text{-}In)AuP(C_6H_5)_3]ClO_4$	(VII)	46.94 (47.08)	3.28 (3.18)	1.24 (1.34)	123	85
$[(COD)Rh(\mu\text{-}In)AuP(2\text{-}MeC_6H_4)_3]ClO_4$	(VIII)	48.75 (47.89)	4.63 (4.24)	1.62 (1.51)	113	93
$[(TFB)Rh(\mu\text{-}In)AuP(2\text{-}MeC_6H_4)_3]ClO_4$	(IX)	47.54 (47.08)	3.46 (3.18)	1.14 (1.34)	113	85
$[(Me_3TFB)Rh(\mu\text{-}In)AuP(2\text{-}MeC_6H_4)_3]ClO_4$	(X)	48.66 (48.57)	3.79 (3.61)	1.17 (1.29)	131	92
$[(COD)Rh(\mu\text{-}In)AuP(4\text{-}MeC_6H_4)_3]ClO_4$	(XI)	48.20 (47.89)	4.56 (4.24)	1.72 (1.51)	121	80
$[(TFB)Rh(\mu\text{-}In)AuP(4\text{-}MeC_6H_4)_3]ClO_4$	(XII)	46.42 (47.08)	3.33 (3.18)	1.32 (1.34)	119	74
$[(Me_3TFB)Rh(\mu\text{-}In)AuP(4\text{-}MeC_6H_4)_3]ClO_4$	(XIII)	48.94 (48.57)	4.01 (3.61)	1.41 (1.29)	128	78
$[(COD)Ir(\mu\text{-}In)AuP(C_6H_5)_3]BF_4$	(XIV)	41.99 (42.43)	3.71 (3.46)	1.10 (1.46)	126	85
$[(COD)Ir(\mu\text{-}In)AuP(2\text{-}MeC_6H_4)_3]BF_4$	(XV)	44.62 (44.24)	4.30 (3.81)	1.17 (1.39)	124	84
$[(COD)Ir(\mu\text{-}In)AuP(4\text{-}MeC_6H_4)_3]BF_4$	(XVI)	43.92 (44.24)	4.21 (3.81)	1.24 (1.39)	132	78

TABLE 3

FRACTIONAL ATOMIC COORDINATES

Atom	*x*	*y*	*z*
Rh	0.2062(1)	0.2500	0.0514(1)
X(1)[a]	0.0548(4)	0.1117(18)	0.2175(13)
C(2)	0.0374(7)	0.2500	0.2959(20)
C(6)	0.1238(3)	0.1683(11)	−0.2014(9)
C(7)	0.1085(3)	0.0808(8)	−0.0600(12)
C(8)	0.0814(3)	0.1657(9)	0.0740(8)
C(1′)	0.4540(6)	0.2500	0.5437(12)
F(1)	0.4353(4)	0.2500	0.7035(8)
C(2′)	0.5301(6)	0.2500	0.5430(15)
F(2)	0.5820(4)	0.2500	0.6968(10)
C(3′)	0.5533(5)	0.2500	0.3908(16)
F(3)	0.6277(3)	0.2500	0.3920(12)
C(4′)	0.4997(5)	0.2500	0.2350(12)
F(4)	0.5243(3)	0.2500	0.0826(8)
C(5′)	0.3609(4)	0.2500	0.0711(8)
C(6′)	0.3080(3)	0.3890(6)	0.0793(7)
C(7′)	0.2826(3)	0.3885(9)	0.2374(8)
C(8′)	0.3127(4)	0.2500	0.3620(10)
C(11′)	0.3996(4)	0.2500	0.3912(10)
C(12′)	0.4242(4)	0.2500	0.2337(10)
C(13′)	0.2795(6)	0.2500	0.5251(14)
C(14′)	0.3066(5)	0.5324(9)	−0.0376(15)
Cl	0.8536(2)	0.2500	0.5532(5)
O(1)	0.9296(7)	0.2500	0.6246(28)
O(2)	0.8294(9)	0.1092(19)	0.4695(18)
O(3)	0.8192(11)	0.2500	0.7004(26)

[a] X = N or C.

much higher for the vinylic protons of the TFB and Me$_3$TFB than for those of COD [9,11,12].

Crystal structure of [(Me$_3$TFB)Rh(η^6-HIn)]ClO$_4$

Although the disorder present in the sample limits the accuracy of the structural data (Tab. 3), the coordination about the Rh atom is not in doubt; the Rh–C

TABLE 4

GEOMETRY OF THE COORDINATION AROUND THE Rh ATOM

Atom	Distance (Å)
Rh–C(2)	> 3.5
Rh–X(1)/X(3)[a]	3.455(10)
Rh–C(6)/C(5)	2.295(6)
Rh–C(7)/C(4)	2.275(6)
Rh–C(8)/C(9)	2.398(5)
Rh–C(6′)/C(10′)	2.140(5)
Rh–C(7′)/C(9′)	2.111(6)

[a] X = N or C.

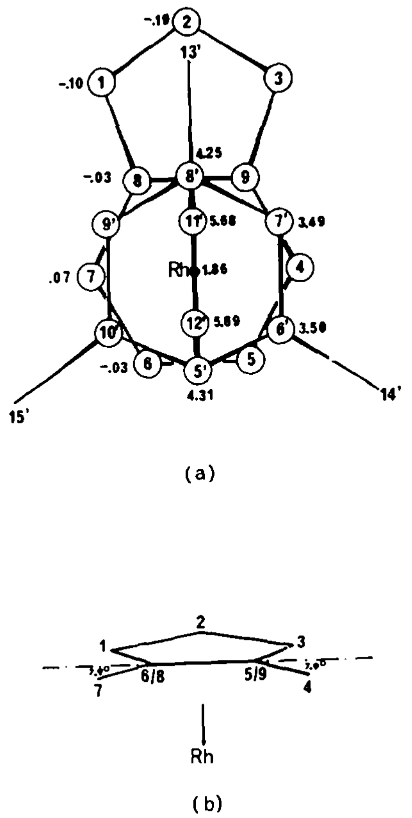


Fig. 2. (a) Rh coordination projected on the mean plane through the arene ring. The deviations of the atoms from this plane are included, only for the asymmetric half. (b) The boat conformation of the arene ring, where 6/8 and 5/9 appear overlapped.

distances are shown in Table 4. The metal atom is coordinated only to the six-membered ring, with the five-membered ring not involved (see Fig. 2a). The arene ring is puckered, to give a boat conformation (see Fig. 2b).

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