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Preliminary communication

INDOLYLGOLD(I) DERIVATIVES AND INDOLE AS π-ARENE LIGANDS IN CATIONIC RHODIUM(I) COMPLEXES

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Summary

The reaction of LAuIn (L = $P(C_6H_5)_3$, $P(2\text{-}MeC_6H_4)_3$ or $P(4\text{-}MeC_6H_4)_3$; In = indolyl group) with the solvated complexes $[(diolefin)Rh(Me_2CO)_x]ClO_4$ gives the novel heterometallic complexes $[(diolefin)Rh(\mu\text{-}In)AuL]ClO_4$. The mononuclear arene derivatives $[(diolefin)Rh(\eta^6\text{-}HIn)]ClO_4$ react with methanolic KOH to give the binuclear complexes $[(diolefin)Rh(\mu\text{-}OMe)]_2$, while $[(COD)Rh(\eta^6\text{-}HIn)]ClO_4$ reacts with KOH in water/acetone to give the hydroxo-bridged complex $[(COD)Rh(\mu\text{-}OH)]_2$.

In transition metal complexes the indole group can act as an N-donor ligand [1] either as η^5-indolyl via its five-membered ring [2,3] or as η^6-indole via its six-membered ring [3,4]. We have taken advantage of these possibilities in order to prepare a novel type of heteronuclear rhodium(I)—gold(I) complexes in which the rhodium atom is π-bonded to the arene ring and the gold atom is σ-bonded to the nitrogen atom.

LAuCl reacts with the potassium salt of indole (prepared in situ by treatment of indole with potassium hydroxide in methanol) to give LAuIn (eq. 1):

$$LAuCl + KIn \rightarrow LAuIn + KCl \quad (1)$$

The solvated complex $[(diolefin)Rh(Me_2CO)_x]ClO_4$ [5] (prepared in situ from $[(diolefin)RhCl]_2$* and silver perchlorate in acetone) reacts quantitative-

*Diolefin = 1,5-cyclooctadiene(COD) [6], tetrafluorobenzobarrelene (TFB) [7] or trimethyltetrafluorobenzobarrelene (Me_3TFB) [7].

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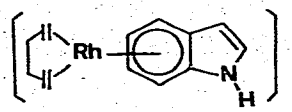
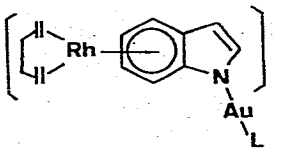
ly with indole and LAuIn to give the corresponding arene complexes (eq. 2 and 3), which are stable as solids and in solution and behave as 1/1 electrolytes in acetone.

$$[(\text{diolefin})\text{Rh}(\text{Me}_2\text{CO})_x]\text{ClO}_4 + \text{HIn} \rightarrow$$



$$+ x\text{Me}_2\text{CO} \qquad (2)$$

$$[(\text{diolefin})\text{Rh}(\text{Me}_2\text{CO})_x]\text{ClO}_4 + \text{LAuIn} \rightarrow$$



$$+ x\text{Me}_2\text{CO} \qquad (3)$$

The proposed bonding for these complexes is supported by their spectroscopic data. The IR spectra show a lowering (76—38 cm^{-1}) of the indole ring stretching vibration on coordination. The ^1H NMR spectra reveal that on coordination the signals corresponding to the protons of the six-membered ring of the indolyl group in the rhodium(I)—gold(I) complexes move upfield.

Attempts to prepare η^5-indolyl derivatives through deprotonation of the indole group by reacting complexes of the type $[(\text{diolefin})\text{Rh}(\eta^6\text{-HIn})]\text{ClO}_4$ with potassium hydroxide in methanol give rise to the formation of methoxy-bridged binuclear complexes (eq. 4). These complexes, prepared by a different route, have been described previously [6,7].

$$[(\text{diolefin})\text{Rh}(\eta^6\text{-HIn})]\text{ClO}_4 + \text{KOH} + \text{MeOH} \xrightarrow{\text{MeOH}}$$

$$1/2[(\text{diolefin})\text{Rh}(\mu\text{-OMe})]_2 + \text{HIn} + \text{KClO}_4 + \text{H}_2\text{O} \qquad (4)$$

On the other hand the reaction of $[(\text{COD})\text{Rh}(\eta^6\text{-HIn})]\text{ClO}_4$ with potassium hydroxide in water/acetone, seems to give $[(\text{COD})\text{Rh}(\mu\text{-OH})]_2$*. This hydroxo-bridged complex can be prepared directly from $[(\text{COD})\text{RhCl}]_2$ (eq. 5).

$$1/2[(\text{COD})\text{Rh}(\mu\text{-Cl})]_2 + \text{KOH} \xrightarrow{\text{H}_2\text{O/Me}_2\text{CO}}$$

$$1/2[(\text{COD})\text{Rh}(\mu\text{-OH})]_2 + \text{KCl} \qquad (5)$$

This complex is an air-stable yellow solid, and is also stable in solution, in spite of the fact that the hydroxo group is a very hard ligand for a metal in low oxidation state. In the solid state it is partially associated via hydrogen bridges, showing ν(OH) at 3550s and 3330s,v(br) cm^{-1} (ν(OD): 2642s and 2400s,v(br) cm^{-1} in a deuteriated sample), but it is not associated in dichloromethane solution.

All the new compounds described gave appropriate analyses.

*A hydroxo-bridged complex of the formula $[(CO)_2\text{Rh}(\mu\text{-OH})]_2$ has previously been postulated as an intermediate in a phase-transfer catalyzed dehydrogenation of alcohols [8].

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