

SYNTHESIS AND PROPERTIES OF CHLOROTRIS(1,3-DIBENZYLIMIDAZOLIDIN-2-YLIDENE)RHODIUM(I) AND OF SOME RELATED COMPOUNDS

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ABSTRACT. The electron-rich alkene $\overline{\text{CNR}(\text{CH}_2)_2\text{NR}}$ (L_2) ($\text{R} = \text{CH}_2\text{Ph}$) has been used as a source of various carbenerhodium(I) complexes: $[\text{RhCl}(\text{cod})(\text{L})]$ (**1**), $[\text{RhCl}(\text{L})_3]$ (**2**), $[\text{RhCl}(\text{CO})(\text{L})_3]$ (**3**), and *trans*- $[\text{RhCl}(\text{CO})(\text{L})_2]$ (**4**), and of the iridium(I) complex $[\text{IrCl}(\text{L})_3]$ (**5**). Compounds (**2**) and (**5**) are of particular interest as they contain no other neutral ligand apart from the carbene $:\overline{\text{CN}(\text{R})(\text{CH}_2)_2\text{NR}}$ (L) ($\text{R} = \text{CH}_2\text{Ph}$); their chemistry is in many ways related to that of the well known complexes $[\text{MCl}(\text{PPh}_3)_3]$ ($\text{M} = \text{Rh}$ or Ir). Thus, compound (**2**) readily loses a carbene ligand upon treatment with either carbon monoxide [ultimately to lead to (**4**)], or O_2 to yield a compound tentatively formulated as $[\text{RhCl}(\text{L})_2(\text{O}_2)]$ (**6**). The X-ray structures of complexes (**2**) and (**4**) have been determined.

1. Introduction

The objectives of this work were to investigate the potential of the electron-rich alkene $\overline{\text{CN}(\text{CH}_2\text{Ph})(\text{CH}_2)_2\text{NCH}_2\text{Ph}}$, abbreviated as $[\text{L}^{\text{CH}_2\text{Ph}}]_2$, particularly in the context of the chemistry of derived carbenometal complexes of rhodium(I) and iridium(I). Previously we have examined extensively a similar series of electron-rich alkenes $[\text{L}^{\text{R}}]_2$ (in which $\text{R} = \text{Me}$, Et , or Ph).¹ A limited amount of work has also been carried out on $[\text{L}^{\text{CH}_2\text{Ph}}]_2$ in the context of Ru^{II} and Os^{II} chemistry.²

In much of the transition metal chemistry of compounds $[\text{L}^{\text{R}}]_2$, the alkene behaved as a C-centred nucleophile giving rise to carbenometal complexes, e.g., the reaction of $[\text{Au}(\text{Cl})\text{PPh}_3]$ with $[\text{L}^{\text{Me}}]_2$ gave $[\text{Au}(\text{L}^{\text{Me}})_2]\text{Cl}$.¹ Thus, it is evident that in many ways the electron-rich alkene behaves in an analogous fashion to a tertiary phosphine. Moreover, some compounds, e.g., *cis*- $[\text{RhCl}(\text{cod})(\text{L}^{\text{Me}})]$ [$\text{L}^{\text{Me}} = \overline{\text{CN}(\text{Me})(\text{CH}_2)_2\text{NMe}}$], have been shown to display catalytic properties similar to their tertiary phosphine equivalents.³

2. Results and Discussion

2.1 SYNTHESIS AND REACTIONS OF RHODIUM(I) AND IRIDIUM(I) COMPLEXES HAVING THE LIGAND 1,3-DIBENZYLIMIDAZOLIDINYLD-2-ENE

The results are summarised in Scheme 1, in which L represents the ligand $:\text{CN}(\text{CH}_2\text{Ph})(\text{CH}_2)_2\text{NCH}_2\text{Ph}$. From this it will be evident that we have obtained rhodium(I) complexes containing one, two, or three of such carbene ligands. Particularly noteworthy is the compound $[\text{RhCl}(\text{L})_3]$ (2), which is free from other neutral ligands. This is the carbene analogue of Wilkinson's compound $[\text{RhCl}(\text{PPh}_3)_3]$. The corresponding iridium compound $[\text{IrCl}(\text{L})_3]$ (5) has also been obtained.

It is interesting that using the alkene $[\text{LCH}_2\text{Ph}]_2$ a range of neutral complexes $[\text{RhCl}(\text{cod})(\text{L})]$ (1), $[\text{RhCl}(\text{CO})(\text{L})_n]$ [$n = 3$ (3), or $n = 2$ (4)], and (2) has been obtained. Using other electron-rich alkenes there is a greater tendency for formation of ionic compounds.¹ For example, whereas treatment of (2) with carbon monoxide yielded the neutral complex (4), a similar reaction starting with $[\text{RhCl}(\text{L}^{\text{Et}})_3]$ [$\text{L}^{\text{Et}} = :\text{CN}(\text{Et})(\text{CH}_2)_2\text{NEt}$] yielded the complex $[\text{Rh}(\text{CO})\text{Cl}(\text{L}^{\text{Et}})_3]\text{Cl}$.³ Another feature which differentiates a benzyl-substituted carbene ligand from a simple alkyl analogue relates to the catalytic activity of derived metal complexes; thus, whereas (2) is an efficient hydrosilylation catalyst, the ethyl analogue is not.³

The reactivity of $[\text{RhCl}(\text{L})_3]$ (2) is of interest for a further reason. Firstly, we demonstrate that it is possible to displace a carbene ligand from the inner co-ordination sphere of the metal. Secondly, in the reaction with dioxygen a compound tentatively formulated as $[\text{RhCl}(\text{L})_2(\text{O}_2)]$ (6) is obtained. As for the first point, there is only limited precedent. Thus, the sterically hindered complex $[\text{RuCl}_2(\text{L}^{\text{Et}})_4]$ readily lost one of its L^{Et} ligands on treatment with an appropriate nucleophile;² however, in general, such carbene ligands are extremely resistant to displacement. Regarding the proposed dioxygen complex, the evidence for the formulation shown for (6) rests on satisfactory microanalysis. However, the isolated complex is paramagnetic and unambiguous identification must await further structural data. Some details of the new compounds (1)-(5) are in Table I.

2.2 STRUCTURAL DATA IN THE 1,3-DIBENZYLIMIDAZOLIDINYLD-2-ENE-RHODIUM(I) AND -IRIDIUM(I) COMPLEXES (1)-(5)

Selected spectroscopic data are in Table II. From the ^1H n.m.r. spectra it will be noted that each of the CH_2Ph groups is revealed as a AB signal for the CH_2 moiety. This arises because of restricted rotation about the $\text{C}_{\text{carb}}-\text{Rh}$ bond.⁴ Variable temperature studies (by D.B. Shaw) on compound (4) shows that the activation energy of rotation about this bond at 343 K is 73.9 kJ mol^{-1} .

In the triscarbene metal complexes (2) and (5), the C_{carb} ^{13}C signal was exceptionally shielded (Table II). In Section 2.1 the distinction was made in reactivity between the ethyl complex