Amides of Rhodium(I) and Ruthenium(II), $[Rh(NR_2)(PPh_3)_2]$ and $[RuH(NR_2)(PPh_3)_2]$ ($R = Me_3Si$): Novel Low Co-ordination Number d^8 and d^6 Metal Complexes

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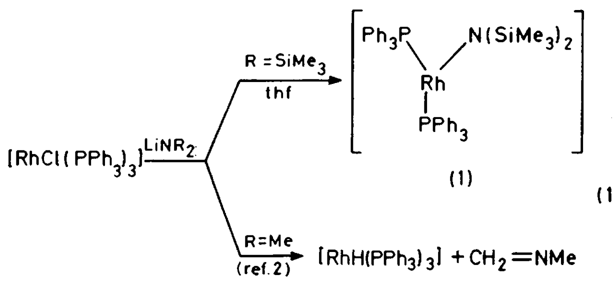
Summary Reaction of $LiNR_2$ ($R = Me_3Si$) with $[RhCl(PPh_3)_3]$ or $[RuH(Cl)(PPh_3)_3]$ in tetrahydrofuran (thf) yields the cyclohexane-soluble, monomeric, diamagnetic amides $[Rh(NR_2)(PPh_3)_2]$ or $[RuH(NR_2)(PPh_3)_2]$, which on heating decompose with elimination of $HN(SiMe_3)_2$; the Ru^{II} compound has equivalent P atoms, but inequivalent $SiMe_3$ environments.

WE report the synthesis and characterisation of the amides (**1**) and (**2**) (see Table). These compounds are of interest for the following reasons. (i) Amides of rhodium or ruthenium were previously unknown.[1] (ii) There is an interesting contrast between the stability of the bis(trimethylsilyl)amides (**1**) and (**2**) and the earlier failure[2] to isolate related dimethylamides, see equations (1) and (2). (iii) Compounds (**1**) and (**2**) are stable in an inert atmosphere in the solid state, but heating in benzene leads to quantitative elimination of $HN(SiMe_3)_2$; for complex (**1**), $t_{\frac{1}{2}}$ at 25 °C in C_6H_6 is *ca.* 12 h. (iv) The co-ordination number of the metal in each of these 14-electron molecules is unusually low. (v) Complex (**2**) has the two phosphorus atoms magnetically equivalent, but the two $SiMe_3$ groups are distinct in C_6D_6 at 30 °C and a dynamic exchange process only becomes apparent upon heating (see Table). (vi) Complexes (**1**) and (**2**), being hydrocarbon-soluble metal amides, are useful starting materials for other Rh^I and Ru^{II} complexes (*cf.*, ref. 1).

TABLE. Data for the rhodium(I) and ruthenium(II) amides, (**1**) and (**2**).

Complex	Colour[a]	Yield/%	M.p. (θ_c/°C)	M[b]	^1H N.m.r.[c] (τ)
(**1**)[d,e]	Green	90	128—130	755 (724)	9·4 (s)
(**2**)[e,f]	Red	73	123—125	727 (786)	9·47 and 9·96 (d),[g] and 27·7, 28·2, and 28·7 (t)[h]

[a] Compounds (**1**) and (**2**) rapidly decompose upon exposure to air, becoming yellow and green, respectively. [b] By cryoscopy in cyclohexane; value calculated for monomer is in parentheses. [c] In C_6D_6 at 30 °C; aromatic protons have been omitted. [d] ^{31}P N.m.r. in C_6D_6 at 30 °C shows a 1 : 1 doublet at δ 78·02 and 82·42 p.p.m. rel. to $P(OMe)_3$, $J(^{31}P-^{103}Rh)$, 180·67 Hz. [e] Satisfactory microanalytical data were obtained. [f] ^{13}C N.m.r. in C_6D_6 at 30 °C shows a broad 1 : 1 doublet at δ +6.1 and −0·4 p.p.m. rel. to $SiMe_4$ (see g); ν(RuH) (Nujol), 2020 cm^{-1}. [g] These are 1 : 1 in intensity and show onset of coalescence at *ca.* 90 °C, indicating magnetic inequivalence of the $SiMe_3$ groups of the amide. [h] This is a 1 : 2 : 1 triplet, $J(^1H-^{31}P)$, 33 Hz.



(1)

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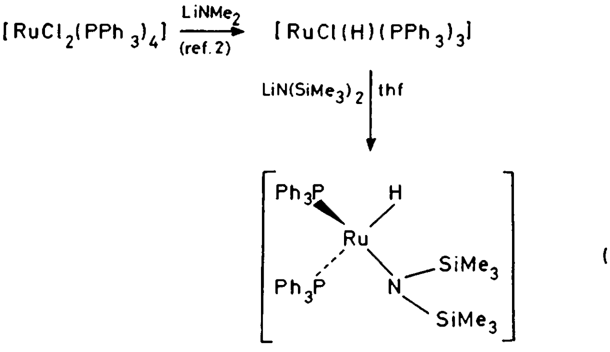


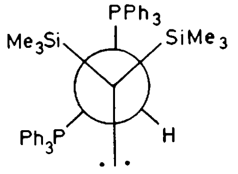
(2)

(2)

As for (i), we note that the only transition elements for which amides now remain unreported are Tc, Os, Ir, Pd, Pm, Tb, Dy, Tm, Pa, and the transuranium elements.[1] The new Rh^I amide (**1**) is isoleptic and isoelectronic with $[Co(NR_2)(PPh_3)_2]$ (C_{2v} $CoNP_2$ framework by *X*-ray),[3] and is therefore probably also trigonal planar about the metal atom.

With regard to (ii) and (iii), the new observations, and especially the data of equations (1) and (2), reinforce the view[2] that the β-elimination pathway has a role not only for decomposition of metal alkyls, but also amides. Furthermore, it is now likely that the thermal stability so often characteristic of the numerous metal and metalloid bis(trimethylsilyl)amides is partly due to the absence of β-hydrogen atoms in the ligand.

Referring to (iv), a few examples of three-co-ordinate Rh^I complexes were previously known, *e.g.*, $[RhH(PR_3)_2]$ ($R = Bu^t$ or C_6H_{11}).[4] However, a four-co-ordinate d^6 complex appears to be without precedent.† The n.m.r. spectroscopic data [see (v)] suggest a non-planar, probably distorted tetrahedral, arrangement of the valences about Ru in (**2**); the dynamic n.m.r. behaviour indicates that there is restricted rotation about the Ru–N bond, *cf.*, the Newman projection (**3**). The low spin d^6 electronic configuration and indeed the diamagnetism, is somewhat unexpected. Some μ-X_2-five-co-ordinate complexes[5] $[\{Ru(H)XL_2\}_2]$ ($X = Cl$ or Br, $L = PPh_3$ or $AsPh_3$) have the same stoicheiometry as (**2**).



(3)

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† There is a reference to unpublished work (including *X*-ray work) on a diamagnetic tetrahedral d^6 Rh^{III} complex $[\overline{Rh(CH_2)_5CH_2}(Cl)PPh_3]$; see P. Binger, B. Çetinkaya, and C. Krüger, unpublished work cited by G. Wilke, *Pure Appl. Chem.*, 1978, **50**, 677.

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