Novel Three-co-ordinate Rhodium(I) Hydrido-compounds, $[RhH(PBu^t_3)_2]$ and $[RhH\{P(cyclohexyl)_3\}_2]$

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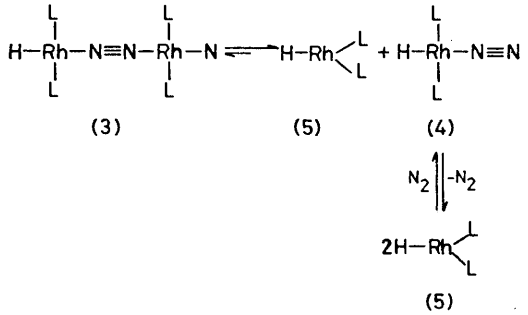
Summary The rhodium(I) hydrido dinitrogen complexes *trans*-$[RhH(N_2)(PBu^t_3)_2]$ and $[\{$*trans*-$RhH[P(cyclohexyl)_3]_2\}_2(\mu\text{-}N_2)]$, prepared by reducing $RhCl_3{\cdot}3H_2O$ with Na–Hg in the presence of the appropriate phosphine, dissociate the co-ordinated dinitrogen to give novel three-co-ordinate complexes $RhHL_2$.

RECENTLY the three-co-ordinate rhodium (I) compounds, $[RhX\{P(cyclohexyl)_3\}_2]^1$ and $[Rh(PPh_3)_3]^{+},^2$ have been reported. In an attempt to prepare two-co-ordinate Rh^I compounds as an extension of our work on ML_2 complexes ($M = Pd$ or Pt),[3] we obtained the hitherto unknown hydrido-bisphosphine Rh^I compounds, $RhHL_2$. The 14 electron system $RhHL_2$ has been postulated to exist in solutions of

$RhHL_3$ ($L = PPh_3$;[4] 5-phenyl-5*H*-dibenzophosphole[5]), but has not been isolated. The extent of phosphine dissociation of these four-co-ordinated compounds was estimated to be extremely low ($K_d < 10^{-5}$ M).[5,6] We have found that *trans*[$RhH(N_2)L_2$] [$L = PBu^t_3$ or P(cyclohexyl)$_3$] and [(*trans*-$RhHL_2)_2(\mu\text{-}N_2)$] [L = P(cyclohexyl)$_3$] complexes serve as precursors of $RhHL_2$.

Reduction of $RhCl{\cdot}3H_2O$ with Na–Hg in the presence of PBu^t_3 in tetrahydrofuran (THF) under N_2 gave *trans*-[$RhH(N_2)(PBu^t_3)_2$] (**1**) as yellow–brown crystals (53% yield). The dinitrogen co-ordination in (**1**) is extremely unstable, releasing dinitrogen even in the solid state under N_2. In n-hexane (**1**) exhibits ν(N≡N) at 2145 cm^{-1} and ν(Rh–H) at 2060 cm^{-1}, while the ^{1}H n.m.r. spectrum shows no hydrido signal even at −70 °C, suggesting a rapid equilibration between two species, (**1**) and [$RhH(PBu^t_3)_2$] (**2**). The latter (**2**) may be isolated as dark brown crystals by recrystallizing (**1**) from n-hexane under argon (70% yield). The monomeric nature of (**2**) was confirmed by molecular weight measurement in benzene (*M*, found 491, calc. 508) as well as by a mass spectrum which shows the molecular ion (*m/e* 508) and fragment ions formed by stepwise loss of Bu^t group of the phosphines as isobutene. The i.r. and ^{1}H n.m.r. spectra of (**2**) show ν(Rh–H) (2065 cm^{-1}) and a hydrido signal [δ −13·9 (dt, $^1J_{H-Rh}$ 10·5 Hz, $^2J_{H-P}$ 18·8 Hz)], respectively. The virtual coupling observed for the Bu^t proton signal [δ 1·37 (t, $^3J_{H-P} + {}^5J_{H-P}$ 11·4 Hz)] appears to suggest considerable distortion from a regular trigonal structure. The structure of [$Rh(PPh_3)_3]^+$ has been shown to be approximately T shaped.[3] The molecular structure of (**2**) is being investigated by *X*-ray diffraction.

Similar reduction of $RhCl_3{\cdot}3H_2O$ in the presence of P(cyclohexyl)$_3$ under N_2 gave a μ-dinitrogen compound [{*trans*-RhH[P(cyclohexyl)$_3$]$_2$}$_2$N$_2$] (**3**) (73% yield) as orange crystals rather than the expected compound, *trans*-[$RhH(N_2)$ {P(cyclohexyl)$_3$}$_2$] (**4**). The latter was obtained as yellow–orange crystals by the reaction of *trans*-[RhH_3 {P(cyclohexyl)$_3$ }$_2$] with N_2 in n-hexane (40% yield). In contrast to (**1**), the dinitrogen co-ordination of (**4**) is stable in the solid state *in vacuo*. On dissolution of (**4**) in benzene, however, partial N_2 evolution was observed even under N_2. The i.r. spectrum of (**4**) in n-hexane showed both ν(Rh–H) (1953 cm^{-1}) and ν(N≡N) (2153 cm^{-1}), while two hydrido n.m.r. signals were observed at δ −13·0 (dt, J_{H-Rh} 18·8 Hz, $^2J_{H-P}$ 20·2 Hz) and −14·9 (dt, $^1J_{H-Rh}$ 18·5 Hz, $^2J_{H-P}$ 22·7 Hz). The latter signal coincides with that of [RhH {P(cyclohexyl)$_3$ }$_2$](**5**) [ν(Rh–H) 1953 cm^{-1} in n-hexane] which was prepared separately by heating (**3**) or (**4**) at 60 °C in benzene under argon. These spectral data of (**4**) indicate that the solution contains (**4**) and (**5**) in a 2 : 3 molar ratio. The i.r. and ^{1}H n.m.r. spectra of (**3**) in solution† also indicate the species present is a mixture of (**4**) and (**5**).



The failure to observe a hydrido signal due to (**3**) may be indicative of complete dissociation into (**4**) and (**5**). A similar dissociation has been reported for [Ni_2{P(cyclohexyl)$_3$}$_4(\mu\text{-}N_2)$].[7] Interestingly, *trans*-[$RhH(N_2)(PPhBu^t_2)_2$][8] showed no tendency to dissociate the co-ordinated dinitrogen. It should be noted that by employing the less bulky phosphines PPr^i_3 and PEt_3, a similar reduction of $RhCl_3{\cdot}3H_2O$ afforded four- and five-co-ordinate complexes, $RhHL_n$ ($n = 3$, $L = PPr^i_3$; $n = 4$, $L = PEt_3$).

The three-co-ordinate hydrido complexes (**2**) and (**5**) as well as their dinitrogen precursors (**1**), (**3**), and (**4**) proved to be extremely versatile. For example, they are efficient catalysts for hydrogenation of unsaturated organic compounds and for the H–D exchange reaction of aromatic compounds with D_2O which occurs through water activation.[9]

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† The i.r. spectrum measured as a Nujol mull showed ν(Rh–H) (1953 cm^{-1}), but no ν(N≡N).

[1] H. L. M. van Gaal and F. L. A. van den Bekerom, *J. Organometallic Chem.*, 1977, **134**, 237.
[2] Y. w. Yared, S. L. Miles, R. Bau, and C. A. Reed, *J. Amer. Chem. Soc.*, 1977, **99**, 7077.
[3] S. Otsuka, T. Yoshida, M. Matsumoto, and K. Nakatsu, *J. Amer. Chem. Soc.*, 1976, **98**, 5850, and references therein.
[4] J. Hjortkjaer, *Adv. in Chem. Ser.*, 1973, **132**, 133.
[5] D. E. Budd, D. G. Holah, A. N. Hughes, and B. C. Hui, *Canad. J. Chem.*, 1974, **52**, 775.
[6] D. F. Shriver, personal communication.
[7] P. W. Jolly, K. Jonas, C. Krüger, and Y. H. Tsay, *J. Organometallic Chem.*, 1971, **33**, 109.
[8] P. R. Hoffman, T. Yoshida, T. Okano, S. Otsuka, and J. A. Ibers, *Inorg. Chem.*, 1976, **14**, 2462.
[9] T. Yoshida and S. Otsuka, to be published.

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