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THE REACTION OF DICHLOROTETRACARBONYLDIRHODIUM, $Rh_2Cl_2(CO)_4$, WITH t-BUTYL ISOCYANIDE *

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Summary

By studying the evolution of CO from $Rh_2Cl_2(CO)_4$ in various solvents with successive additions of t-BuNC and by measuring the conductances and infrared spectra of these solutions, the course of the reaction and the nature of the intermediates have been established. The intermediates $RhCl(CO)_2$(t-BuNC) and RhCl(CO)$(t\text{-BuNC})_2$ in the formation of $[Rh(t\text{-BuNC})_4]Cl$ were isolated as blue-black solids from yellow solutions.

Introduction

Additions of organic isocyanides to $Rh_2Cl_2(CO)_4$ have been shown to give various products. The cationic complexes $[Rh(RNC)_4]^+$ were the first and easiest to obtain [1] since an excess of the ligand readily replaces all the originally coordinated ligands. The colour of these complexes depends on the counter-ion in the crystal or on the solvent and concentration in solution. This was originally believed [1] to be due to equilibria involving four-coordinated and five-coordinated complexes with coordinated solvent molecules, but recently it has been shown that the mononuclear complexes $[Rh(RNC)_4]^+$ have a strong tendency to oligomerise to give deep purple or blue dimers or trimers linked by Rh—Rh bonds [2—7]. Similarly the intense blue-black complex $[Ir(MeNC)_4]^+$ on photolysis in solution becomes orange-red. This was originally thought to be due to uptake of solvent [8] but has been shown to be a photo-induced dissociation of an intensely coloured oligomer [9].

If, instead of adding RNC in excess to $Rh_2Cl_2(CO)_4$, an appropriately reduced proportion is added then $RhCl(CO)(RNC)_2$ may be isolated as the presumed intermediate in the formation of $[Rh(RNC)_4]^+$. When R = aryl, the complex $RhCl(CO)(ArNC)_2$ is colourless and presumed reasonably to be mononuclear [10].

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* No reprints available.

In this work we have attempted by measuring CO evolution, conductances and infrared spectra as t-BuNC is added to $Rh_2Cl_2(CO)_4$ in various solvents to identify intermediates in this reaction and to isolate these where possible.

Results and discussion

The infrared spectra (2300—1700 cm^{-1}) of a solution of $Rh_2Cl_2(CO)_4$ in ethanol-free chloroform saturated with carbon monoxide (1 atm) were measured after successive additions of t-BuNC (L) had been made. The overall reaction occurs in three separate stages. When the ratio of ligand molecules to rhodium atoms (L/Rh) is 1.00, absorptions due to the starting material had been totally replaced by just three absorptions (2223, 2101 and 2033 cm^{-1}) which we assign to *cis*-RhCl(CO)$_2$(t-BuNC) (see Fig. 1). As the L/Rh ratio is increased from 1.00 to 2.00 these three absorptions decrease in intensity and are totally replaced by two new ones (2181 and 2011 cm^{-1}); at this stage in the reaction (L/Rh = 2.00) the only species in solution is *trans*-RhCl(CO)(t-BuNC)$_2$.

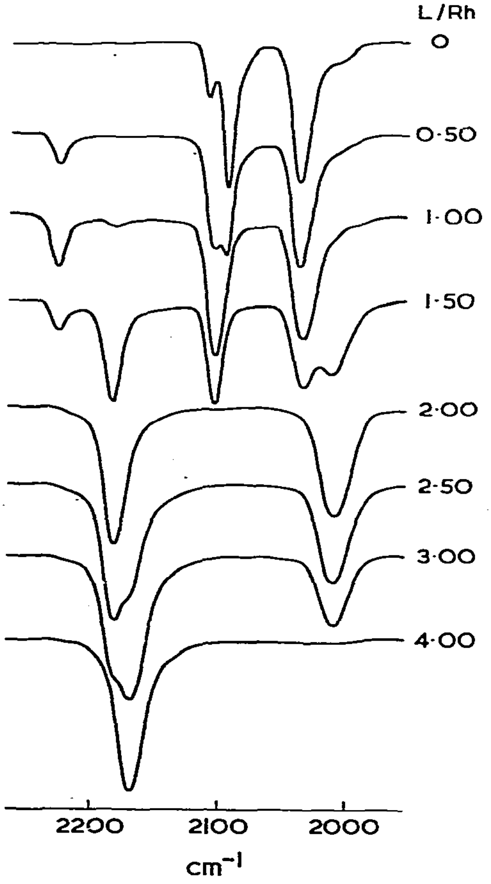
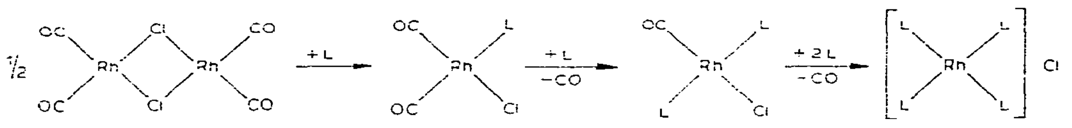


Fig. 1. Infrared spectra of solutions obtained by addition of t-BuNC (L) to $Rh_2Cl_2(CO)_4$ in ethanol-free chloroform under CO (1 atm.)

Finally as the L/Rh ratio is increased from 2.00 to 4.00 the remaining CO group is replaced so that no absorption remains in the range 2150 to 1700 cm^{-1} and the final spectrum contains the single absorption at 2167 cm^{-1} assignable to $[Rh(t\text{-}BuNC)_4]Cl$. This complex cation was isolated as its chloride or perchlorate salt. The very simple reaction sequence below is shown by these results, each step occurring quantitatively:



(1)

The chloroform solution is varying intensities of yellow throughout the course of the additions so that oligomerisations of these species does not appear to occur. Only two rhodium complexes are in solution at any time. If, however, the experiment is repeated with N_2 bubbling through the solution, more complex spectra are obtained in the intermediate stages but the final spectrum when L/Rh = 4.00 is the same as under CO. Clearly $RhCl(CO)_2(t\text{-}BuNC)$ and/or $RhCl(CO)(t\text{-}BuNC)_2$ are involved in chemical equilibria involving free carbon monoxide.

Reaction sequence 1 was confirmed, in toluene solution at least, by measurement of the CO evolved as t-BuNC is added to $Rh_2Cl_2(CO)_4$. Figure 2 shows that the first addition of t-BuNC (▽ curve) do not lead to much CO evolution so that when L/Rh = 1.00 little CO is formed and this corresponds with the formation of $RhCl(CO)_2(t\text{-}BuNC)$ and subsequent stages of the reaction from L/Rh = 1.00 to 2.00 and from 2.00 to 4.00 confirm the infrared results. The combined results show that there is no measurable concentration of any intermediate between $RhCl(CO)(t\text{-}BuNC)_2$ and $[Rh(t\text{-}BuNC)_4]Cl$. Thus the graph (Fig. 2, ▽) is linear in the range L/Rh = 2.00 to 4.00 with half the slope found between L/Rh = 1.00 to 2.00, whereas significant concentrations of the inter-

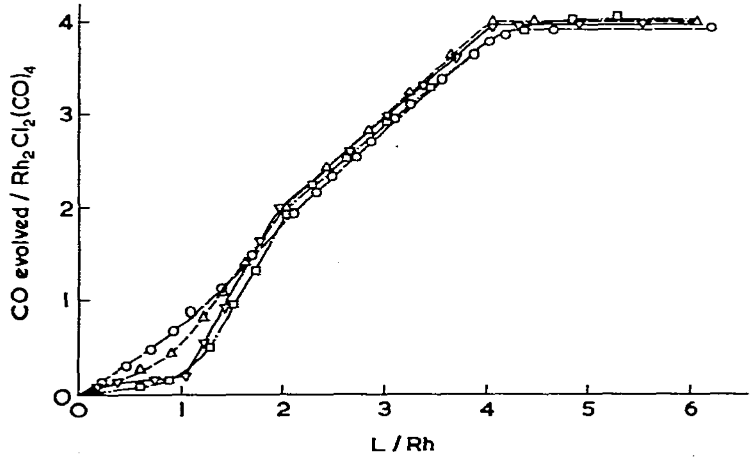
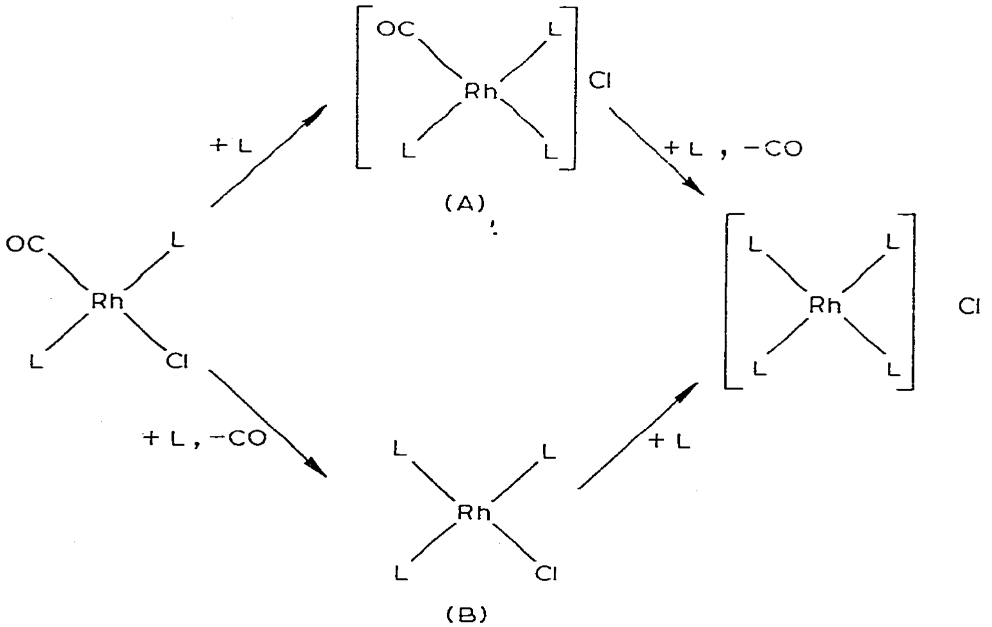


Fig. 2. Graph of CO evolution {mol CO evolved per mol $Rh_2Cl_2(CO)_4$} against t-BuNC molecules added per Rh atom (L/Rh) to $Rh_2Cl_2(CO)_4$ in toluene (▽), DMF (○), butanol (△) or cyclohexane (□) under CO (1 atm).

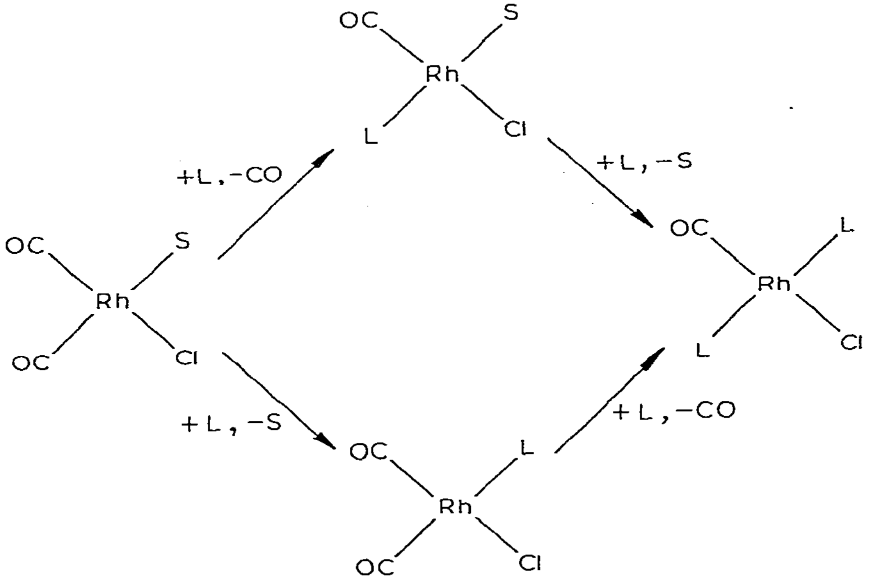
mediates A or B would lead to deviations from linearity. Contrasting behaviour



(2)

is found on addition of RNC (R = 2,6-dimethylphenyl) to $Rh_2Cl_2(COD)_2$ (COD = cycloocta-1,5-diene) [11]. Addition of the appropriate amount of RNC allows the isolation of $RhCl(RNC)_3$ which gives $[Rh(RNC)_4]Cl$ on further addition of RNC. It is probable that the good leaving properties of monodentate COD account for the difference. There is nothing intrinsically unstable about $RhCl(RNC)_3$, but in the presence of CO the complex must be unstable with respect to an equimolar mixture of $RhCl(CO)(t\text{-}BuNC)_2$ and $[Rh(t\text{-}BuNC)_4]Cl$. We can discuss product formation in terms of favourable or unfavourable equilibria because the reactions discussed so far are all very rapid; each addition of t-BuNC leads to a rapid adjustment of the concentrations of species in solution and in experiments used to obtain Fig. 2 volume measurements could be made 3 min after each addition of t-BuNC. The reversibility of the reactions was demonstrated by mixing yellow ethanol-free chloroform solutions of $[Rh(t\text{-}BuNC)_4]Cl$ and of $Rh_2Cl_2(CO)_4$ (mol ratio 2/1) under an atmosphere of CO. An immediately formed dark red colour was discharged in a few seconds after mixing and the infrared spectrum of the resulting pale-yellow solution which was recorded a few minutes later showed only $RhCl(CO)(t\text{-}BuNC)_2$; with the above proportion of reactants this complex may be formed by simple redistribution rather than overall loss or gain of ligands. We have made no attempt to determine the nature of the red intermediate in this reaction.

Figure 2 shows that the reaction up to L/Rh = 2.00 is dependent upon the solvent, CO being lost at an earlier state in DMF (○) and n-butanol (△) compared with toluene solution (▽). The $\nu(CO)$ spectra of $Rh_2Cl_2(CO)_4$ in a wide range of solvents show that this species only exists in non-coordinating solvents (toluene, cyclohexane, dry ethanol-free dichloromethane or chloroform) but that in coordinating solvents the ν(CO) spectrum consists of two equal intensity absorptions consistent with the chloro-bridge cleaved species $RhCl(CO)_2(S)$ where S = solvent; ν(CO) = 2089, 2014 (n-butanol); 2091, 2016 (MeOH); 2088, 2012 (MeCOMe); 2085, 2010 (EtCOEt); 2071, 1994 (THF) cm^{-1}. In diethyl ether there appears to be a mixture of $Rh_2Cl_2(CO)_4$ and $RhCl(CO)_2(S)$. It is not simply that the spectrum of $Rh_2Cl_2(CO)_4$ has a different appearance in different solvents. For instance, the spectrum of the dimer (0.015 g) in EtOH-free chloroform (10 cm^3) is as shown in Fig. 1; but successive additions of n-butanol lead to a gradual replacement of these absorptions by two new ones at 2089 and 2014 cm^{-1}. When n-butanol (0.6 cm^3) is added to the original solution, $Rh_2Cl_2(CO)_4$ and $RhCl(CO)_2(S)$ have approximately equal concentrations, but there are only traces of $Rh_2Cl_2(CO)_4$ remaining when n-butanol (2.0 cm^3) had been added. From such experiments and the lack of CO evolution on dissolving $Rh_2Cl_2(CO)_4$ in DMF or n-butanol we know that in neat DMF or n-butanol the complex exists totally as $RhCl(CO)_2(S)$. On addition of t-BuNC to these solutions a non-linear curve (Fig. 2) for L/Rh = 0 up to 2.00 is obtained, which we interpret as resulting from a competition between the reactions shown in scheme 3.



(3)

In DMF the intermediate RhCl(CO)(DMF)(t-BuNC) predominates when Rh/L = 1.00; approximately 0.75 mol CO are displaced per mol Rh at this point. For L/Rh >2.00, the reaction appears to be independent of solvent. Monitoring the reaction of t-BuNC with $Rh_2Cl_2(CO)_4$ in n-butanol by measuring conductance changes (Fig. 3) it can be seen that when L/Rh = 2.00 the neutral complex $RhCl(CO)(t\text{-}BuNC)_2$ must be formed and the linearity of the plot for L/Rh = 2.00 up to nearly 4.00 again agrees with the observation already made that no intermediate in the conversion of $RhCl(CO)(t\text{-}BuNC)_2$ to $[Rh(t\text{-}BuNC)_4]Cl$ is formed in significant concentrations.

In Fig. 2 it can be seen that CO is evolved very similarly from cyclohexane solutions (□ curve) as from toluene (▽ curve) and this would, of course, suggest

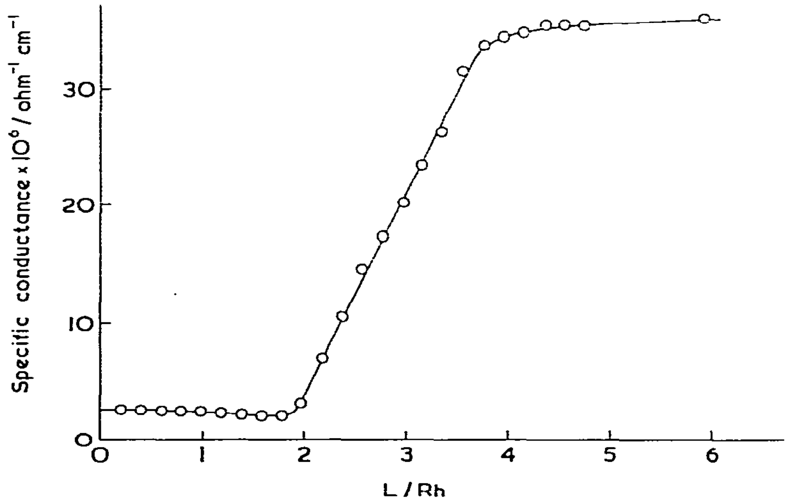


Fig. 3. Specific conductance of a solution of $Rh_2Cl_2(CO)_4$ (1.78×10^{-3} mol dm^{-3}) in butanol at 23°C against molecules of L per Rh atom (L/Rh).

that the same intermediates were involved. However, while the toluene solution remains homogeneous and yellow throughout, the cyclohexane solution gave precipitates. From the first addition of t-BuNC to $Rh_2Cl_2(CO)_4$ in cyclohexane a deep blue-black precipitate was formed which persisted and thickened as more ligand was added up to L/Rh = 2.00, the supernatant liquid remaining yellow. With further additions of t-BuNC the deep coloured precipitate redissolved to be replaced by a yellow one. When L/Rh = 4.00 the colour of the solution had been almost discharged and the yellow precipitate remaining was shown to be $[Rh(t\text{-}BuNC)_4]Cl$. The nature of the blue-black precipitate will now be discussed.

Isolation of intermediates. We have been able to isolate $RhCl(CO)_2(t\text{-}BuNC)$ and $RhCl(CO)(t\text{-}BuNC)_2$ both as intensely purple-black powders as well as the yellow crystalline complexes $[Rh(t\text{-}BuNC)_4]Cl$ and $[Rh(t\text{-}BuNC)_4]ClO_4$.

$RhCl(CO)_2(t\text{-}BuNC)$. Addition of t-BuNC to a solution of $Rh_2Cl_2(CO)_4$ in petroleum ether (b.p. 30—40°C) under an atmosphere of CO (L/Rh = 0.50) gave a blue-black precipitate which was separated by filtration. Addition of a further equal amount of L to the filtrate gave more blue-back precipitate. These materials analyse fairly closely for $RhCl(CO)_2(t\text{-}BuNC)$ (Experimental) but we were unable to recrystallise the complex to obtain totally satisfactory data. Both precipitates dissolve in CO-saturated chloroform to give yellow solutions with the expected $\nu(CO)$ spectra for $RhCl(CO)_2(t\text{-}BuNC)$ and Fig. 4 shows how CO is evolved from this complex on addition of t-BuNC to a yellow toluene solution. These results indicate that the complex is indeed $RhCl(CO)_2$-(t-BuNC) but slightly impure since only 1.90 mol CO were calculated to be displaced. The curve follows closely that shown in Fig. 2 for L/Rh >1.00. Thus although $RhCl(CO)_2(t\text{-}BuNC)$ exists as a yellow solute (probably mononuclear) it gives an intensely coloured solid which either contains discrete oligomers as for $[Rh(RNC)_4]^+$ or extended chains with Rh—Rh bonding as in $IrCl(CO)_3$ [11]. We were unable to obtain suitable crystals for an X-ray diffraction study.

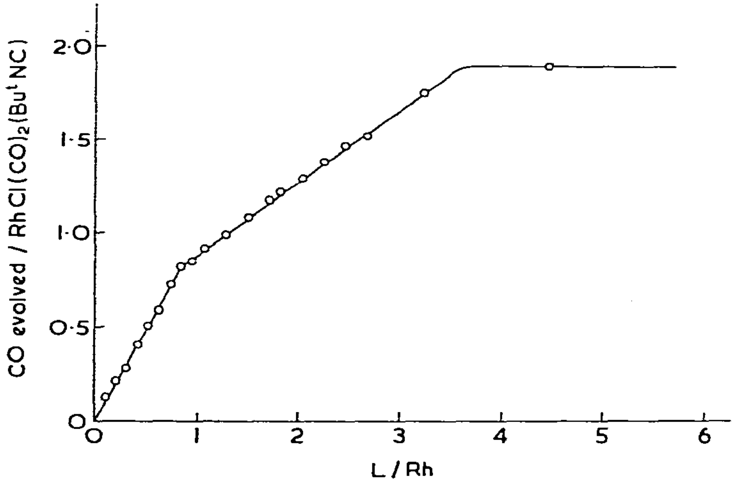


Fig. 4. Graph of molecules of CO evolved per Rh atom against t-BuNC molecules added per Rh atom of $RhCl(CO)_2$(t-BuNC) (L/Rh) for reaction in toluene under CO (1 atm). No CO was absorbed or evolved on dissolving the rhodium complex in toluene before addition of L.

Bubbling N_2 through an ethanol-free chloroform solution of $RhCl(CO)_2$(t-BuNC), prepared by adding the appropriate amount of t-BuNC to $Rh_2Cl_2(CO)_4$, gave gradual changes in the infrared spectrum. After bubbling N_2 for 180 min the original absorptions at 2223, 1101 and 2033 cm^{-1} are totally replaced by new absorptions at 2182, 2093, 2029 and 2011 cm^{-1}; one ν(CN) and three ν(CO) absorptions. Bubbling CO into a sample of this solution gave almost complete regeneration of $RhCl(CO)_2$(t-BuNC). Attempts to isolate solid products gave a blue-black solid which on redissolving in chloroform gave the same four absorptions but with those at 2182 and 2011 cm^{-1} with increased relative intensity. Clearly this is a mixture possibly containing RhCl(CO)(t-BuNC)$_2$ (2182, 2011 cm^{-1}) and another compound or compounds which were unidentified but which are probably binuclear species with chlorobridges.

RhCl(CO)(t-BuNC)$_2$. A mixture of [Rh(t-BuNC)$_4$]Cl and $Rh_2Cl_2(CO)_4$ (2/1 mol ratio) in chloroform gives RhCl(CO)(t-BuNC)$_2$ in solution (infrared spectrum). Removal of the solvent and addition of hexane to the residual red oil gave a blue-back solid. This dissolves to give a yellow chloroform solution with the ν(CO) spectrum as expected for RhCl(CO)(t-BuNC)$_2$. Although the solid and solution have very different colours the ν(CO) spectra of the crystals [2178, 2000 cm^{-1} (Nujol)] and the solution [2181, 2010 cm^{-1} ($CHCl_3$)] are quite similar. In contrast crystals of RhCl(CO)(ArNC)$_2$ are colourless. Probably there are Rh—Rh interactions in crystals of the t-BuNC complex, but not in those of the ArNC complex. $RhCl(CO)_2$(t-BuNC) and RhCl(CO)(t-BuNC)$_2$ give solids with very similar appearance and presumably they are structurally related.

Experimental

Infrared spectra were recorded on a Perkin—Elmer 257 spectrometer and frequencies were calibrated against water vapour absorptions (± 1 cm^{-1}), and conductances were measured with a Philips PR9500 bridge using shiny Pt electrodes. Measurements of CO evolution were made in a thermostatted (20°C) hydrogenation-type apparatus. Solid samples (~ 0.1 g) of the starting complex in a small glass bucket were dropped into stirred solvent (20 cm^3) in a 50 cm^3 flask containing CO gas (1 atm) after thermal equilibrium had been attained. t-BuNC was then introduced with a microsyringe through a rubber serum cap and changes in the gas volume measured.

$RhCl(CO)_2(t\text{-}BuNC)$. t-BuNC (0.0214 g, 1 mol per $Rh_2Cl_2(CO)_4$) was added to a solution of $Rh_2Cl_2(CO)_4$ (0.1006 g) in petroleum ether (b.p. 30—40°C) through which CO gas was slowly bubbled. The instantaneously formed blue-black precipitate (0.0504 g) was removed by filtration and dried under vacuum. Addition of further t-BuNC (0.0214 g) to the yellow filtrate gave more of the blue-black precipitate (0.0695 g). These precipitates were identified as $RhCl(CO)_2$(t-BuNC) (total yield 84%) (Found: First crop; C, 29.7; H, 3.9; N, 5.8; Cl, 13.95; second crop; C, 27.9; H, 4.05; N, 5.7; Cl, 13.2. $C_7H_9ClNO_2Rh$ calcd.: C, 30.3; H, 3.25; N, 5.05; Cl, 12.8%). ν(CO) (CO-saturated $CHCl_3$) 2101s, 2033s; ν(CN), 2223 cm^{-1}. Addition of an excess of t-BuNC gave a calculated 1.90 mol CO per Rh based on above formulation.

$RhCl(CO)(t\text{-}BuNC)_2$. Solutions of $[Rh(t\text{-}BuNC)_4]Cl$ (0.0568 g) and $Rh_2Cl(CO)_4$ (0.0235 g), each in ethanol-free chloroform (15 cm^3), were mixed and the ν(CO) spectrum of the final solution showed the desired product. The solution was evaporated to dryness under reduced pressure and addition of hexane to the deep red residual oil gave a blue-black solid on scratching (0.048 g, 60%) (Found: C, 39.45; H, 5.6; N, 8.35; Cl, 11.45. $C_{11}H_{18}ClN_2ORh$ calc.: C, 39.7; H, 5.45; N, 8.4; Cl, 10.45%). ν(CO) 2000 (Nujol), 2010 ($CHCl_3$) and ν(CN) 2178 (Nujol), 2181 ($CHCl_3$) cm^{-1}.

Acknowledgements

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