Ruthenium Complexes Containing $Ph_2PCH_2CH_2SPh$ as a Mono- or Bidentate Ligand or Both

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Reaction of $[RuCl_2(CO)_3]_2$ with $Ph_2PCH_2CH_2SPh$ (L) gives successively $[RuCl_2(CO)_3(L)]$ and $[RuCl_2(CO)_2(L)_2]$, in each of which L is coordinated by the phosphorus atom alone. In contrast, the complexes $[RuCl_3(L)]$, and $[RuCl_2(L)_2]$ each contain L as a bidentate ligand. The complex $[RuCl_2(CO)(L)_2]$ contains L as both a monodentate and a bidentate chelating ligand.

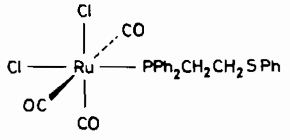
Introduction

Reactions of equivalent or greater amounts of $Ph_2PCH_2CH_2SPh$ (L) [1] with Rh^I [2], Pd^{II} [3], or Pt^{II} [3] give products containing L as either a monodentate (P) or bidentate (P, S) ligand. Herein we report the formation of a similar series of complexes of ruthenium(II) or ruthenium(III), and a novel complex containing both monodentate and bidentate L.

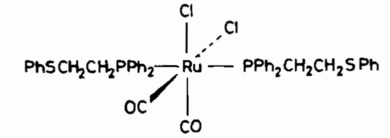
Results and Discussion

At room temperature in solution in dichloromethane the dinuclear complex $[RuCl_2(CO)_3]_2$, (*1*), is cleaved by reaction with an equimolar or greater amount of L to form *cis*-$[RuCl_2(CO)_3(L)]$, (*2*), in which L is coordinated to ruthenium by only the phosphorus donor atom. This white, crystalline complex exhibits carbonyl bands in the IR spectrum (ν(CO) = 2130(m), 2056(s), 1995(s) cm^{-1}; ν(RuCl) = 307, 282 cm^{-1}) similar to those exhibited by *cis*-$[RuCl_2(CO)_3(PPh_3)]$ [4], but the product is considerably more stable to loss of CO. This stability is all the more surprising considering the facile preparation of the chelated 2-diphenylphosphinopyridine (L') complex *cis*-$[Ru(L')Cl_2(CO)_2]$ by the reaction of chlorine with $[Ru(L')(CO)_3]_3$ [5]. In a separate experiment, a benzene solution of complex *1* and excess L was refluxed for 48 hours under an atmosphere of dinitrogen. After removal of solvent and subsequent attempted recrystallization of the product from dichloromethane/diethyl ether, impure $[Ru(L)_2Cl_2(CO)_2]$, (*3*), was obtained in relatively poor yield as a white powder (ν(CO) = 2056, 1993 cm^{-1}); (ν(RuCl) = 301, 279 cm^{-1}). This product is analogous to both $[RuCl_2(CO)_2(PPh_3)_2]$ [6] and $[RuCl_2(CO)_2(L')_2]$ [5]. The infra-red spectrum indicated that the pairs of carbonyl or chloro-ligands are each mutually *cis*. The ^{31}P NMR spectrum (δ(P) = +16.4 ppm *vs.* 85% H_3PO_4) demonstrates that the phosphorus atoms are equivalent. Therefore the ligands L are mutually *trans*. It is interesting to note that complexes (*2*) and (*3*) each contain L as a monodentate (P) ligand.

When equimolar quantities of $[RuCl_3 \cdot 3H_2O]$ and L react under an atmosphere of N_2 the initial grey-



(2)



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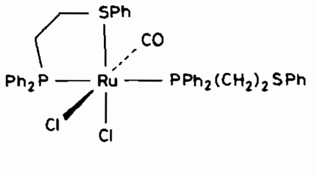

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green product is $[RuCl_3(L)]$, (*4*, ν(RuCl) = 326(s,b) cm^{-1}), contaminated with other products from which it can be purified by extraction with CH_2Cl_2, addition of diethyl ether, and slow evaporation of the green solution. However, reaction of $[RuCl_3{\cdot}3H_2O]$ with greater amounts of *L* gives more highly substituted complexes, with concomitant subsequent reduction of the central metal atom to ruthenium(II). When an ethanolic solution of $[RuCl_3{\cdot}3H_2O]$ and excess *L* was refluxed for a prolonged time under an atmosphere of dinitrogen the pink product was $[RuCl_2(L)_2]_x$, (*5*; ν(RuCl) = 311(s) cm^{-1}). Each *L* is probably bidentate (P, S), thereby affording a 6-coordinate (18-electron) complex. This product is of such low solubility in all solvents as to preclude determination of its molecular weight. When the above experiment was performed at lower temperatures, or for shorter periods, mixtures of products were obtained.

The initial light-brown precipitate formed when an ethanolic solution of $[RuCl_3{\cdot}3H_2O]$ reacts with CO and an equivalent or greater amount of *L* has a composition consistent with formulation as impure $[Ru_2Cl_4(CO)_2(L)_3]$, (*6*), which would be analogous to $[Ru_2Cl_4(CO)_2\{Ph_2P(CH_2)_4PPh_2\}_3]$ [7]. The molecular weight of *6* also indicates that the product is a dinuclear complex which is partially dissociated in solution in CH_2Br_2 (*M*, 1298 calculated, 1566). When a similar reaction mixture is refluxed under an atmosphere of CO the product is instead the mononuclear complex $[RuCl_2(CO)(L)_2]$, (*7*). Complex *7* is a non-electrolyte. The carbonyl band in the infra-red spectrum (ν(CO) = 1969 cm^{-1}; ν(RuCl) = 308, 256 cm^{-1}) is of a value appropriate for a carbonyl ligand *trans* to a chloro-ligand [7]. The value of the coupling constant between the inequivalent phosphorus atoms ($\delta(P^1)$ = 16.4 ppm; $\delta(P^2)$ = −13.9 ppm; $^2J(P^1{-}P^2)$ = 349.1 Hz) shows that they are mutually *trans* [8]. The two ligands *L* are therefore dissimilar, one being monodentate (P) and the other bidentate (P, S).

In contrast to related complexes of rhodium(I) [9], the chloro-complexes herein described are not efficient catalysts for either the hydrogenation or hydroformylation of alkenes, having very low activity at moderate temperatures and atmospheric pressure. It is anticipated that hydrido-complexes derived from the above systems will be more active.

Experimental

The ligand $Ph_2PCH_2CH_2SPh$ was prepared as described in the literature [1]. Complexes $[RuCl_2(CO)_3]_2$ and $[RuCl_3{\cdot}xH_2O]$ (x ~ 3) were purchased from Strem Chemicals Inc., and were used without further purification. Solvents were dried, distilled, and flushed with the appropriate gas (CO or N_2).

Infra-red spectra of products were obtained from Nujol mulls using a Perkin-Elmer 283 instrument, and ^{31}P NMR spectra were obtained using a Bruker WP80 instrument. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Germany.

The specific conditions for each reaction arre described in the text.

Example 1

Under an atmosphere of N_2 a mixture of $[RuCl_3{\cdot}3H_2O]$ (0.065 g, 0.25 mmol) and $Ph_2PCH_2CH_2SPh$ (0.242 g, 0.75 mmol) in ethanol was successively refluxed for 52 hours, cooled to room temperature, filtered, and the precipitate dried under vacuum to yield, as a pink powder, $[RuCl_2(Ph_2PCH_2CH_2SPh)_2]_x$ (Yield = 91%).

Example 2

A mixture of $[RuCl_2(CO)_3]_2$ (0.061 g, 0.12 mmol) and $Ph_3PCH_2CH_2SPh$ (0.163 g, 0.51 mmol) in benzene (30 ml) was refluxed (2 h) under an atmosphere of N_2 and then allowed to successively cool and evaporate to dryness. The sticky product was stirred with diethyl ether (1.5 h), and the mixture was filtered to give, as a pale, creamy-white powder, $[RuCl_2(CO)_2(Ph_2PCH_2CH_2SPh)_2]$. The material was recrystallized from dichloromethane/diethyl ether (Yield ~45%).

Example 3

Under an atmosphere of CO a mixture of $[RuCl_3{\cdot}3H_2O]$ (0.065 g, 0.25 mmol) and $Ph_2PCH_2CH_2SPh$ (0.242 g, 0.75 mmol) in ethanol (50 ml) was refluxed for 4 hours. The mixture was successively allowed to cool to room temperature, filtered, and the precipitate dried under vacuum to give, as a pale brown powder, $[RuCl_2(CO)(Ph_2PCH_2CH_2SPh)_2]$. Slow evaporation of 25% of the mother liquor under a stream of CO gave a second crop of similar material (IR) as a fine off-white powder, (total yield ~40%). Subsequent material precipitated by evaporation of the solvent was impure, and included unreacted starting material.

When the mixture was refluxed under CO for much longer periods the major product was $[RuCl_2(CO)_2(Ph_2PCH_2CH_2SPh)_2]$, identified by comparison with the product of Example 2 above.

Elemental Analyses of Products (calculated values in parentheses):

(*2*): C, 47.51 (47.76); H, 3.42 (3.31); Cl, 12.05 (12.26); S, 5.57 (5.54)%.

(*3*): C, 56.44 (57.79); H, 4.46 (4.39); Cl, 7.98 (8.12); P, 7.03 (7.10); S, 7.10 (7.35)%.

(*4*): C, 45.48 (45.34); H, 3.76 (3.61); P, 5.98 (5.85); S, 6.15 (6.05)%

(*5*): C, 58.73 (58.82); H, 4.78 (4.69); Cl, 8.28 (8.68); P, 7.40 (7.58); S, 7.54 (7.85)%.

(*6*): Cl, 10.63 (10.37); P, 6.74 (6.80); S, 6.95 (7.03)% (C analyses were inconsistent).

(*7*): C, 57.56 (58.29); H, 4.95 (4.53); Cl, 7.89 (8.39); P, 7.18 (7.33); S, 7.43 (7.59)%.

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