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Preliminary communication

REACTIONS OF A DICHLOROCARBENE-RUTHENIUM COMPLEX, $RuCl_2(CCl_2)(CO)(PPh_3)_2$

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Summary

The dichlorocarbene ligand, in the new complex $RuCl_2(CCl_2)(CO)(PPh_3)_2$, readily undergoes substitution reactions in which the integrity of the metal—carbon bond is maintained. Reactions with species H_2X ($X = O, S, Se$) give chalcocarbonyl complexes $RuCl_2(CX)(CO)(PPh_3)_2$ while RXH ($X = O, S$) give new carbene complexes $RuCl_2[C(XR)_2](CO)(PPh_3)_2$. Ammonia reacts to give a cyanide-containing complex, $RuCl(CN)(CO)(NH_3)(PPh_3)_2$, and primary amines, an isocyanide complex, or in the case of certain primary diamines cyclic carbene complexes. $RuCl_2(CNNMe_2)(CO)(PPh_3)_2$ is formed in the reaction with *N,N*-dimethylhydrazine. Secondary amines, R_2NH, react to give chloroamino-carbene complexes, $RuCl_2[C(Cl)NR_2](CO)(PPh_3)_2$.

Dihalocarbene complexes are rare but interesting because of the potential for the halogens to act as good leaving groups in substitution reactions. Some of the diversity of ligands that may be formed has been explored in the tetraphenylporphyrin-iron system where reactions converting the dichlorocarbene ligand to carbonyl and isocyanide ligands have been reported [1]. Other reactions have been described for the osmium complex $OsCl_2(CCl_2)(CO)(PPh_3)_2$ in which novel tellurocarbonyl and carbyne complexes were formed [2].

We have recently prepared, by a reaction analogous to that used for the osmium complex, a new dichlorocarbene complex $RuCl_2(CCl_2)(CO)(PPh_3)_2$, containing a more reactive dichlorocarbene ligand than in the osmium case.

The reaction of the dichlorocarbene-ruthenium complex with amines is the most facile of the reactions reported here. A benzene solution of the complex rapidly loses the bright orange colour when exposed to ammonia, and white crystals of the cyanide complex $RuCl(CN)(CO)(NH_3)(PPh_3)_2$ result. The coordinated ammonia is readily substituted by CO to give the dicarbonyl complex (see Scheme 1).

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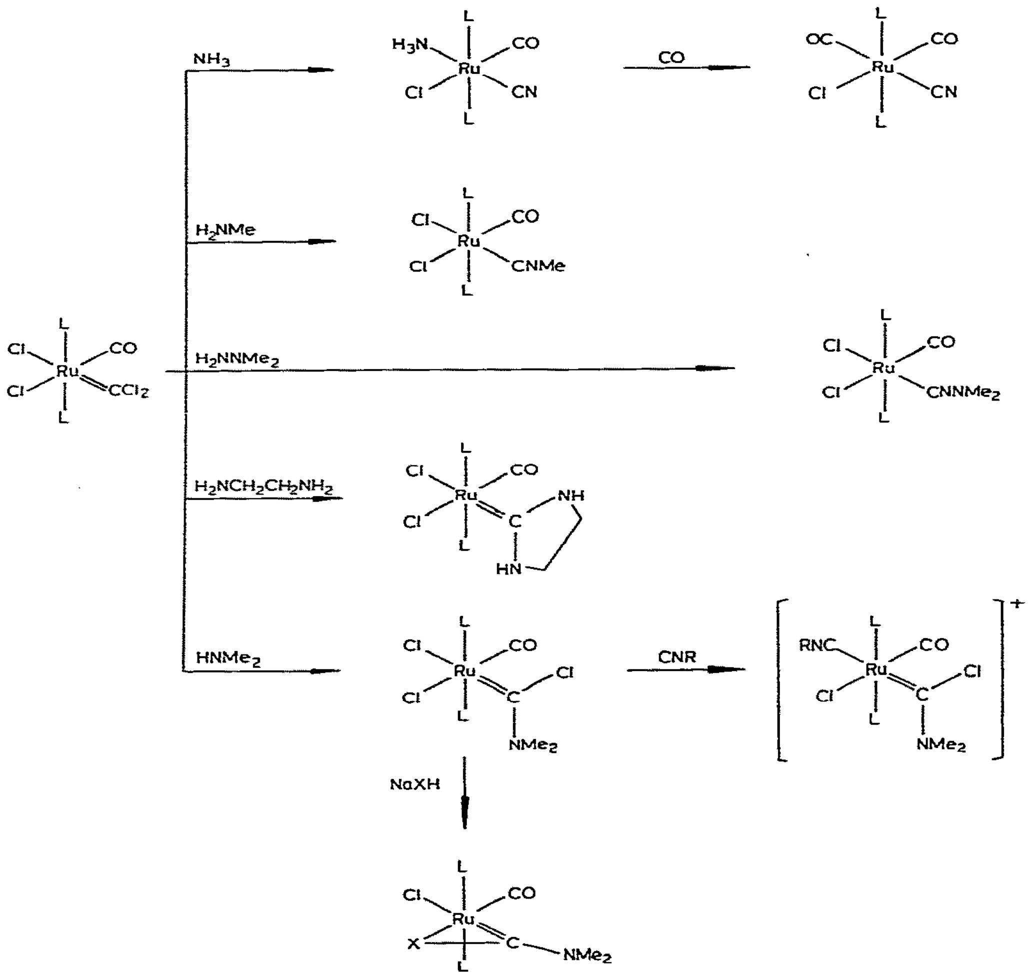
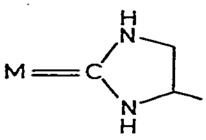


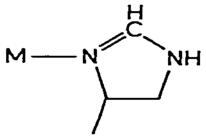
SCHEME 1: Reaction of $RuCl_2(CCl_2)(CO)(PPh_3)_2$ with amines ($L = PPh_3$; R = *p*-tolyl; X = S, Se, Te).

Simple primary amines also react rapidly at room temperature to give the isocyanide complexes $RuCl_2(CNR)(CO)(PPh_3)_2$ (R = Me, *p*-tolyl). The scope of this reaction has been tested using H_2NNMe_2 which gave the dimethylamino isocyanide complex, a product related to the previously reported $CNNH_2$-containing complex [3].

Cyclic diaminocarbene ligands are produced from reactions with primary diamines with the dichlorocarbene ligand. The product from the reaction with 1,2-diaminopropane has been characterised as the carbene complex (A) rather than the nitrogen-bound rearrangement product (B) from the ^{13}C NMR spectrum which shows a triplet signal at δ 197 ppm, typical of metal-bound carbene-carbon atoms.

Secondary amines such as dimethylamine substitute a single chloride to give the chloroaminocarbene complex $RuCl_2[C(Cl)NMe_2](CO)(PPh_3)_2$. Similar complexes, prepared by different methods, have been isolated by Lappert [4]


(A)


(B)

and by Fischer [5]. One of the metal-bound chlorides is sufficiently labile to be substituted at room temperature by *p*-tolyl isocyanide, giving the cationic complex $[RuCl\{C(Cl)NMe_2\}(CO)(CN\text{-}p\text{-}tolyl)(PPh_3)_2]ClO_4$.

Reactions involving the carbene ligand are also possible. Reagents of the type NaXH (X = S, Se, Te) react with the complex to give the series of *dihapto*-chalcocarboxamido-complexes $R\overline{u[C(X})NMe_2]Cl(CO)(PPh_3)_2$.

As with the osmium case, the dichlorocarbene complex reacts with H_2X (X = O, S, Se) (see Scheme 2) to give the chalcocarbonyl complexes [6]. The comparative reactivity of the two complexes is indicated by the milder conditions required for the hydrolysis of the ruthenium complex. A simple model involving nucleophilic attack by the base at the electrophilic carbene carbon followed by elimination of two equivalents of HCl suffices to explain the reaction products and is applicable to all the results described herein.

Thiols react with the complex to give the disubstituted carbene complex in all the cases tried. The reactions require heating, unlike the amine reactions, but conversion to the yellow dithiocarbene complex is then quantitative. The complexes add to the already large and well-studied group of dithiocarbene complexes [7].

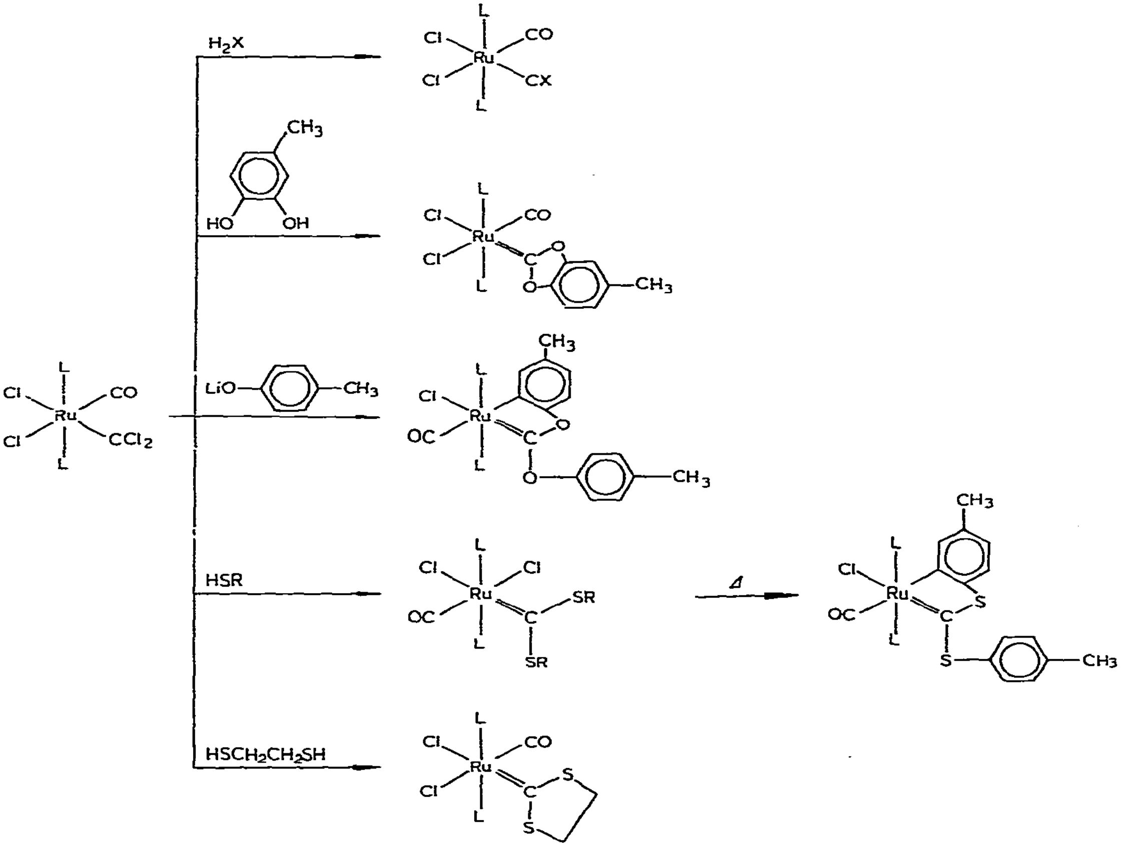
TABLE 1

IR DATA[a] FOR RUTHENIUM COMPLEXES[b]

Compound	ν(CO)	Other bands
$RuCl_2(CCl_2)(CO)(PPh_3)_2$	(2030,2005)[c]	ν(CCl) 860,(790,780)[c]
$RuCl(CN)(CO)(NH_3)(PPh_3)_2$	1955	ν(CN) 2100
$RuCl(CN)(CO)_2(PPh_3)_2$	2065,2005	ν(CN) 2120
$RuCl_2(CNNMe_2)(CO)(PPh_3)_2$	(1974,1943)[c]	ν(CN) 2165
$RuCl_2(\overline{CNHCH_2CH_2NH})(CO)(PPh_3)_2$	(1940,1925)[c]	
$RuCl_2(CClNMe_2)(CO)(PPh_3)_2$	1980	ν(CCl) 795
$[RuCl(CClNMe_2)(CNC_6H_4Me\text{-}4)(CO)(PPh_3)_2]ClO_4$	1990	ν(CCl) 814
$R\overline{u(CS}NMe_2)Cl(CO)(PPh_3)_2$	1920	ν(CS) 847
$R\overline{u(CSe}NMe_2)Cl(CO)(PPh_3)_2$	1918	ν(CSe) 800
$R\overline{u(CTe}NMe_2)Cl(CO)(PPh_3)_2$	1920	ν(CTe) 762
$RuCl_2(CO)[C(SMe)_2](PPh_3)_2$	1950	
$RuCl_2(CO)(\overline{CSCH_2CH_2S})(PPh_3)_2$	1945	
$RuCl_2(CO)[\overline{COC_6H_3(Me\text{-}4)O}](PPh_3)_2$	1985	
$R\overline{u[C(OC_6H_4Me\text{-}4)OC}_6H_3Me\text{-}4]Cl(CO)(PPh_3)_2$	1964	
$RuCl_2(CO)[C(SC_6H_4Me\text{-}4)_2](PPh_3)_2$	(1968,1936)[c]	
$R\overline{u[C(SC_6H_4Me\text{-}4)(SC}_6H_3Me\text{-}4)]Cl(CO)(PPh_3)_2$	1975	
$RuCl_2(CNCH_2CH_2OH)(CO)(PPh_3)_2$	1995	ν(CN) 2200
$RuCl_2(\overline{CNHCH_2CH_2O})(CO)(PPh_3)_2$	1960	

[a] In cm^{-1} measured as Nujol mulls. [b] All compounds have satisfactory carbon and hydrogen analyses. [c] Twin of absorptions due to solid-state splitting.

The reaction with phenols proceeds less readily. Although the reaction with catechol gives the expected cyclic carbene ligand, it is necessary to use the preformed lithium salt for satisfactory reaction with *p*-cresol. The product is not the simple carbene, but rather contains one of the aromatic rings σ-bound to the metal (see Scheme 2). A similar *ortho*-metallated product has been characterised by Lappert in his studies of carbenes formed from electron-rich olefins [8].



SCHEME 2: Reactions of $RuCl_2(CCl_2)(CO)(PPh_3)_2$ with other nucleophiles ($L = PPh_3$; X = O, S, Se; R = Me or *p*-tolyl).

The intermediacy of the simple carbene complex can be inferred from the reaction of the dichlorocarbene complex with *p*-toluenethiol. In this case the simple carbene can be isolated and *ortho*-metallation induced by vigorous heating in xylene.

The relative reactivity of moieties containing nucleophilic nitrogen and oxygen atoms is given by the reaction with ethanolamine. The reaction proceeds at room temperature, and rapid purification of the product produces the isocyanide complex exclusively, while slow recrystallisation gives the cyclic carbene. The interconversion of related isocyanide and carbene complexes has been observed previously with Pd and Pt complexes [9].

Some IR data for the ruthenium complexes obtained are reported in Table 1.

References

1 D. Mansuy, Pure Appl. Chem., 52 (1980) 681.

2 G.R. Clark, K. Marsden, W.R. Roper and L.J. Wright, J. Amer. Chem. Soc., 102 (1980) 1206; ibid., 102 (1980) 6570.

3 W.P. Fehlhammer, P. Buracas and K. Bartel, Angew. Chem. Int. Ed Engl., 16 (1977) 707.

4 A.J. Hartshorn, M.F. Lappert and K. Turner, J. Chem. Soc. Chem. Commun., (1975) 929.

5 E.O. Fischer, W. Kleine and F.R. Kreissl, J. Organometal. Chem., 107 (1976) C23.

6 $RuCl_2(CO)_2(PPh_3)_2$, J.P. Collman and W.R. Roper, J. Amer. Chem. Soc., 87 (1965) 4008; $RuCl_2(CO)(CS)(PPh_3)_2$, K.R. Grundy, R.O. Harris and W.R. Roper, J. Organometal. Chem., 90 (1975) C34; $RuCl_2(CO)(CSe)(PPh_3)_2$, G.R. Clark, K.R. Grundy, R.O. Harris, S.M. James and W.R. Roper, ibid., 90 (1975) C37.

7 For example: F.B. McCormick and R.J. Angelici, J. Organometal. Chem., 205 (1981) 79.

8 P.B. Hitchcock, M.F. Lappert, P.L. Pye and S. Thomas, J. Chem. Soc Dalton Trans., (1979) 1929.

9 K. Bartel, W.P. Fehlhammer, Angew. Chem. Int. Ed. Engl., 13 (1974) 599.