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Preliminary communication

COMBINED DECARBOXYLATION OF THE FORMATO LIGAND AND REDUCTIVE ELIMINATION OF HYDRIDO AND ARYL GROUPS IN THE SYNTHESIS OF RUTHENIUM(0) COMPLEXES. METHYLATION OF RUTHENIUM(0) WITH FORMALDEHYDE

W.R. ROPER* and L.J. WRIGHT
Department of Chemistry, University of Auckland, Auckland (New Zealand)

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Summary

The formato ligand is readily introduced into the 5-coordinate complexes $MRCl(CO)(PPh_3)_2$ (M = Ru or Os, R = *o*-tolyl) giving 6-coordinate $MR(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$. In the presence of excess PPh_3 thermal decarboxylation of the osmium complex leads to the stable aryl, hydride, $OsRH(CO)(PPh_3)_3$. A similar reaction with $RuR(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$ is accompanied by reductive elimination of RH and formation of "$Ru(CO)(PPh_3)_3$" which as a solid is *ortho*-metallated, i.e. exists as $Ru(C_6H_4PPh_2)H(CO)(PPh_3)_2$. Decarboxylation and reductive elimination in the presence of bis(diphenylphosphino)ethane (dppe) give the zerovalent $Ru(CO)(dppe)_2$. "$Ru(CO)(PPh_3)_3$" undergoes a most unusual reaction with formaldehyde forming $Ru(CH_3)(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$.

Several preparative routes to zerovalent complexes of ruthenium and osmium involve intermediate divalent hydrido complexes. Of the following three possible routes:

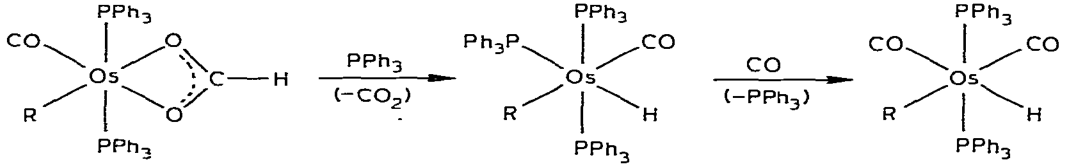
$$L_5M^{II}H]^+ \xrightarrow[-H^+]{\text{base}} L_5M^0 \qquad (1)$$

$$L_4M^{II}H_2 \xrightarrow[-H_2]{L} L_5M^0 \qquad (2)$$

$$L_4M^{II}RH \xrightarrow[-RH]{L} L_5M^0 \qquad (3)$$

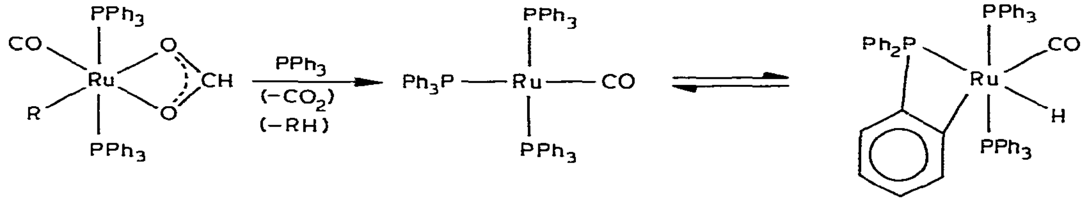
(1) has been used with some success, e.g. for $Ru(CO)_2(CN\text{-}p\text{-tolyl})(PPh_3)_2$ [1], $Ru(CO)_2(PPh_3)_3$ and $Os(CO)_2(PPh_3)_3$ [2], and for $Os(CO)(CS)(PPh_3)_3$ [3]. A possible complication when the ligands include groups like CS or carbene is attack by base at the ligand rather than a deprotonation at the metal. A general observation, relevant for methods (2) and (3) is that reductive elimination of RH is often more facile than reductive elimination of H_2 [4]. Method (3) is therefore appealing provided that the required L_4MRH precursors are accessible. We describe here a simple synthesis of several L_4MRH complexes from thermal decarboxylation of the corresponding formates, and the further reductive elimination of RH leading to ruthenium(0) complexes. The R group chosen was the rather bulky *o*-tolyl group in order to facilitate elimination. In addition, a reaction of a ruthenium(0) complex with formaldehyde which leads to a ruthenium(II) methyl derivative is reported.

The red 5-coordinate complexes $MRCl(CO)(PPh_3)_2$ result from reaction of $MHCl(CO)(PPh_3)_3$ with HgR_2 [5]. Further reaction with sodium formate introduces the formato ligand in $MR(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$. The *dihapto* nature of the formato ligand is indicated by the pale-yellow colour of these molecules, suggesting 6-coordination and IR data (see Table 1) supports this conclusion. When $OsR(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$ is heated in benzene under reflux in the presence of PPh_3, CO_2 is lost and colourless $OsRH(CO)(PPh_3)_3$ is formed. $OsH_2(CO)_2(PPh_3)_2$ similarly results from $Os(\eta^1\text{-}O_2CH)_2(CO)_2(PPh_3)_2$ [6]. Carbonylation of $OsRH(CO)(PPh_3)_3$ readily replaces a labile phosphine giving $OsRH(CO)_2(PPh_3)_2$.



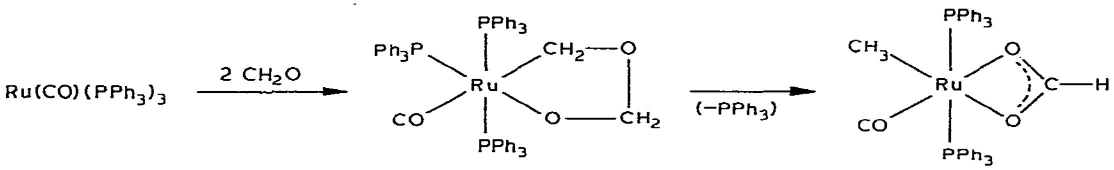
These compounds join $Os(CH_3)H(CO)_2(PPh_3)_2$ [7] as further examples of stable *cis*-hydrido-alkyl (or -aryl) complexes of osmium(II).

A similar decarboxylation of $RuR(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$, best carried out in t-butanol, is accompanied by reductive elimination of RH and leads directly to "$Ru(CO)(PPh_3)_3$". As a solid this material is formulated as $\overline{Ru(C_6H_4P}Ph_2)H(CO)(PPh_3)_2$ since IR activity at 1554 and 1415 cm^{-1} is characteristic of *ortho*-metallated triphenylphosphine [8]. The complex also exhibits an IR band at 1949 cm^{-1} assigned to $\nu(RuH)$.



Benzene solutions of this complex react as zerovalent $Ru(CO)(PPh_3)_3$ which is isoelectronic with $RhCl(PPh_3)_3$. H_2 gives $RuH_2(CO)(PPh_2)_3$. HCl gives

$RuHCl(CO)(PPh_3)_3$, CO gives $Ru(CO)_3(PPh_3)_2$ and aldehydes are decarbonylated giving $Ru(CO)_2(PPh_3)_3$. An intriguing reaction with formaldehyde gives a ruthenium(II) methyl derivative.



Any 1/1 formaldehyde complex $Ru(\eta^2\text{-}CH_2O)(CO)(PPh_3)_3$, analogous to $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ [9], which may be formed initially, must undergo a ring-expansion reaction with a further molecule of formaldehyde forming the metallacycle depicted before rearrangement to the observed product $Ru(CH_3)(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$. A metallacycle similar to the postulated intermediate is formed by hexafluoroacetone on nickel(0) [10].

TABLE 1

IR[a] AND ^{1}H NMR DATA FOR RUTHENIUM AND OSMIUM COMPLEXES

Compound[b]	ν(CO) (cm^{-1})	Other bands (cm^{-1})	Chemical shift (τ)[c]
$OsR(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$	1901	1548, 1360 (formate)	
$RuR(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$	1913	1548, 1358 (formate)	
$OsRH(CO)(PPh_3)_3$	1903	2220w ν(OsH)	
$OsRH(CO)_2(PPh_3)_2$	2026,1968	1914 ν(OsH)	15.09, t, 1H, Os*H* ^2J(HP) 23 Hz
"$Ru(CO)(PPh_3)_3$"	1922	1949m ν(RuH)	
"$Os(CO)(PPh_3)_3$"	1913	2022w ν(OsH)	
$Ru(CO)(dppe)_2$	1833		
cis-$[RuH(CO)(dppe)_2]^+$	1982		17.80 dq, 1H, Ru*H* $^2J(HP)_{trans}$ 70; $^2J(HP)_{cis}$ 20 Hz
$RuCH_3(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$	1915	1549, 1352 (formate)	9.55, t, 3H CH_3 ^3J(HP) 5.5 Hz 3.10, t, 1H, O_2CH, ^4J(HP) 1.9 Hz

[a] Measured as Nujol mulls; all bands strong unless indicated otherwise. [b] Satisfactory elemental analyses obtained for all compounds. [c] In $CDCl_3$ solution.

If the decarboxylation of $RuR(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$ is carried out in the presence of dppe the yellow-orange, very air-sensitive, $Ru(CO)(dppe)_2$ is formed. This is readily protonated by acids to *cis*-$[RuH(CO)(dppe)_2]^+$ (see Table 1 for data relating to these compounds).

$OsRH(CO)(PPh_3)_3$ also undergoes slow reductive elimination upon prolonged heating under reflux in benzene (0.5 h) forming $\overline{Os(C_6H_4P}Ph_2)H(CO)(PPh_3)_2$.

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References

1 D.F. Christian and W.R. Roper, Chem. Commun., (1971) 1271.
2 B.E. Cavit, K.R. Grundy and W.R. Roper, J. Chem. Soc. Chem. Commun., (1972) 60.
3 T.J. Collins and W.R. Roper, J. Organometal. Chem., 139 (1977) C56.
4 J.R. Norton, Accounts Chem. Res., 12 (1979) 139.
5 W.R. Roper and L.J. Wright, J. Organometal. Chem., 142 (1977) C1.
6 K.R. Laing and W.R. Roper, J. Chem. Soc. A, (1969) 1889.
7 C.E.L. Headford and W.R. Roper, J. Organometal. Chem., 198 (1980) C7.
8 D.J. Cole-Hamilton and G. Wilkinson, J. Chem. Soc. (Dalton), (1979) 1283.
9 K.L. Brown, G.R. Clark, C.E.L. Headford, K. Marsden and W.R. Roper, J. Amer. Chem. Soc., 101 (1979) 503.
10 M. Green, S.K. Shakshooki and F.G.A. Stone, J. Chem. Soc. (Dalton), (1971) 2828.