Oxidation of Alcohol to Co-ordinated Carboxylate with a Dioxygen Complex of Ruthenium. Examples of Reversible Hydrogen Transfer to an Isocyanide Ligand

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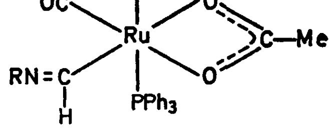
Summary The dioxygen complex, $Ru(O_2)(CO)(CNR)(PPh_3)_2$ (R = *p*-tolyl), reacts with alcohols, $R'CH_2OH$ (R′ = Me, Et, or Ph) forming $Ru(O_2CR')(CHNR)(CO)(PPh_3)_2$; when the bidentate carboxylate group is replaced by iodide the ruthenium hydride $RuHI(CO)(CNR)(PPh_3)_2$ results which reacts with acetate with returns of hydride to the isocyanide ligand forming $Ru(O_2CMe)(CHNR)(CO)(PPh_3)_2$.

DIOXYGEN complexes of Group VIII metals, have been shown to bring about many oxidations,[1] some catalytically.[2] In the course of our study of the properties of dioxygen bound to a metal we discovered an unusual reaction with alcohols. When $Ru(O_2)(CO)(CNR)(PPh_3)_2$[3] is heated in ethanol, pale yellow crystals (I), m.p. 186—187 °C are formed (50%). Structure (I) was confirmed by i.r. and n.m.r. spectra and by complete *X*-ray structure determination.

The i.r. spectrum shows a single ν (CO) at 1939 cm^{-1} and no absorptions above 2000 cm^{-1} expected for ν (CN) for an isocyanide ligand. However, there is a strong band at 1556 cm^{-1} attributed to ν (C=N) of the *N*-(*p*-tolyl)formimidoyl-ligand. Bands associated with the OCO stretching modes of the chelate acetate occur at 1527 and 1451 cm^{-1} [*cf.* 1526 and 1451 cm^{-1} for $RuH(O_2CCH_3)(PPh_3)_3$[4]]. The



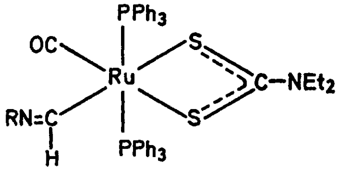
(I)

^1H n.m.r. spectrum (in $CDCl_3$) shows signals at τ 9·45 (s, 3H, Me of bidentate acetate), 7·86 (s, 3H, Me of *p*-tolyl), and −0·32 [t, 1H, single hydrogen of the formimidoyl ligand coupled with two ^{31}P nuclei, *J*(P–H) 2 Hz].

Crystals of (I) are monoclinic; $a = 9{\cdot}927(4)$, $b = 14{\cdot}651(4)$, $c = 27{\cdot}957(5)$ Å, $\beta = 92° 5'$; space group $P2_1/c$; D_c 1·358 g cm^{-3} for $Z = 4$, $D_m = 1{\cdot}34$. Intensity data were collected on a Hilger and Watts automated four-circle diffractometer using Mo-K_α *X*-radiation. Initial least-squares refinement using isotropic thermal parameters has lowered the *R*-factor to 0·08 for 2542 observed reflections. The analysis has confirmed the structure shown; ∠(Ru–C–N) = 132 ± 1° d(Ru–CHNR) = 1·97 ± 0·01 d(Ru–CO) = 1·79 ± 0·01 Å. The hydrogen atom of the formimidoyl ligand has not yet been located.

Like other $>C=NR$ groups σ-bonded to transition metals $Ru(O_2CMe)(CHNR)(CO)(PPh_3)_2$ is reversibly protonated by acids[5] to form carbene complexes; *e.g.* with HCl, $RuCl(O_2CCH_3)(CHNHR)(CO)(PPh_3)_2$ is formed.

Reaction of $Ru(O_2)(CO)(CNR)(PPh_3)_2$ with n-propanol or benzyl alcohol produces compounds analogous to (I) with bidentate propionate and benzoate respectively, but reaction with acetaldehyde or acetic acid results only in $Ru(O_2CMe)_2(CO)(CNR)(PPh_3)_2$.



(II)

The acetate is readily cleaved from (I) by sodium diethyldithiocarbamate and the product (II) retains the unusual formimidoyl ligand.

$Ru(S_2CNEt_2)(CHNR)(CO)(PPh_3)_2$, m.p. 130—131 °C, has ν (CO) at 1916 cm^{-1} and the ^1H n.m.r. spectrum again shows the formimidoyl proton as a triplet at τ −0·29 [J(P–H) 3 Hz]. An alternative synthesis of this compound is from $RuH(OClO_3)(CO)(CNR)(PPh_3)_2$[3] with sodium diethyldithiocarbamate, when replacement of perchlorate by the bidentate dithiocarbamate induces hydride migration from ruthenium on to the isocyanide ligand. The ethyl groups in this chelate dithiocarbamate are non-equivalent demonstrating that there is restricted rotation about the C–N band of the dithiocarbamate as observed in other complexes of this ligand.[6]

When acetate is cleaved from (I) by iodide, hydride moves to the metal and the isocyanide ligand is regenerated in $RuHI(CO)(CNR)(PPh_3)_2$, m.p. 120 °C; ν (CO), 1987, ν (CN), 2125 cm^{-1}; ^1H n.m.r. τ 15·6 [t, J(P–H) 20 Hz]. This hydride reacts with excess of acetate, hydride returning to the isocyanide reforming (I).

The formimidoyl ligand has not been reported previously associated with transition metals but N-(cyclohexyl)-formimidoyltrimethylsilane results from the addition of trimethylsilane to cyclohexylisocyanide.[7] Other examples of hydrogen transfer from metal to ligand are not common but transfer to nitrosyl ligand,[8] ketimido-ligand,[9] and coordinated acetylene[10] are known. Corresponding transfer to the carbonyl ligand has not been reported although $HCOMn(CO)_4$ has been suggested to account for the fast CO exchange in $HMn(CO)_5$.[11]

Elemental analyses are consistent with the above formulae.

(*Received*, 10*th February* 1972; *Com.* 218.)

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