

## Cationic Formyl Complexes of Ruthenium(II)

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Low temperature reductions of  $[\text{Ru}(\text{CO})_2(\text{P-P})_2][\text{SbF}_6]_2$  [ $\text{P-P} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm) or  $(\text{Ph}_2\text{PCH}_2)_2$  (dppe)] with  $\text{NaHB}(\text{OEt})_3$  or  $\text{LiHBEt}_3$  afford the formyl complexes,  $[\text{Ru}(\text{CHO})(\text{CO})(\text{P-P})_2]\text{X}$  ( $\text{X} = [\text{SbF}_6]^-$  or  $[\text{BET}_4]^-$ ), which are fully characterised by spectroscopic means.

Although complexes of ruthenium are among the few that have been shown<sup>1-3</sup> unequivocally to catalyse the homogeneous reduction of carbon monoxide by hydrogen, no fully characterised formyl complexes of ruthenium have been isolated, despite the fact that they have often been invoked as intermediates in such reductions. Short-lived formyls, formed by the reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with  $\text{LiHBEt}_3$  or of  $[\text{HRu}_3(\text{CO})_9\text{S}]^-$  with  $\text{KHB}(\text{OPr}^i)_3$  have been identified<sup>4</sup> spectroscopically and the unstable complex  $[\text{RuH}(\text{CHO})(\text{PPh}_3)_3\text{S}]$  ( $\text{S} = \text{solvent}$ ) has been reported.<sup>5</sup> Furthermore, although neutral and anionic formyl complexes are well-known,<sup>6-8</sup>  $[\text{IrH}(\text{CHO})(\text{PMe}_3)_4]^+$  represents the only reported<sup>9</sup> cationic metal formyl complex.

We now report the facile synthesis of cationic formyl complexes of ruthenium *via* nucleophilic attack of hydride on  $[\text{Ru}(\text{CO})_2(\text{P-P})_2]^{2+}$ .<sup>10</sup>

Reactions of *trans*- $[\text{Ru}(\text{CO})_2(\text{dppe})_2][\text{SbF}_6]_2$  or *cis*- $[\text{Ru}(\text{CO})_2(\text{dppm})_2][\text{SbF}_6]_2$  with  $\text{NaHB}(\text{OEt})_3$  in nitromethane or dichloromethane at  $-30^\circ\text{C}$  afford smooth conversion into

$[\text{Ru}(\text{CHO})(\text{CO})(\text{P-P})_2][\text{SbF}_6]$ .<sup>†</sup> For  $\text{P-P} = \text{dppm}$ , the unstable product precipitates from  $\text{CH}_3\text{NO}_2$  whereas  $[\text{Ru}(\text{CHO})(\text{CO})(\text{dppe})_2][\text{SbF}_6]$ <sup>‡</sup> is sufficiently stable for crystallisation.

Attempts to promote a second hydridic reduction of these mono-formyl complexes by treatment of  $[\text{Ru}(\text{CO})_2(\text{P-P})_2]^{2+}$  with the more nucleophilic  $\text{LiHBEt}_3$  have, as yet, proved unsuccessful. Although the products of these reactions do not contain  $[\text{SbF}_6]^-$ ; their spectroscopic properties show them once again to contain  $[\text{Ru}(\text{CHO})(\text{CO})(\text{P-P})_2]^+$  and resonances in their  $^1\text{H}$  and  $^{11}\text{B}$  n.m.r. spectra are identical with those

<sup>†</sup> Although the isolated products from  $\text{MeNO}_2$  and  $\text{CH}_2\text{Cl}_2$  are the same,  $^{31}\text{P}$  n.m.r. studies suggest that small amounts of other compounds, presumably derived from *e.g.*  $[\text{CH}_2\text{NO}_2]^-$ , are formed in  $\text{MeNO}_2$ .

<sup>‡</sup> Satisfactory microanalytical data have been obtained for this compound.

reported<sup>11,12</sup> for  $[\text{BEt}_4]^-$ . This anion is presumably formed by intermolecular boron ethyl transfer but the transition state evidently involves the hydride since treatment of  $[\text{Ru}(\text{CO})_2(\text{dppe})_2][\text{SbF}_6]_2$  with  $\text{LiDBEt}_3$  slowly affords  $[\text{Ru}(\text{CDO})(\text{CO})(\text{dppe})_2][\text{SbF}_6]$  (rather than with  $[\text{BEt}_4]^-$  as the counter anion). *trans*- $[\text{Ru}^{13}\text{CHO}^{13}\text{CO}(\text{dppe})_2][\text{BEt}_4]$  is formed on treatment of  $[\text{Ru}^{13}\text{CO}_2(\text{dppe})_2][\text{SbF}_6]_2$  with an excess of  $\text{LiHBEt}_3$ .

The dppm complexes are too unstable for complete characterisation but the presence of the formyl group [ $\nu(\text{C}=\text{O})$  at 1600 and  $\nu(\text{C}-\text{H})$  at 2585  $\text{cm}^{-1}$ ], the carbonyl group [ $\nu(\text{C}=\text{O})$  at 1970  $\text{cm}^{-1}$ ], and  $[\text{SbF}_6]^-$  are confirmed by i.r. studies. A broad formyl proton resonance at  $\delta$  13.5 is also observed on treating a mixture of *cis*- and *trans*- $[\text{Ru}(\text{CO})_2(\text{dppm})_2][\text{SbF}_6]_2$  with  $\text{NaHB}(\text{OEt})_3$  in an n.m.r. tube and immediately measuring the spectrum at  $-30^\circ\text{C}$ .

The dppe complexes, on the other hand, are less labile and have been fully characterised. The assignment of the i.r. spectra is assisted by the labelled compounds. Thus, the formyl  $\nu(\text{C}-\text{H})$  moves from 2550 to 1918  $\text{cm}^{-1}$  on deuteration [ $\nu(\text{C}-\text{H}) \div \nu(\text{C}-\text{D}) = 1.33$ ] and the  $^{13}\text{C}$ -labelled complex has  $\nu(\text{C}-\text{H})$ ,  $\nu(\text{C}=\text{O})$ , and  $\nu(\text{C}=\text{O})$  at 2505, 1928, and 1558  $\text{cm}^{-1}$ , respectively (cf. 2550, 1978, and 1596  $\text{cm}^{-1}$  for the  $^{12}\text{C}$ -analogue).

$^1\text{H}$  N.m.r. studies confirm the presence of the formyl complex [ $\delta$  13.6 (quint,  $J_{\text{FH}} 8 \text{ Hz}$ )] which has a half-life of *ca.* 30 min in  $\text{CD}_3\text{NO}_2$  at room temperature. The low temperature ( $-30^\circ\text{C}$ )  $^{13}\text{C}$  n.m.r. spectrum of  $[\text{Ru}^{13}\text{CHO}^{13}\text{CO}(\text{dppe})_2][\text{BEt}_4]$  (92% enriched) shows two low field resonances, one from the formyl group at  $\delta$  261.9 p.p.m. (dq,  $J_{\text{FC}} 9.5$ ,  $J_{\text{CC}} 22.12 \text{ Hz}$ )<sup>13</sup> and the other from the carbonyl ligand at  $\delta$  198.7 p.p.m. (dq,  $J_{\text{FC}} 9.5 \text{ Hz}$ ). These assignments are confirmed since only the lower field resonance splits into a further doublet on off-resonance decoupling.

All of the above formyl complexes readily decompose in solution and preliminary results suggest that the main products for  $\text{P}-\text{P} = \text{dppe}$  are *trans*- $[\text{RuH}(\text{CO})(\text{dppe})_2]^+$  and a

compound we believe to contain  $[\text{Ru}(\text{CO})(\text{dppe})]^{2+}$ . Similar decomposition products are obtained from  $[\text{Ru}(\text{CHO})(\text{CO})(\text{dppm})_2][\text{SbF}_6]$ , although the major decomposition product is apparently  $[\text{RuH}(\text{CO})_2(\text{dppm})_2]^+$  with *cis*-carbonyl groups and a monodentate dppm ligand.

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