In situ spectroscopic evidence for facile, carbon monoxide mediated, reversible cleavage of neutral heterobimetallic rhodium–ruthenium complexes into ionic mononuclear complexes

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In situ IR and NMR spectroscopic evidence is presented for the facile and reversible cleavage of ligand-bridged metal–metal bonds in heterobimetallic Rh–Ru complexes of the type $[(C_5R_5)Ru(\mu\text{-}CO)_2(\mu\text{-}LL)RhX_2]$ [R = H, Me; LL = $Ph_2PCH_2PPh_2$ (dppm), $Me_2PCH_2PMe_2$ (dmpm) or $Ph_2PC(=CH_2)PPh_2$ (dppee); X = Cl, I] upon reaction with carbon monoxide under mild conditions to form $[Ru(C_5R_5)(CO)_2(\eta^1\text{-}LL)]^+$ and $[RhX_2(CO)_2]^-$; an intermediate species in the cleavage process, $[(C_5H_5)(CO)_2Ru(\mu\text{-}Me_2PCH_2PMe_2)Rh(CO)Cl_2]$, is detected by NMR spectroscopy.

The preparation and characterization of heterobimetallic complexes has attracted considerable interest in the context of potential applications as homogeneous catalyst precursors.[1] This interest derives mainly from the idea that adjacent metal centres offer the possibility of cooperative reactivity (synergism) which may lead to different patterns of activity and/or selectivity. The approach has, however, been restricted to some extent by the lack of stability of the metal-atom framework under catalytic reaction conditions, in particular the tendency for metal–metal bond cleavage (fragmentation). One strategy to at least retard such behaviour involves the use of diphosphine ligands which bridge the two metals and thus strengthen their overall interaction. Indeed the ligand-bridged metal–metal bond has often been cited as being a stabilised metal–metal bond.

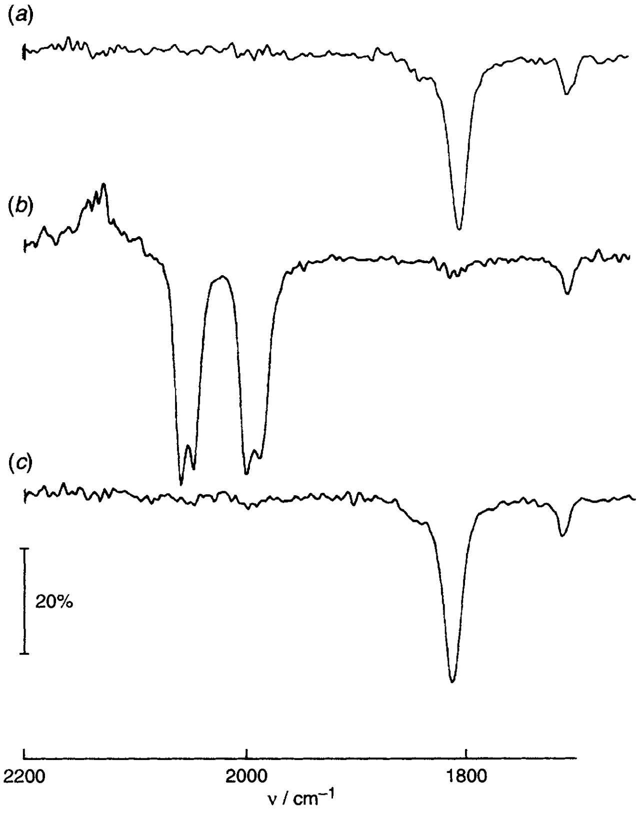


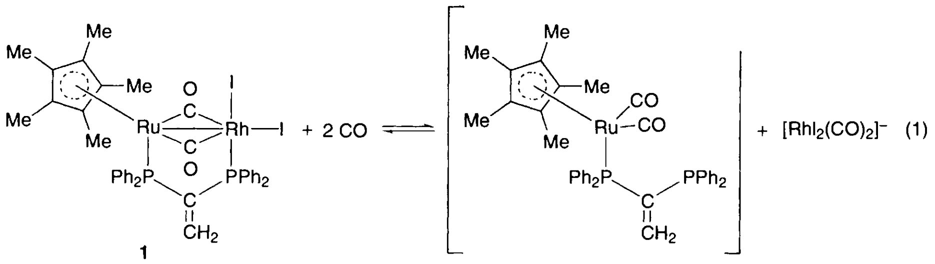
Fig. 1 (*a*) IR spectrum of $[(C_5Me_5)Ru(\mu\text{-}CO)_2(\mu\text{-}dppee)RhI_2]$ **1** in CH_2Cl_2 under N_2; (*b*) spectrum of **1** in CH_2Cl_2 under CO (100 psi), subtracted from the spectrum of CO (100 psi) in CH_2Cl_2; (*c*) spectrum of the sample shown in (*b*) after removing CO and flushing the IR cell twice with N_2 (100 psi)

The synthesis and structural characterization of a range of rhodium–ruthenium heterobimetallic complexes $[(C_5R_5)Ru(\mu\text{-}CO)_2(\mu\text{-}LL)RhX_2]$ [R = H, CH_3; LL = $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PC(=CH_2)PPh_2$ (dppee), $Me_2PCH_2PMe_2$ (dmpm); X = Cl, I] has been carried out.[2,3] These complexes are readily prepared in high yield by the reaction of, for example, the complex $[RhCl(CO)_2]_2$ with $[Ru(C_5H_5)Cl(dppee)]$ *via* a ring-opening reaction of the bidentate phosphine ligand. Structural characterization by X-ray diffraction (and molecular modelling) has demonstrated that these complexes are very congested sterically

Table 1 Spectroscopic data

Complex	IR[a] $\nu(CO)/cm^{-1}$	$^{31}P\{^1H\}$ NMR, δ[b]
$[(C_5Me_5)Ru(\mu\text{-}CO)_2(\mu\text{-}dppee)RhI_2]$ **1**	1812s	52.8 (dd, J_{PP} 132, J_{PRh} 5.4), 43.0 (dd, J_{PP} 132, J_{PRh} 126)
$[(C_5Me_5)Ru(\mu\text{-}CO)_2(\mu\text{-}dppee)RhCl_2]$ **2**	1815s	56.4 (dd, J_{PP} 128, J_{PRh} 6), 45.5 (dd, J_{PP} 128, J_{PRh} 124)
$[(C_5H_5)Ru(\mu\text{-}CO)_2(\mu\text{-}dppee)RhCl_2]$ **3**	1859w, 1820s	56.8 (dd, J_{PP} 120, J_{PRh} 9.8), 43.6 (dd, J_{PP} 120, J_{PRh} 118)
$[(C_5H_5)Ru(\mu\text{-}CO)_2(\mu\text{-}dmpm)RhCl_2]$ **4**[c]	1819s	40.7 (dd, J_{PP} 60, J_{PRh} 8.5), 43.2 (dd, J_{PP} 60, J_{PRh} 113.5)
$[(C_5H_5)(CO)_2Ru(\mu\text{-}dmpm)Rh(CO)Cl_2]$ **5**		16.6 (s), 1.4 (d, J_{PRh} 114)
$[(C_5H_5)Ru(\mu\text{-}CO)_2(\mu\text{-}dppm)RhCl_2]$	1855w, 1818s	55.9 (d, J_{PP} 69), 45.5 (dd, J_{PP} 69, J_{PRh} 124)
$[(C_5H_5)Ru(\mu\text{-}CO)_2(\mu\text{-}dppm)RhI_2]$	1821s	54.3 (d, J_{PP} 75), 45.9 (dd, J_{PP} 75, J_{PRh} 124)
$[RhI_2(CO)_2]^-$	2059s, 1989s	
$[RhCl_2(CO)_2]^-$	2070s, 1994s	
$[Ru(C_5Me_5)(CO)_2(\eta^1\text{-}dppee)]^+$	2047s, 2002s	
$[Ru(C_5H_5)(CO)_2(\eta^1\text{-}dppee)]^+$	2068s, 2022s	
$[Ru(C_5H_5)(CO)_2(\eta^1\text{-}dmpm)]^+$	2059s, 2011s	
$[Ru(C_5H_5)(CO)_2(\eta^1\text{-}dppm)]^+$	2067s, 2022s	
$[Ru(C_5H_5)(CO)_2(PPh_3)]^+$	2069, 2022[d]	

[a] In CH_2Cl_2 solution. [b] In $CDCl_3$ solution; chemical shifts δ relative to 85% H_3PO_4. Coupling constants in Hz. [c] In $(CD_3)_2SO$ solution. [d] Ref. 5.



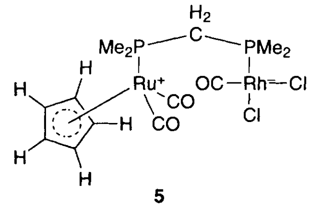
and that facile chemical reactivity seems relatively unlikely. Nevertheless we have observed some dramatic (and unexpected) changes whilst monitoring the spectra of such complexes under modest pressures of carbon monoxide in a high-pressure IR cell.[4] For example, on stirring a dichloromethane solution of $[(C_5Me_5)Ru(\mu\text{-}CO)_2(\mu\text{-dppee})RhI_2]$ **1** under as little as 10 psi CO at room temperature, weak absorptions appear in the terminal ν(CO) stretching region as the absorptions due to the bridging carbonyl groups at 1859 and 1820 cm^{-1} decrease slightly in intensity. Incremental increases in the CO pressure to 100 psi result in the complete disappearance of these bridging carbonyl peaks and the observation of four peaks of approximately equal intensity at 2059, 2048, 2001 and 1989 cm^{-1} (see Fig. 1). Moreover, venting of the CO followed by stirring under similar pressures of dinitrogen leads to a rapid reversal of the reaction and the reappearance of the initial bridging carbonyl absorptions of the parent heterobimetallic complex. The reaction is thus quantitatively reversible.

Similar behaviour has been observed with the chloro analogue **2** and the cyclopentadienyl derivative **3**, although rather more severe reaction conditions (950 and 1500 psi, respectively) are required for complete reaction. Also, in some cases the two new absorptions in the 2060 cm^{-1} region overlap and coalesce into a single broad peak with approximately twice the intensity of the two distinct peaks at *ca.* 2000 cm^{-1} (see Table 1).

A comparison with literature data of the band positions of the new ν(CO) absorptions observed in the reaction of complex **1** with CO shows that the bands observed at 2059 and 1989 cm^{-1} correspond exactly with those displayed by the well known dicarbonyldiiodorhodium anion $[RhI_2(CO)_2]^-$. Thus it seems reasonable to assume that the neutral heterobimetallic complex is readily cleaved to give two mononuclear ionic species. The nature of the cationic species is most likely to be $[Ru(C_5Me_5)(CO)_2(\eta^1\text{-dppee})]^+$ in which one phosphorus atom remains uncoordinated. A ruthenium cyclopentadienyl triphenylphosphine complex $[Ru(C_5H_5)(CO)_2(PPh_3)][BF_4]$ is the closest known analogue[5] and displays ν(CO) absorptions at 2069 and 2022 cm^{-1}.

Confirmation of this suggestion has been obtained from an examination of the reaction of the ruthenium complex $[RuCl(C_5Me_5)(\eta^2\text{-dppee})]$ with carbon monoxide. After treatment with 1000 psi CO at 50 °C, two ν(CO) absorptions of similar intensities at 2047 and 2002 cm^{-1} (*cf.* 2048 and 2001 cm^{-1} in the reaction of complex **1** with CO) are observed. A ^{31}P NMR spectrum of the reaction solution indicated the presence of two inequivalent P atoms [two doublets, δ 52.7 and −11.4 ($^2J_{PP}$ 113.0 Hz)] consistent with η^1-coordination of dppee. The spectroscopic data are thus consistent with the formation of $[Ru(C_5Me_5)(CO)_2(\eta^1\text{-dppee})]Cl$ from the reaction of CO with $[RuCl(C_5Me_5)(\eta^2\text{-dppee})]$. This reaction appears to be irreversible; once formed the ionic product is stable at room temperature under dinitrogen.

Overall therefore we have demonstrated the facile displacement of equilibrium (1) to the right-hand side by the application of CO pressure.



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Although the displacement of equilibrium (1) to either the left or the right hand side is particularly facile it does form part of a general reaction scheme which has been found to apply to a range of Rh–Ru heterobimetallic complexes containing different diphosphines, halides and cyclopentadiene substituents.

The mechanism by which the metal–metal bond cleavage occurs is unclear at present. However, *in situ* ^{31}P NMR studies of the reaction of CO with $[(C_5H_5)Ru(\mu\text{-}CO)_2(\mu\text{-dmpm})RhCl_2]$ **4** under ambient conditions have provided evidence for an intermediate species, $[(C_5H_5)(CO)_2Ru(\mu\text{-dmpm})Rh(CO)Cl_2]$ **5** in which the two halves of the molecule remain intact. Thus, bubbling CO through a solution of the heterobimetallic complex **4** at room temperature leads to the formation of a species that has a ^{31}P NMR spectrum consisting of a singlet at δ 16.6 and a doublet at δ 1.4 ($^1J_{RhP}$ 114 Hz). This clearly shows that the dmpm ligand is still coordinated to both the Rh and Ru atoms. It is often the case that J_{PP} is very small when a diphosphine ligand bridges two metal atoms which are not bonded, it is therefore not surprising that the P–P coupling is approximately zero in complex **5**.

The facile nature of some of these fragmentation reactions in such sterically congested complexes is unprecedented and is of direct significance to investigations of 'heterobimetallic catalysis' in reactions involving carbon monoxide.

Footnote

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