Lewis Acid Promoted Terminal-to-Bridge Carbonyl Shift in $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$

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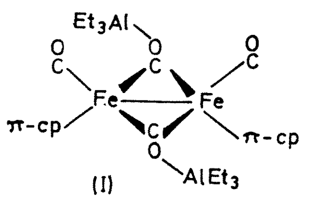
Summary Solution i.r. spectra demonstrate that in the presence of AlR_3 the non-bridged form of $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$ is converted into CO-bridged adducts containing AlR_3 co-ordinated to the oxygen(s) of the bridging carbonyls.

CHANGES in temperature,[1] solvent,[2] or ancillary ligands[3,4] may cause the CO ligand to shift between bridging and terminal positions in certain polynuclear carbonyls, but there is at present no systematic chemical method for effecting this transformation. For example, substitution by PPh_3 causes a shift of bridging CO groups to terminal positions in $Co_2(CO)_8$,[3] but causes the opposite in $MeC[Co(CO)_3]_3$.[4] We report that the basicity of the bridging $>$CO group[5] provides a driving force for terminal-to-bridge CO interchange.

While the terminal CO group has been known to serve as a base toward a Lewis acid,[6,7] an *X*-ray single-crystal structure determination of $[(\pi\text{-cp})Fe(CO)_2]_2,2AlEt_3$ (I) (cp = C_5H_5) shows only bridging >CO groups co-ordinated to triethylaluminium.[5] Bridging >CO appears, therefore, to be more basic than terminal CO.



(I)

I.r. spectra of $[(\pi\text{-cp})Fe(CO)_2]_2$ in heptane solution with various concentrations of tri-isobutylaluminium reveal three types of concentration dependence for the CO stretching bands.

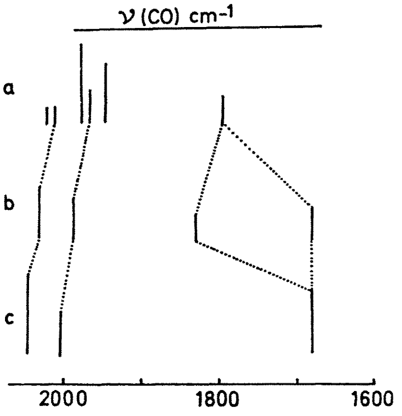
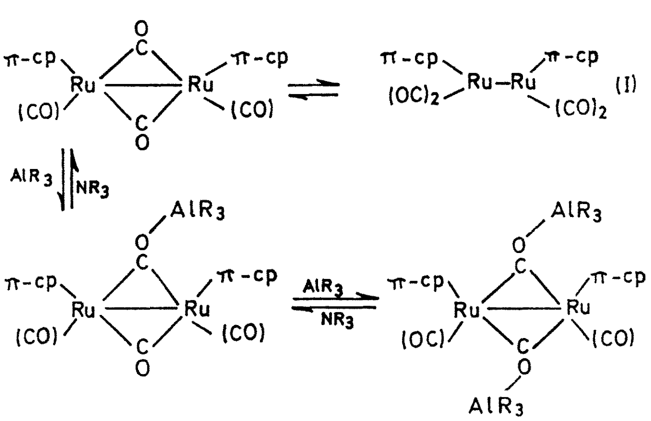


FIGURE. *Correlation of bands for the* $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2\text{-}AlBu^i_3$ *system. Ratio of* $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$ *to* $AlBu^i_3$, a, 1 : 0; b, 1 : 1; c, 1 : 2.

Intensities of Type a bands, which are characteristic of the parent iron dimer (2005, 1962, and 1794 cm^{-1}), decrease monotonically with added $AlBu^i_3$, Type b bands (2026, 1985, 1828, and 1682 cm^{-1}) first increase and then decrease in intensity, and finally Type c bands (2042, 2004, and 1682 cm^{-1}) increase monotonically. From the concentration dependence, number, and relative positions of component bands, these three band types correspond to parent carbonyl, a 1 : 1, $[(\pi\text{-cp})Fe(CO)_2]_2:AlBu^i_3$, adduct, and a 1 : 2 adduct, respectively.

On the basis of the $[(\pi\text{-cp})Fe(CO)_2]_2\text{-}AlBu^i_3$ spectra it is possible to interpret the more complicated $[(\pi\text{-cp})Ru(CO)_2]_2\text{-}AlBu^i_3$ system. In hydrocarbon solution, the spectrum of the parent compound, $[(\pi\text{-cp})Ru(CO)_2]_2$ unlike that of its iron analogue shows the presence of *ca.* 50% non-bridged form in equilibrium with the CO bridged species.[8,9]

Hydrocarbon solutions of the ruthenium dimer are much less stable in the presence of trialkylaluminium than are those of the iron analogue. However, satisfactory results were obtained when the i.r. cells were thermostatted at *ca.* −3 °C and spectra were obtained within a few minutes of aluminium alkyl addition. As with the iron system, the i.r. bands fall into three categories (Figure), which can be identified with the parent isomers (1795, 1945, 1967, 1976, 2011, and 2021 cm^{-1}), a 1 : 1 complex in the bridged form (1680, 1831, 1988, and 2006 cm^{-1}), and a 1 : 2 complex (1680, 2006, and 2045 cm^{-1}) also in the bridged form. At concentrations of $2{\cdot}2 \times 10^{-3}$M $[(\pi\text{-cp})Ru(CO)_2]_2$ and $1{\cdot}8 \times 10^{-2}$M tri-isobutylaluminium, the primary species present in solution is the bridged 1 : 2 complex with minor amounts of the bridged 1 : 1 complex and no parent observable. However, the spectrum reverts to that of the parent $[(\pi\text{-cp})Ru(CO)_2]_2$ on addition of an excess of triethylamine. Thus the formation of oxygen-co-ordinated bridging carbonyls serves as a driving force for the isomerization of the non-bridged ruthenium compound [equation (1)].



The reaction may provide a general method of inducing a terminal-to-bridge carbonyl shift in poly-nuclear carbonyls. The recent data of McArdle and Manning show a similar trend in that the proportion of non-bridged $[(\pi\text{-cp})Ru(CO)_2]_2$ decreases with increasing hydrogen-bonding propensity of the solvent.[10] In this case however, the potential for the reaction may originate from either hydrogen bonding with the bridging carbonyls, or less specific interactions which favour the *cis*-bridged isomer in polar solvents.[10]

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