Site Exchange Between the Single Bridging and Terminal Carbonyl Groups in $[(C_5H_5)_2Rh(CO)_2P(OPh)_3]$

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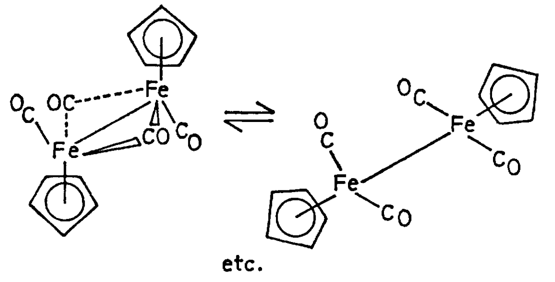
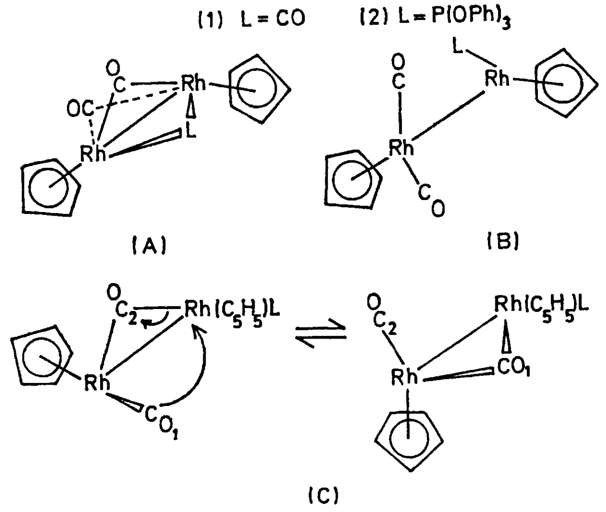
Summary Site exchange between the single bridging and terminal carbonyl groups in $[(C_5H_5)_2Rh_2(CO)_2P(OPh)_3]$ has been observed; a synchronous mechanism is favoured.

Bridge–terminal site exchange of the type shown in Scheme 1,[1] affords a sound basis for our understanding of CO scrambling in binuclear double carbonyl bridge systems such as $[(C_5H_5)_2Fe_2(CO)_4]$. It also provides a satisfactory pathway for the *cis–trans* isomerism also observed in that complex. For binuclear systems containing a single carbonyl bridge, as in $[(C_5H_5)_2Rh_2(CO)_3]$ (**1**),[2,3] the mechanism of CO transfer is less clear. Three mechanisms could be envisaged for carbonyl site exchange in such systems (Scheme 2); (a) *via* a triply bridged intermediate (A), (b) *via* an unbridged intermediate (B), (c) a synchronous process(C). Mechanism (c) has been postulated for $[RhCo_3(CO)_{12}]$.[4] Type (a) has been stressed by Cotton[5] for site exchange in (**1**) owing to the absence of any direct evidence for one of exchange of single bridging and terminal groups. We have synthesised $[(C_5H_5)_2Rh_2(CO)_2P(OPh)_3]$ (**2**), from the reaction of (**1**) and a stoicheiometric quantity of the phosphite, in the hope of observing such a process. The i.r. spectrum of (**2**) in cyclohexane exhibits two ν_{CO} absorptions, at 1979 and 1815 cm^{-1}, due to the single terminal and bridging groups respectively. A 45% ^{13}CO enriched sample was similarly prepared from a labelled sample of (**2**), to be used for ^{13}C n.m.r. studies.



Scheme 1



Scheme 2

A slow exchange ^{13}C n.m.r. spectrum of the carbonyl region was obtained in $CHFCl_2$ at −105 °C [δ 239.4 (m, ${}^{1}J_{\mathrm{Rh(1)-C}}$ 41 Hz, ${}^{1}J_{\mathrm{Rh(2)-C}}$ 50 Hz, ${}^{2}J_{\mathrm{P-C}}$ 19 Hz, bridging CO), 190·4 (d, ${}^{1}J_{\mathrm{Rh(1)-C}}$ 85 Hz, terminal CO)]; warming the sample to −85 °C [in CD_2Cl_2 with added $Cr(acac)_3$][6] caused broadening of the resonances and a coalescence temperature of −65 ± 10 °C was observed ($\Delta G^{\ddagger}_{208}$ 8·8 ± 0·5 kcal mol^{-1}).

The fast exchange spectrum was observed at 25 °C, consisting of an eight-line multiplet at 218·5 p.p.m. This demonstrates that site exchange between the bridging and terminal carbonyl groups occurs rapidly at room temperature, requiring a similar $\Delta G^{\ddagger}$ to that for $[(C_5H_5)_2Rh_2(CO)_3]$ (**1**).[3] The complexity of the pattern requires that the Rh–P bond remains intact throughout the process. This point was further demonstrated by the ^1H and ^{31}P n.m.r. spectra of an unlabelled sample of (**2**). The ^{31}P (CD_2Cl_2, 141·2 p.p.m. downfield of H_3PO_4, d, J_{Rh-P} 327 Hz) and the ^1H n.m.r. spectra [$CDCl_3$, τ 2·70 (m, 15 H), 4·41 (s, 5H), 5·32 (d, J 2 Hz, 5H)] are temperature invariant between −90 and 20 °C, and clearly indicate that the phosphite is associated with one rhodium atom. Clearly mechanism (a), which would involve a phosphite bridge, is eliminated by the evidence above and while definitive proof remains elusive, we favour (c), a synchronous process and suggest that this pathway may also be operating in (**1**). As a generality, single bridge–terminal exchange, possibly occurring as a one-step process, must now be considered as viable in other systems, unless there is definitive evidence to the contrary.

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