Unusual Intermolecular Ligand Exchange Process in Octakis(trimethyl phosphite)dirhodium(0), $Rh_2[P(OMe)_3]_8$

By RENÉ MATHIEU and JOHN F. NIXON*

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, *and U.E.R. Chimie Inorganique, Université Paul Sabatier, Toulouse, France)*

Summary. The new complex $Rh_2[P(OMe)_3]_8$ which has a bicapped trigonal antiprismatic structure at room temperature undergoes a specific equatorial intermolecular ligand exchange at higher temperatures rather than any intramolecular ligand exchange between equatorial and axial sites.

THERE is current interest in the fluxional behaviour of five-co-ordinate transition-metal complexes.[1-4] We report the preparation of the pale yellow crystalline complex octakis(trimethylphosphite)dirhodium(0) $Rh_2[P(OMe)_3]_8$ (I), m.p. 75° (decomp.), (60%) by displacement of the cyclopentadienyl group and ethylene from π-$C_5H_5Rh(C_2H_4)_2$ with excess of trimethyl phosphite at 60°.

The proton-decoupled ^{31}P n.m.r. spectrum of (I) [Figure (a)] at room temperature is of the A_3BX type (A and B $= {}^{31}P$ nuclei, X $= {}^{103}Rh$, 100% natural abundance) indicating that (I) has a non-fluxional symmetrical bicapped trigonal antiprismatic structure (each rhodium having local C_{3v} symmetry). This is similar to that reported very recently for the non-fluxional cobalt complex $Co_2[P(OMe)_3]_8$.[4] Analysis of the ^{31}P n.m.r. spectrum yields: J_{AB} 122, J_{AX} 200, $J_{BX} \approx J_{AB} = 122$ Hz.

The temperature dependence of the ^{31}P n.m.r. spectrum of (II) has been studied between room temperature and 100°. Both sets of signals broaden around 50° and near 100° the A part of the spectrum becomes a sharp singlet [Figure (c)] while the B part appears as a doublet separated by 122 Hz (J_{BX}). There is no change in the chemical shift difference δ_A—δ_B over the temperature range and the original spectrum is regained on cooling the sample to room temperature.

These results indicate that the molecule is *not* undergoing an intramolecular exchange of phosphite ligands and the loss of rhodium-phosphorus coupling only for resonance A implies that there is a specific intermolecular ligand exchange in the equatorial positions at higher temperatures. The lack of intermolecular ligand exchange at room temperature is confirmed by adding a small amount of free trimethyl phosphite to a solution of (I). The resulting room temperature ^{31}P n.m.r. spectrum [Figure (b)] consists of a simple superposition of the spectrum of (I) and that of the free phosphite. As the temperature is raised to 100° there is a coalescence of the A part of the spectrum and the single line of the free ligand to give a spectrum similar to the Figure (c). The B part remains as a 1-1 doublet owing to coupling with rhodium.

This appears to be the first example of a five-co-ordinate complex undergoing a reversible intermolecular ligand exchange specifically with the equatorial set of ligands rather than an intramolecular exchange process between equatorial and axial sites where the barriers are usually low (5-15 kcal/mol).

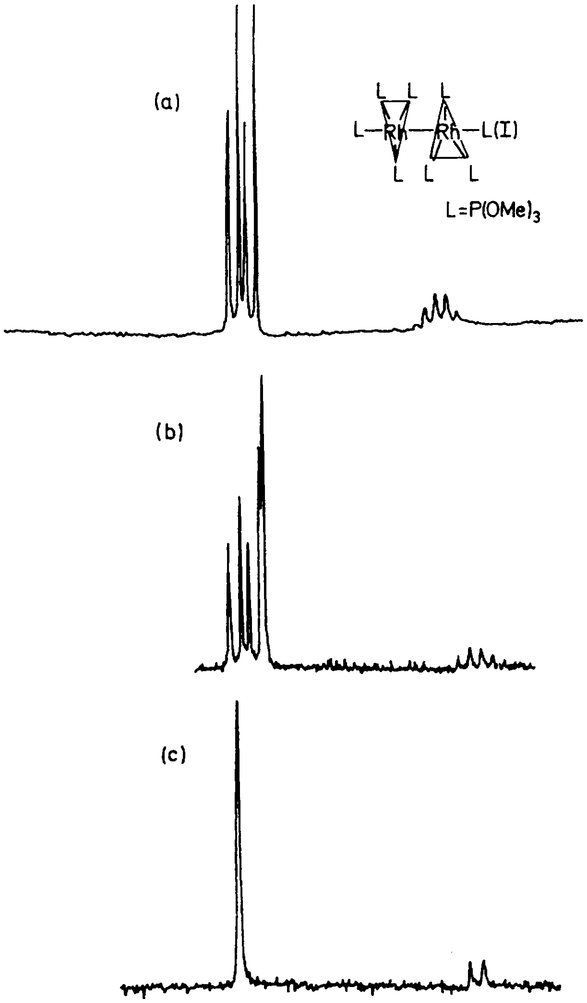

FIGURE. 40·49 MHz ^{31}P {H} n.m.r. spectrum of $Rh_2[P(OMe)_3]_8$: (a) at 32°; (b) with added $P(OMe)_3$ at 32°; (c) at 100°.

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