

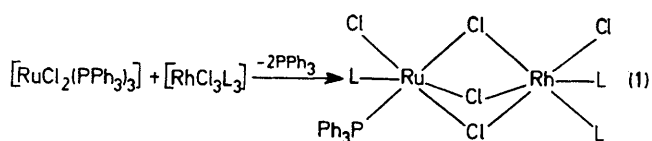
## Triple Chloro-bridged Heterobimetallic Phosphine Complexes Containing Ruthenium(II) and Rhodium(III)†

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**Summary** A series of triple chloro-bridged heterobimetallic phosphine complexes of the type  $[(PPh_3)_2LClRuCl_2RhClL_2]$  ( $L = PMe_2Ph, PEt_2Ph, PBu^n_2Ph, PBu^n_3,$  or  $PPh_3$ ) have been prepared from the mononuclear complexes  $[RuCl_2(PPh_3)_3]$  and  $[RhCl_3L_3]$ ; these reactions involve phosphine-ligand transfer from rhodium to ruthenium.

RECENTLY<sup>1</sup> we reported the synthesis of the triple chloro-bridged diruthenium(II) complex,  $[(PF_3)(PPh_3)_2RuCl_2RuCl(PF_3)(PPh_3)]$ , from the reaction between  $[RuCl_2(PPh_3)_3]$  and *cis*- $[RuCl_2(PF_3)_2(PPh_3)_2]$ . An interesting feature of the reaction was the  $PF_3$  ligand transfer from one ruthenium atom to the other. We now describe the synthesis of a



series of triple chloro-bridged heterobimetallic complexes of the type  $[(PPh_3)_2LClRuCl_2RhClL_2]$  (I) ( $L = PMe_2Ph, PEt_2Ph, PBu^n_2Ph, PBu^n_3,$  or  $PPh_3$ ) containing ruthenium(II) and rhodium(III) which are formed in high yields from the reactions of  $[RuCl_2(PPh_3)_3]$  with the appropriate *mer*- $[RhCl_3L_3]$  compound as shown in equation (1). Complex (I;  $L = PPh_3$ ) is also obtained from the reaction of  $[RhCl_3(PF_3)(PPh_3)_2]$  {prepared by careful chlorination of *trans*- $[RhCl(PF_3)(PPh_3)_2]$ } with  $[RuCl_2(PPh_3)_3]$ .

The structures of the complexes (I), which form deep-red or purple crystals, have been assigned on the basis of elemental analysis, molecular weight measurements, and <sup>31</sup>P n.m.r. spectra (see below). The formation of the hetero-

nuclear bimetallic complexes appears to involve a transfer of one phosphine ligand, L, from rhodium to ruthenium.

The proton decoupled <sup>31</sup>P n.m.r. spectrum of (I;  $L = PBu^n_2Ph$ ) (Figure) is typical of the series of complexes studied. The resonances of the two different phosphines on ruthenium constitute an AX spin system and give the expected 1:1 doublet patterns [<sup>2</sup>J(P-Ru-P') 40.0 Hz], the phosphorus chemical shifts being 85.5 p.p.m. (PPh<sub>3</sub>) and 101.0 p.p.m. (PBu<sup>n</sup><sub>2</sub>Ph), relative to P(OMe)<sub>3</sub>. The two magnetically non-equivalent<sup>1</sup> PBu<sup>n</sup><sub>2</sub>Ph ligands co-ordinated to rhodium give rise to an AB pattern of lines [δ 177.0 (P<sup>1</sup>), 114.7 (P<sup>2</sup>) <sup>2</sup>J(P<sup>1</sup>-P<sup>2</sup>) 22 Hz], each being split further into doublets by the <sup>103</sup>Rh nucleus [ $I = \frac{1}{2}$ , 100% natural abundance, <sup>1</sup>J(P<sup>1</sup>-Rh) = <sup>1</sup>J(P<sup>2</sup>-Rh) = 117.2 Hz]. The directly bonded P-Rh coupling constants in (I) are similar to those measured in typical mononuclear rhodium(III)-phosphine complexes.<sup>2</sup>

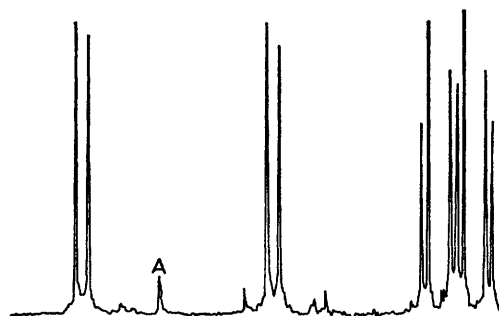


FIGURE. 40.5 MHz <sup>31</sup>P{<sup>1</sup>H} n.m.r. spectrum of (I;  $L = PBu^n_2Ph$ ). The signal marked A is due to a trace of  $[RuCl_2(PPh_3)_3]$ .

Preliminary results indicate that analogous mixed ruthenium-iridium complexes may also be obtained. On

† Reprints not available

the other hand, the reaction between  $[\text{PtCl}_4(\text{PBU}^n_2\text{Ph})_2]$  and  $[\text{RuCl}_2(\text{PPh}_3)_3]$  readily affords high yields of the monomeric platinum(II) complex *trans*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ .<sup>3</sup>

These results are of interest in connection with recent reports by Masters *et al.*<sup>4,5</sup> on the bimetallic complexes

$[\text{PtPdCl}_4\text{L}_2]$  ( $\text{L} = \text{PBU}^n_3$  or  $\text{PPr}^n_3$ ), identified by <sup>31</sup>P n.m.r. studies on  $[(\text{PtCl}_2\text{L})_2]$  and  $[(\text{PdCl}_2\text{L})_2]$  mixtures.

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<sup>2</sup> J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345.

<sup>3</sup> R. A. Head, J. F. Nixon, and A. Al-Ohaly, unpublished results.

<sup>4</sup> C. Masters and J. P. Visser, *J.C.S. Chem. Comm.*, 1974, 932.

<sup>5</sup> A. A. Kiffen, C. Masters, and J. P. Visser, *J.C.S. Dalton*, 1975, 1311.