^{31}P Nuclear Magnetic Resonance Study of Conformers of *trans*-[MCl(CO)(PBu$^t_2$R)$_2$] (M=Rh or Ir; R=Me, Et, or Pr^n)

By B. E. MANN, C. MASTERS, B. L. SHAW,* and R. E. STAINBANK
(*School of Chemistry, The University, Leeds* LS2 9JT)

Summary The low temperature ^{31}P n.m.r. spectra of the complexes *trans*-[MCl(CO)(PRBu$^t_2$)$_2$] (M = Rh or Ir; R = Me, Et, or Pr^n) show the presence of three rotamers with very different chemical shifts.

RESTRICTED rotation about metal–phosphorus bonds has been postulated to explain the occurrence of extra bands in the i.r. spectrum of *cis*-[Mo(CO)$_4$(PHPh$_2$)$_2$][1] and also to explain the ^{1}H n.m.r. patterns of complexes of type *trans*-[MX$_2$(PHBu$^t_2$)$_2$] (M = Pd or Pt; X = Cl, Br, or I).[2] We now show, by low-temperature ^{31}P n.m.r. spectroscopy, that complexes of the type *trans*-[MCl(CO)(PBu$_2$R)$^t_2$] (R = Me, Et, or Pr^n) exist as rotational conformers. Thus, the ^{31}P resonance patterns of *trans*-[RhCl(CO)PBu$^t_2$Et)$_2$], with random noise decoupling of the hydrogens, consists of two very broad resonances at 28° but a series of sharp resonances at −60° (Figure). The spectrum at −60° is made up of two A$_2$X and one ABX patterns which we assign to the three conformers (rotamers) (Ia), (Ic), and (Ib). Conformer (Ib) has non-equivalent phosphorus nuclei and gives the ABX patterns [J(P–P) = 306 Hz]; the other two conformers have equivalent P nuclei and give A$_2$X patterns. The other rhodium complexes *trans*-[MCl(CO)(PBu$^t_2$R)$_2$] (M = Rh) show similar spectra and the iridium complexes (M = Ir) give two singlets and an AB pattern at −60°. The data are given in the Table. We have also examined the low-temperature (−60°) ^{31}P n.m.r. spectra of *trans*-

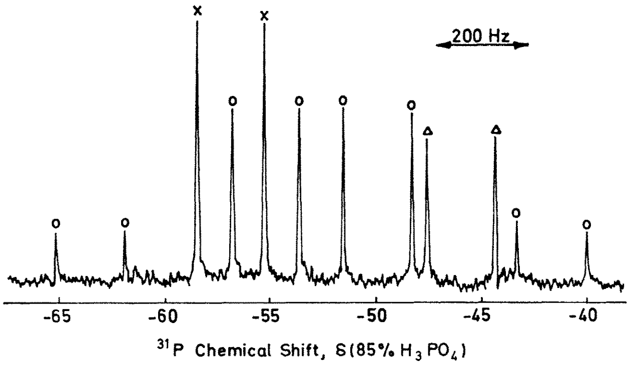
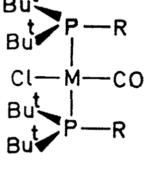
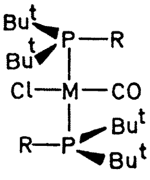


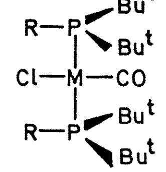
FIGURE. ^{31}P *N.m.r. patterns for the three conformers,* (Ia), (Ib), and (Ic) *of* trans-[RhCl(CO)(PBu$_2$Et)$_2$] *at* −60° *in* CH$_2$Cl$_2$ *solution. The three patterns are marked* ×, ○, and △ [*only the pattern for* (Ib) *is assigned*].



(Ia)



(Ib)



(Ic)

TABLE

^{31}P *N.m.r. spectral data for the complexes* trans-[MCl(CO)-(PRBu$^t_2$)$_2$] (M = Rh or Ir; R = Me, Et or Pr^n) *measured in* CH$_2$Cl$_2$ *at* −60 °C, *with respect to* 85% H$_3$PO$_4$ *and with complete decoupling of the protons.*

	δ(H$_3$PO$_4$) (±0·2)	^1J(Rh–P) (±0·2)/Hz	^2J(P–P) (±0·2)/Hz
trans-RhCl(CO)(PMeBu$^t_2$)$_2$]	−29·0	120·4	
	−45·1	117·9	
ABX system	−30·7 −46·6	122·3 117·0	317·0
trans-[IrCl(CO)(PMeBu$^t_2$)$_2$]	−22·3	—	
	−36·6	—	
AB system	−22·9 −39·1	— —	311·8
trans-[RhCl(CO)(PEtBu$^t_2$)$_2$]	−46·0	120·5	
	−57·1	119·1	
ABX system	−47·2 −58·2	121·4 117·7	306·0
trans-[IrCl(CO)(PEtBu$^t_2$)$_2$]	−38·7	—	
	−49·0	—	
AB system	−39·1 −50·9	— —	303·0
trans-[RhCl(CO)(PPr^{n}Bu$^t_2$)$_2$]	−43·4	120·6	
	−54·7	119·2	
ABX system	−44·5 −55·9	121·1 117·7	307·6
trans-[IrCl(CO)(PPr^{n}Bu$^t_2$)$_2$]	−35·9	—	
	−46·6	—	
AB system	−36·3 −48·5	— —	304·1

[RhCl(CO)L_2] (L = $PMePh_2$, $PBu^t_2Me_2$, and $PBu^tPr^n_2$) but in each case the resonance is a doublet showing that rotation is very probably occurring. *trans*-{RhCl(CO)[PBu^t_2(*p*-tolyl)]$_2$} at −60° gave a ^{31}P n.m.r. pattern similar to that of *trans*-[RhCl(CO)(PBu^t_2Et)$_2$], but badly resolved.

We have shown that complexes of these bulky tertiary-di-t-butylphosphines have a very different chemistry from complexes of less bulky tertiary phosphines. Thus, they favour low co-ordination numbers, *e.g.* five-co-ordinate rhodium(III)[3,4] or iridium(III)[5] hydrides and four-co-ordinate rhodium(II)[3,4] complexes, and they also promote conversions of metal halides into metal hydrides[3,5] and internal metallation reactions.[6] Our present observations show that in complexes of type *trans*-[MCl(CO)(PBu^t_2R)$_2$] there must be an energy barrier to rotation about the M–P bond of several kcal mol^{-1}, owing to interaction with the *cis* Cl or CO ligands. There will be similar strong interactions with *cis*-ligands in other complexes of tertiary di-t-butylphosphines and the unusual reactions or co-ordination numbers mentioned above are probably associated with a relief of steric strain around the metal.

Our observations also have important implications for the interpretation of ^{31}P n.m.r. data. The results show that there can be large differences in ^{31}P chemical shifts between conformers of the same substance (up to 16·2 p.p.m., see Table). Thus for bulky and asymmetric phosphine ligands ^{31}P chemical shifts can be markedly dependent on the probabilities of existence of the various conformers, and this should be borne in mind when interpreting data.

We thank the S.R.C. and Johnson Matthey Ltd. for generous support.

(*Received, July 2nd,* 1971; *Com.* 1117.)

[1] J. G. Thompson and J. G. Smith, *J. Chem. Soc.* (*A*), 1967, 1694.

[2] A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 1826.

[3] C. Masters, W. S. McDonald, G. Raper, and B. L. Shaw, *Chem. Comm.*, 1970, 210.

[4] C. Masters and B. L. Shaw, *J. Chem. Soc.* (*A*), in the press.

[5] C. Masters, B. L. Shaw, and R. E. Stainbank, *Chem. Comm.*, 1970, 209.

[6] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *Chem. Comm.*, 1970, 1176.