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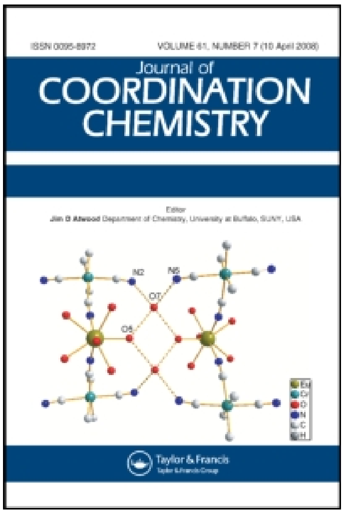

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Samuel O. Grim[a]; Robert A. Ference[a]
[a] Department of Chemistry, University of Maryland, College Park, Maryland

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PHOSPHORUS-31 MAGNETIC RESONANCE SPECTRA OF TERTIARY PHOSPHINE COMPLEXES OF IRIDIUM(III) CHLORIDE[1,2]

SAMUEL O. GRIM and ROBERT A. FERENCE

Department of Chemistry, University of Maryland, College Park, Maryland 20742

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Phosphorus-31 chemical shifts are reported for eleven compounds of the type *mer*-[Ir($Ph_nR_{3-m}P)_3Cl_3$] where R is alkyl and *n* is 0, 1, or 2. The occurrence of two peaks in the ratio of 2:1 in the phosphorus-31 magnetic resonance spectra confirms the meridional stereochemistry for the compounds. The chemical shift upon coordination is upfield from the free ligand, which is somewhat unusual for tertiary phosphine coordination compounds. Some proton magnetic resonance spectra and electronic spectra are also reported.

INTRODUCTION

The utility of phosphorus magnetic resonance in the study of coordination compounds has been well documented.[3] We have reported earlier studies[4,5] on rhodium compounds of the type L_3RhCl_3, where L is a tertiary phosphine. The meridional stereochemistry for these compounds was originally proposed from dipole moment measurements[6] and confirmed by pmr spectra of certain methylphosphine compounds by the phenomenon of virtual coupling.[7] More recently the utility of carbon-13 magnetic resonance has been shown to be useful in structural studies of t-butylphosphine complexes.[8] Since phosphorus-31 magnetic resonance can provide unequivocal stereochemical structural proof between the facial and meridional isomers for any phosphine complex, if sufficiently soluble, we have examined a series of compounds of the type L_3IrCl_3, where L is a tertiary phosphine.

EXPERIMENTAL

Microanalyses were carried out by Galbraith Laboratories, Knoxville, Tennessee. Phosphorus-31 nmr measurements were made in methylene chloride solution with a Varian DP60 spectrometer at 24.3 MHz as previously described.[9] Chemical shifts are accurate to $\pm$ 0.4 ppm. Proton magnetic resonance spectra were obtained with a Varian A-60A spectrometer. Spectra in the visible-ultraviolet region were measured with a Cary model 14 spectrophotometer.

All tertiary phosphines except commercially available $(C_6H_5)_3P$ and $(n\text{-}C_4H_9)_3P$ were synthesized[10] via the Grignard method from PCl_3, $(C_6H_5)PCl_2$, or $(C_6H_5)_2PCl$.

The synthesis of the iridium compounds was based on the methods of previous workers.[6,11,12] All manipulations with tertiary phosphines were carried out in a nitrogen atmosphere. Melting points and analytical data for the L_3IrCl_3 compounds are given in Table I.

The general synthesis is as follows: To a 500 ml one-necked flask equipped with a gas inlet tube with a side arm was added hydrated iridium chloride (1.0 g, 2.8 mm) and a solution of 2-methoxyethanol (100 ml) and water (5 ml). The red-brown solution was heated on a steam bath while gaseous hydrogen chloride was bubbled through at a moderate rate (2–4 bubbles/sec) until the solution became green (about 6 hr). The flask was placed on a rotary evaporator for 10 min and nitrogen was bubbled through the solution for another 10 min to remove the excess HCl. An Allihn condenser with nitrogen inlet tube was partially inserted into the neck of the flask and the apparatus swept with N_2 for 10 min. Four equivalents of the tertiary phosphine were injected into the flask and the condenser was lowered into place. The solution was refluxed for 1.5 hr under N_2, then was cooled. Generally, the compounds containing phenyl phosphines precipitated on cooling, and were collected by filtration and recrystallized from the appropriate solvent (Table I). The trialkylphosphine compounds generally did not precipitate upon cooling, so the volume was reduced to about 25 ml with a rotary evaporator.

TABLE I

Preparative and analytical data for *mer*-L_3IrCl_3 compounds

L	mp(°C)	Calculated C	Calculated H	Calculated Cl	Found C	Found C	Found Cl	Recrystallization Solvent
Bu_3P	148–149	47.74	9.03	11.74	47.90	9.20	11.50	CH_3COOH
Pr_3P	234–240 (236–242)[a]	41.66	8.05	13.66	41.48	8.11	13.49	C_2H_5OH
Et_3P	111–115 (113–115)[a]	33.10	6.96	16.28	33.27	7.01	16.09	Petroleum ether 90–100°
Bu_2PhP	159–162 (155–158)[a]	52.24	7.22	11.01	52.50	7.40	11.00	CH_3OH
Pr_2PhP	239–241 (230–236)[a]	49.05	6.53	12.07	48.89	6.45	12.17	C_2H_5OH
Et_2PhP	238–239 (235–241)[a, b]	45.20	5.70	13.34	45.16	5.84	13.29	$CH_3COC_2H_5$
Me_2PhP	231–235 (238–241)[c]	40.42	4.67	14.92	40.55	4.80	14.83	CH_3OH
$BuPh_2P$	229–231	56.21	5.61	10.37	56.03	5.43	10.63	CCl_4
$PrPh_2P$	248–250	54.96	5.24	10.81	55.06	5.43	10.95	$CH_3COC_2H_5$
$EtPh_2P$	221–223	53.59	4.83	11.40	53.39	5.00	11.09	C_2H_5OH
$MePh_2P$	242–244 (240–246)[c]	52.09	4.38	11.83	52.06	4.41	11.62	$CH_3COC_2H_5$

[a] Ref. 6;
[b] Ref. 11;
[c] Ref. 12.

Water (10 ml) was added and the solution then extracted with CH_2Cl_2. Evaporation of the CH_2Cl_2 solution gave the solid compounds which were recrystallized.

DISCUSSION

The phosphorus-31 nuclear magnetic resonance spectrum of each of the L_3IrCl_3 compounds prepared as described consists of two peaks with relative intensity 2:1, which confirms the meridional structure for these compounds, since two of the phosphorus ligands (P_1,P_3) are mutually *trans* and the other phosphorus (P_2) is *trans* to a chlorine. Because the phosphorus atoms are not equivalent, phosphorus-phosphorus spin-spin coupling is expected, although with our moderate resolution it was not observed, as it had been in the case of the analogous rhodium compounds.[3–5]

The ^{31}P chemical shift data for the eleven compounds are given in Table II. There are several points of interest. First, with the exception of the downfield peak in the spectrum of the dimethylphenylphosphine compound, all the other phosphorus shifts are upfield from the uncomplexed

TABLE II

Phosphorus-31 NMR data for *mer*-L_3IrCl_3 compounds (chemical shifts are in ppm relative to H_3PO_4)

L	δ^a free ligand	$\delta_{P_{1,3}}{}^b$	$\delta_{P_2}{}^c$	$\Delta_{P_{1,3}}{}^d$	$\Delta_{P_2}{}^d$
Bu_3P	+32.3	+37.6	+39.9	+5.3	+7.6
Pr_3P	+33	+37.4	+40.0	+4.4	+7.0
Et_3P	+20.4	+33.0	+35.5	+12.6	+15.1
Bu_2PhP	+26.2	+37.9	+41.4	+11.7	+15.2
Pr_2PhP	+27.7	+37.8	+41.1	+10.1	+13.4
Et_2PhP	+16	+33.3	+36.7	+17.3	+20.7
Me_2PhP	+46	+40.4	+49.5	−5.6	+3.5
$BuPh_2P$	+17.1	+29.5	+35.0	+12.4	+17.9
$PrPh_2P$	+17.6	+29.9	+35.1	+12.3	+17.5
$EtPh_2P$	+12	+27.5	+31.6	+15.5	+19.6
$MePh_2P$	+26	+41.8	+55.2	+15.8	+29.2

[a] ref, 10;
[b] $P_{1,3}$ are mutually *trans* phosphines;
[c] P_2 is *trans* to chlorine;
[d] Δ (coordination chemical shift) = δ complex −δ free ligand.

ligand. Although this behaviour has been noted before[3] and is quite common for organophosphites upon coordination[3,13] or protonation,[14] and phosphorus halides on coordination,[3,15] it is rather unusual for tertiary phosphines.

Secondly, the chemical shift of P_2 is in all cases upfield from that of $P_{1,3}$. In the case of R_3P the difference ($\delta_{P2} - \delta_{P1,3}$) is about +2.5 ppm; in R_2PhP (except when R is methyl), it is about +3.4 ppm; and in PRh_2P (except when R is methyl) the difference is about +5 ppm. The methyl derivatives are unusual in that the differences between $P_{1,3}$ and P_2 are quite a bit larger, *viz.*, +9.1 (Me_2PhP) and +14.4 ppm ($MePh_2P$). In the rhodium compounds[5] the corresponding differences ($\delta_{P2} - \delta_{P1,3}$) are about −15.5 for R_3P, −13.5 for R_2PhP, and about −9 for RPh_2P (when R is ethyl, *n*-propyl, or *n*-butyl). The reason for the P_2 chemical shift being downfield from $P_{1,3}$ in rhodium compounds but upfield in the iridium compounds is not understood at this time. The same phenomenon is observed in *cis* and *trans* isomers of palladium[16] and platinum.[9] In the second transition series, the phosphorus *trans* to chlorine has its chemical shift downfield from that of the mutually *trans* phosphorus atoms, whereas in the third transition series (iridium, platinum) the reverse is true.

The proton magnetic resonance spectra are of interest in that they show only limited utility for assigning stereochemistries. In certain instances, *e.g.*, with dimethylphenylphosphine, the pmr spectra are definitive in structural determinations and stereochemical studies have been extensively and elegantly carried out by Shaw[17,18] and others.[19] In cases where two methylphosphines are mutually *trans*, the methyl group appears as a 1:2:1 triplet, which is ascribed to "virtual coupling", arising from the fact that $^2J_{P-P}$ is large. When the methylphosphine is not *trans* to another phosphorus, the methyl resonance is the expected doublet, due to splitting by phosphorus. The compound, *mer*-trichlorotris(dimethylphenylphosphine)iridium(III) has been discussed previously.[18] The doublet due to P_2 [τ, 8.78 (8.75[18]) ppm; J, 10.8 (11.0[18])Hz] is well separated from the triplet due to $P_{1,3}$ [τ, 8.23 (8.10[18])ppm; J_A, 4.2 (4.35[18])Hz]. J_A is defined as the separation between the lines

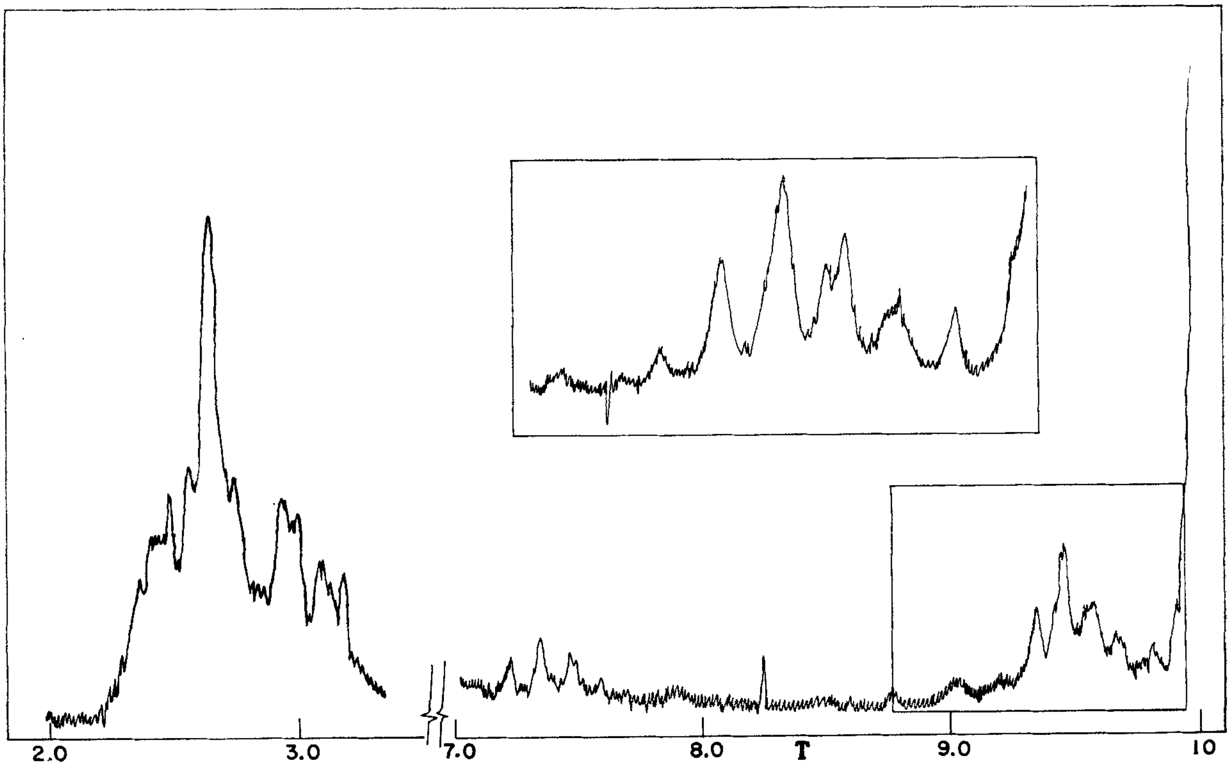

FIGURE 1 Proton spectrum of *mer*-$(EtPh_2P)_3IrCl_3$.

in the triplet (see ref. 18 for a discussion of the relationship of J_A and J_{PCH} and refs. 20 and 21 for a general discussion of X_nAAX_n spectra).

For *mer*-trichlorotris (diphenylmethylphosphine) iridium(III), the doublet from P_2 (τ, 8.05 ppm; J, 10.4 Hz), approaches the triplet from $P_{1,3}$ (τ, 7.87 ppm; J_A, 4.0 Hz) so that the neighboring lines begin to overlap but the assignments are quite clear.

"Virtual coupling" has also been noted for ethylphosphine[19] compounds. The methyl region of mutually *trans* diethylphenylphosphine in *mer*-$(Et_2PhP)_3IrCl_3$ is characterized by a 1 : 4 : 6 : 4 : 1 quintet [τ, 9.03 (8.98[19]) ppm; J_A, 7.3 (7.4[19]) Hz], which results from splitting and overlap of a triplet of triplets, i.e., by coupling to the methylene protons and to the "virtually coupled" phosphorus atoms. On the other hand, the diethylphenylphosphine *trans* to chlorine gives a five line 1:2:2:2:1 pattern [τ, 9.72 (9.73[19]) ppm; $^3J_{PCCH}$ 16.6 (14.8[19]) Hz; $^3J_{HCCH}$, 7.2 (7.4[19]) Hz] which results from the overlap of a doublet (phosphorus coupling) of triplets (methylene proton coupling). However in the case of *mer*-$(EtPh_2P)_3IrCl_3$, the methyl regions overlap so that the two types of ligands are not distinguishable (Figure 1). Further, in the case of *mer*-$(Et_3P)_3IrCl_3$ (Figure 2) the pmr of the methyl region is a broad quintet. This could result from the accidental magnetic equivalence of the ethyl groups or from chemical equivalence of the ligands caused by ligand exchange. It is interesting to note in this regard that of the twelve *mer*-L_3RhCl_3 compounds studied earlier, only when L was triethylphosphine and methyldiphenylphosphine was there no P–P coupling observed between P_2 and $P_{1,3}$. Again this could be explained by ligand exchange.

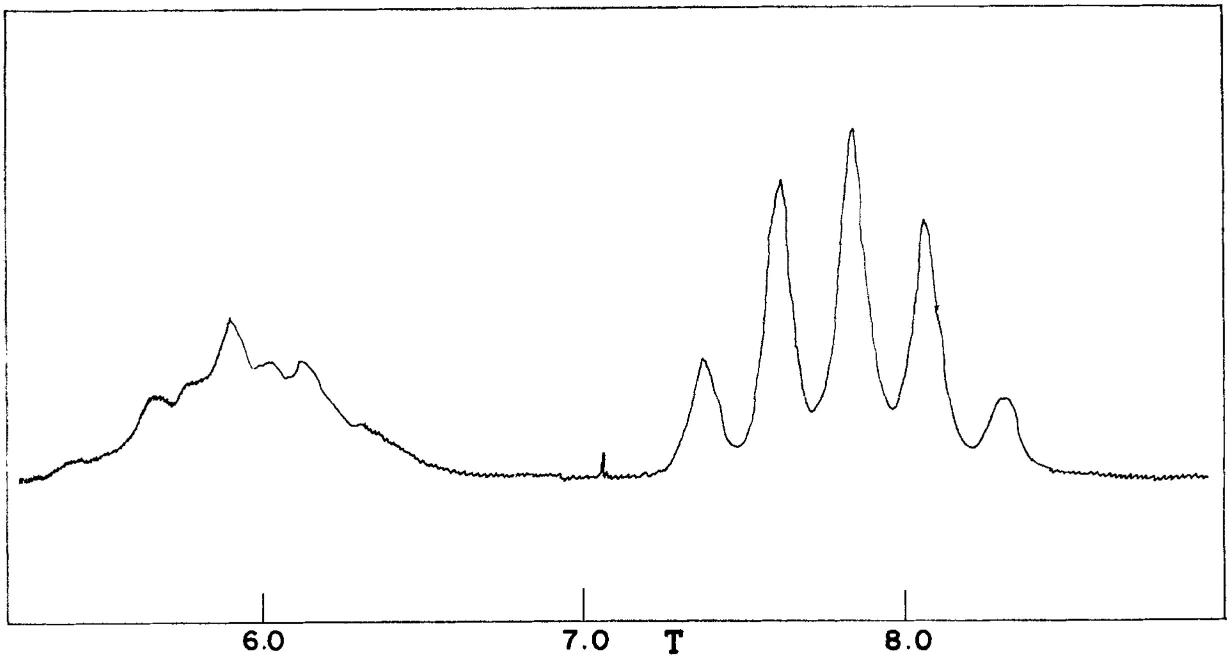

FIGURE 2 Proton spectrum of *mer*-$(Et_3P)_3IrCl_3$.

A present limiting factor in the applicability of ^{31}P magnetic resonance is the low solubility of some complexes, but this will be overcome with Fourier transform nmr. Recently, INDOR techniques have been used with some iridium dimethylphenylphosphine compounds of low solubility to measure phosphorus chemical shifts and phosphorus-phosphorus coupling constants.[22] However, this method is restricted also to special compounds with a particular arrangement of protons and phosphorus atoms.

In conclusion, the earlier work on stereochemical assignment by pmr, although extremely useful and unequivocal in optimum circumstances, is not as widely applicable for a variety of tertiary phosphines as is ^{31}P nmr.

The results of the electronic spectra are tabulated in Table III. It is noted that the transition energy is in the order of basicities, $R_3P > R_2PhP > RPh_2P$ (R = ethyl, *n*-propyl, *n*-butyl). The methyl compounds cause slightly higher energies. These are the same trends observed with the analogous rhodium compounds.

TABLE III

Electronic absorption spectra of *mer*-L_3IrCl_3 compounds

L	λ(Å)	Δ E(cm^{-1})	ϵ max(lit/mole—cm)
PBu_3	4280	23,360	80
PPr_3	4280	23,360	80
PEt_3	4280	23,360	70
PBu_2Ph	4340	23,040	75
PPr_2Ph	4340	23,040	65
PEt_2Ph	4350	22,980	60
PMe_2Ph	4210	23,750	80
$PBuPh_2$	~4400[a]	22,730	<100
$PPrPh_2$	~4400[a]	22,730	<100
$PEtPh_2$	~4400[a]	22,730	<100
$PMePh_2$	4310	23,200	80

[a] shoulders on charge transfer band.

REFERENCES

1. Supported by the U.S. Office of Scientific Research under Grant No. AF-AFOSR-782-67.
2. (a) Taken in part from the Ph.D. thesis of Robert A. Ference, University of Maryland, 1968; (b) Presented at the Third Middle Atlantic Regional Meeting, ACS, Philadelphia, February, 1968, Abstracts of papers, F9.
3. J. F. Nixon and A. Pidcock, *Annual Review of NMR Spectroscopy*, E. F. Mooney, ed., Vol. 2, Academic Press, New York, N.Y., 1969, pp. 346–422.
4. S. O. Grim and R. A. Ference, *Inorg. Nucl. Chem. Letters* **2**, 205 (1966).
5. S. O. Grim and R. A. Ference, *Inorg. Chim. Acta* **4**, 277, (1970).
6. J. Chatt, A. E. Field, and B. L. Shaw, *J. Chem. Soc.* 3371 (1963).
7. P. R. Brookes and B. L. Shaw, *J. Chem. Soc.* (A), 1079 (1967).
8. B. E. Mann, B. L. Shaw and R. E. Stainbank, *Chem. Commun.* 151 (1972).
9. S. O. Grim, R. L. Keiter and W. McFarlane, *Inorg. Chem.* **6**, 1133, (1967).
10. S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem.* **32**, 781 (1967).
11. J. W. Collier and F. G. Mann, *J. Chem. Soc.* 1815 (1964).
12. J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* 6789 (1965).
13. P. R. McAllister, Ph.D. Thesis, University of Maryland, 1968.
14. W. McFarlane and R. F. M. White, *Chem. Commun.* 744 (1969).
15. L. S. Meriwether and J. R. Leto, *J. Amer. Chem. Soc.* **83**, 3192 (1961).
16. S. O. Grim and R. L. Keiter, *Inorg. Chim. Acta* **4**, 56 (1970).
17. J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.* 279 (1963).
18. J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (A), 1407 (1966).
19. E. W. Randall and D. Shaw, *Mol. Phys.* **10**, 41 (1965).
20. R. K. Harris, *Can. J. Chem.* **42**, 2275 (1964).
21. R. D. Bertrand, F. B. Ogilvie and J. G. Verkade, *J. Amer. Chem. Soc.* **92**, 1908 (1970).
22. B. E. Mann, C. Masters, and B. L. Shaw, *J. Chem. Soc. Dalton* **48** (1972).