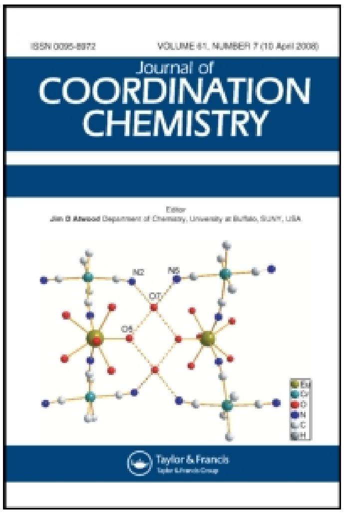

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Samuel O. Grim[a]; Larry C. Satek[a]
[a] Department of Chemistry, University of Maryland, College Park, Maryland

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PREPARATION AND PHOSPHORUS NMR STUDIES OF SOME FACIAL RHODIUM(III) AND IRIDIUM(III) COMPLEXES

SAMUEL O. GRIM and LARRY C. SATEK

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

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A series of fifteen compounds of the type *fac*- $\{M(Ph_nR_{3-n})_3Cl_3]$ where R is alkyl, n is 0, 1, or 2, and M is Rh or Ir has been prepared. The phosphorus-31 magnetic resonance data for the soluble compounds are reported. The compounds. Rhodium-phosphorus coupling constants are compared to the J_{Rh-P}'s in the previously reported meridional complexes. The somewhat unusual upfield chemical shifts upon coordination of tertiary phosphines previously observed in meridional iridium complexes are also found in the analogous facial complexes. Some proton magnetic resonance data are reported.

INTRODUCTION

Studies of uncharged octahedral rhodium(III) and iridium(III) tertiary phosphine complexes[2,3,4] have shown that the meridional or *trans* configuration is usually the dominant or exclusive product, although generally lower yields of various ionic compounds, dimers, and facial or *cis* isomers also are obtained under varying reaction conditions.[2,4,5] The comprehensive study of rhodium compounds by Intille summarizes these reactions and products.[4] Brooks and Shaw[6] have demonstrated the photochemical isomerization of some meridional rhodium(III) and iridium(III) tertiary phosphine and arsine complexes to the facial configurations. They attributed the formation of some previously reported facial isomers to photochemical isomerization.

We have prepared several facial rhodium(III) and iridium(III) tertiary phosphine complexes from the series *mer*- $M(Ph_nR_{3-n})_3Cl_3$ where M is Rh, Ir, n is 0, 1, or 2, and R is Me, Et, *n*-Pr, or *n*-Bu, and have recorded their phosphorus-31 nmr spectra where solubilities permitted.

EXPERIMENTAL

Phosphorus-31 nmr spectra were recorded on a Varian Associates DP-60 spectrometer operating at 24.3 MHz as described previously.[7] Chemical shifts (ppm vs. H_3PO_4) are accurate to ±0.4 ppm and coupling constants to ±8 Hz. Because of the limited solubility of the complexes in CH_2Cl_2, our usual solvent, $CHCl_2CN$ was employed. Where possible, spectra were also recorded in CH_2Cl_2. Within experimental error, the same chemical shifts and coupling constants are observed.

Proton magnetic resonance spectra were recorded on a Varian Associates A-60-A spectrometer or a Perkin-Elmer Hitachi R-20-A spectrometer in $CDCl_3$, CH_2Cl_2, or $CHCl_2CN$ with TMS as an internal standard.

Microanalyses were performed by Dr. Franz Kasler of the University of Maryland.

Melting points were obtained with a Mel-Temp melting point apparatus and are reported uncorrected.

Reactions were carried out in a benzene or a benzene-cyclohexane solution of the appropriate meridional isomer. A Sylvania 275 watt sunlamp, a PCQ (Ultraviolet Products, Inc., San Gabriel, Calif.) internal uv source, and laboratory fluorescent lights were all used as light sources; however, best results were obtained by placing a stoppered flask containing the solution on a south window ledge (spring-summer) in direct sunlight for periods of several hours to eight weeks. The solid was removed by filtration, washed with benzene, and vacuum-dried (room temperature and 0.2 torr). Recrystallizations, when necessary, were performed rapidly from CH_2Cl_2-hexane. Preparation of the meridional complexes are reported elsewhere.[8,9]

DISCUSSION

The melting points, yields, analyses, and approximate lengths of reaction time are recorded in Table I. Although no attempt was made to standardize reaction times, it can be observed from the yields and reaction times that the formation of the facial isomers correlates roughly inversely with the solubilities or the expected solubilities of the complexes. The compounds expected to be most soluble due to the numerous alkyl groups, i.e., *fac*-$(PBu_3)_3RhCl_3$, *fac*-$(PPr_3)_3RhCl_3$, and *fac*-$(PBu_3)_3IrCl_3$, did not form even after several months of exposure to direct sunlight. Phosphorus-31 nmr spectra of the residues demonstrated that only the meridional isomers were present. An attempt to prepare *fac*-$(PBu_3)_3RhCl_3$ from *fac*-$(CH_3CH)_3RhCl_3$[10] and Bu_3P resulted in the formation of *mer*-$(PBu_3)_3RhCl_3$ as identified by its phosphorus-31 nmr spectrum.

Attempts to prepare *fac*-$(PPh_2R)_3RhCl_3$ (R=Me, Et, n-Pr, n-Bu) resulted in what appeared to be a mixture of products, none of which was identified.

Phosphorus-31 nmr data are recorded in Table II. Also listed for convenience are the chemical shifts, the coupling constants, and coordination chemical

TABLE I

Preparative and analytical data for *fac*-L_3MCl_3 compounds

L_3RhCl_3

	CARBON		HYDROGEN					
L	CALC.	FOUND	CALC.	FOUND	MP (°C)	% YIELD	COLOR	Rx.TIME
Me_3P	24.70	24.89	6.23	6.08	260-70[a]	90	cream	1 day
Et_3P	38.34	38.60	8.06	8.02	164-66[b,f]	70	yellow	2 weeks
Me_2PhP	46.21	46.02	5.34	5.31	216-17[c,g]	60	yellow	1 day
Et_2PhP	50.90	50.64	6.42	6.25	174-78	62	yellow	2 days
Pr_2PhP	54.58	54.45	7.27	6.98	168-73	30	yellow	2 days
Bu_2PhP	57.56	56.74	7.95	7.76	153-56	30	yellow	8 weeks
					L_3IrCl_3			
Et_3P	33.10	32.95	6.96	6.75	257-59[d]	95	white	6 days
Pr_3P	41.66	41.76	8.15	8.06	248-52	94	white	5 days
Me_2PhP	40.42	40.90	4.67	3.90	298-302	100	white	5 days
Et_2PhP	45.20	44.90	5.70	5.61	252-56	90	white	2 days
Pr_2PhP	49.05	48.30	6.53	6.38	230-33	71	white	2.5 hours
Bu_2PhP	52.20	52.50	7.20	7.17	230-33	57	lt. yellow	2 days
$MePh_2P$	52.09	52.18	4.38	4.25	185-87	100	lt. yellow	1 day
$EtPh_2P$	53.59	52.85	4.83	4.68	239-43	95	lt. yellow	2 days
$PrPh_2P$	54.91	55.20	5.22	5.34	262-67	85	lt. yellow	2 days

(a) 160-170, ref. 4; (b) 160-170, ref. 4; (c) 210-215, ref. 4; 261-64, ref. 3; (e) 255-65, ref. 3; (f) 169-74; J. Chatt, N. P. Johnson and B. L. Shaw, J. Chem. Soc. 2508 (1964); (g) 215-226, ref. 2.

TABLE II

Phosphorus-31 nmr data for *fac*-$(Ph_nR_{3-n})_3RhCl_3$ and *fac*-$(Ph_nR_{3-n})_3IrCl_3$

L_3RhCl_3

L	δ_P[a]	δ_P[d] complex	Δ[e]	J_{P-Rh}[f]	δ_{P_2} mer	ΔP_2 mer	J_{P_2-Rh} mer
Et_3P	+20.4[b]	-24.3(3)	-44.7	114(7)	-20.0[g] (-20.0)[h]	-40.4	109[g] (112.1)[h]
Me_3P	+62[b]	-7.9(4)	-70	113(10)	-7.6[g] --	-70	103[g] --
Bu_2PhP	+26.2[b]	-10.0(3)	-36.2	122(7)	-12.7[g] (-12.8)[h]	-38.9	113[g] (111.0)[h]
Pr_2PhP	+27.2[c]	-9.5(2)	-36.7	117(5)	-12.7[g] (-12.7)[h]	-39.9	115[g] (110.9)[h]
Et_2PhP	+16[b]	i	--	i	-17.5[g] (-17.1)[h]	-33	108[g] (111.1)[h]
Me_2PhP	+46[b]	i	--	i	-4.4[g] (-3.7)[h]	-50	112[g] (112.3)[h]

L_3IrCl_3

L	δ_P	δ_P complex	Δ	δ_{P_2} mer	ΔP_2 mer
Et_3P	+20.4[b]	+26.2(3)	+5.8	+35.5[j] (+36.1)[h]	+15
Pr_3P	+33[b]	+31.9(2)	-1	+40.0[j] --	+7
Me_2PhP	+46[b]	i	--	+49.5[j] (+50.1)[h]	+4
Et_2PhP	+16[b]	+34.8(5)	+19	+36.7[j] (+37.5)[h]	+21
Pr_2PhP	+27.7[c]	+39.3(2)	+11.6	+41.1[j] (+41.6)[h]	+14
Bu_2PhP	+26.2[b]	+39.4(2)	+13.2	+41.4[j] --	+15
$MePh_2P$	+28[b]	i	--	+55.2[j] (+55.2)[h]	+29
$EtPh_2P$	+12[b]	+37.3(3)	+25	+31.6[j] --	+20
$PrPh_2P$	+17.6[c]	+38.6(2)	+21.0	+35.1[j] --	+18.5

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[a] ppm relative to 85% H_3PO_4.

[b] S.O. Grim and W. McFarlane, Nature, 208, 995 (1965).

[c] S.O. Grim, W. McFarlane, and E. Davidoff, J. Org. Chem., 32, 781 (1967).

[d] Values in parenthesis are standard deviations in the last digit.

[e] δ complex - δ ligand.

[f] In Hz.

[g] Ref. 8.

[h] Ref. 11.

[i] Too insoluble to be observed.

[j] Ref. 9.

shifts of the phosphorus atoms *trans* to the chlorine atom in the meridional isomers. The facial isomers have three equivalent phosphorus atoms, each *trans* to a chlorine atom. Thus a phosphorus-31 nmr spectrum should consist of a single line. Further splitting should be observed for the rhodium complexes since ^{103}Rh (100% abundance) has a spin I = 1/2(Figure 1). It is apparent that $J_{Rh\text{-}P}$ values for the facial complexes are similar to the $J_{Rh\text{-}P}$ values for the phosphorus atom *trans* to a chlorine atom in the meridional isomer, and quite different from the $J_{Rh\text{-}P}$ coupling constants observed for the mutually *trans* phosphorus atoms (*ca.* 84 Hz).[8,11]

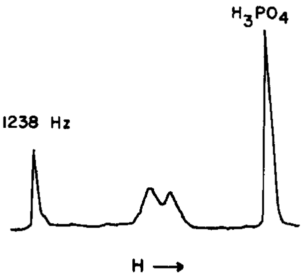

FIGURE 1 ^{31}P NMR spectrum of *fac*-$(Et_3P)_3RhCl_3$ with 85% H_3PO_4 external standard and calibration sideband at 1238 Hz downfield from H_3PO_4.

TABLE III

PMR data for methyl and ethyl substituted *fac*-RhL_3Cl_3 and *fac*-IrL_3Cl_3[a]

Compound	Signal	τ (ppm)	Assignment
$(Me_3P)_3RhCl_3$	triplet[b]	8.27	CH_3
$(Et_3P)_3RhCl_3$	quintet[c]	7.79	CH_2
	quintet[c]	8.69	CH_3
$(Me_2PhP)_3RhCl_3$	triplet[b]	8.09	CH_3
	multiplet	2.5	C_6H_5
$(Et_2PhP)_3RhCl_3$	multiplet	9.1	CH_3
	multiplet	7.8	CH_2
	multiplet	2.9	C_6H_5
$(Et_3P)_3IrCl_3$	quintet[c]	8.75	CH_3
	quintet	7.85	CH_2
$(Et_2PhP)_3IrCl_3$	multiplet	9.3	CH_3
	multiplet	7.2	CH_2
	multiplet	2.6	C_6H_5
$(EtPh_2P)_3IrCl_3$	multiplet	9.3	CH_3
	multiplet	7.3	CH_2
	multiplet	2.8	C_6H_5

[a] $(Me_2PhP)_3RhCl_3$ was dissolved in $CF_3CHOHCF_3$. All others were dissolved in $CHCl_2CN$. The Ir complexes of Me_2PhP and $MePh_2P$ were too insoluble to obtain spectra.

[b] The separation between the two outside lines is 10 Hz which means an apparent coupling constant of 5 Hz. For a discussion of the actual J see ref. 18.

[c] The separation between the two outside lines of the quintet is 28 Hz which means an apparent coupling constant of 7 Hz. For a discussion of the actual J see ref. 18.

The two other points should be noted for the rhodium compounds. First, the $J_{Rh\text{-}P}$ values average 6.5 Hz larger in the facial complexes than the corresponding meridional complexes. Second, the most basic phosphines have the smallest $J_{Rh\text{-}P}$ coupling constants. This trend was previously noted[8] for the meridional compounds, although a recent paper[11] has noted some reversals of the trend. However, the differences between the observed values observed in both points are approximately the size of the error of measurement and therefore probably not significant.

The *fac*-tris(triorganophosphine)iridium(III)-chloride compounds, except for tri-*n*-propylphosphine, exhibit the same upfield chemical shifts from the free ligands as previously observed in the meridional compounds.[9,11] While this effect is commonly observed for organophosphites[12,13] and phosphorus halides[12,14] on coordination and organophosphites on protonation[15], it has only occasionally been noted in other teritary phosphine complexes.[12]

One other trend in the phosphorus-31 nmr spectra of the iridium compounds should be noted. For the R_3P complexes, the coordination chemical shifts average 8.5(4) ppm less than the corresponding P_2 phosphine[16] of the meridoinal compounds. The R_2PhPcomplexes average 1.9(1) ppm less than their corresponding P_2 phosphines in the meridional compounds, and the RPh_2P complexes average 4.6(1) ppm more than their corresponding P_2 phosphines. Thus each substitution of an alkyl group with a phenyl group produces a 6.5 ppm increase in the relative coordination chemical shifts. Such behavior could be due to increased steric effects in the compounds.

Proton magnetic resonance data for the methyl and ethyl substituted compounds appear in Table III. They are of interest because they are not simple spectra due to the complex spin system coupling commonly known as 'virtual coupling', which is usually observed in compounds with methyl[17,18] or ethyl[19] phosphines mutually *trans*. Virtual coupling arises because J_{PP} in these compounds is considerably larger than zero. Several papers[20,21,22,23] have reported, however, the observation of a complex pmr spectrum for mutually *cis* methylphosphine complexes, which again have $J_{PP} > 0$.

The pmr spectrum of *fac*(Me$_3$P)RhCl$_3$ appears in Figure 2. This spectrum is somewhat different from that reported for the same compound prepared by an alternate route[4], and the reported color and melting point are also different; however, the colors and melting points of *fac*-(Et$_3$P)$_3$RhCl$_3$ and *fac*-(Me$_2$Ph)$_3$RhCl$_3$ are similar and the pmr spectrum of *fac*-(Et$_3$P)$_3$RhCl$_3$ is similar to that reported here. Reference 4 did not report the pmr spectrum of *fac*(Me$_2$PhP)$_3$RhCl$_3$ which we found to be similar to Fig. 2, although the central "line" was not quite as well formed.

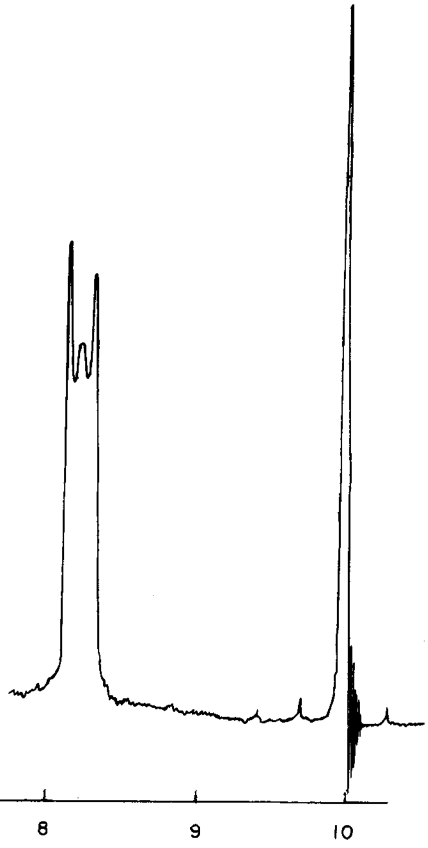

FIGURE 2 Pmr spectrum of *fac*-(Me$_3$P)$_3$RhCl$_3$ with TMS (τ = 10 ppm) internal reference.

The ethyl substituted phosphine compounds have complex pmr spectra, with a methyl region multiplet that appears different than the expected 1:2:2:2:1 quintet[8,9] (arising from the overlap of a doublet of triplets, where the doublet is due to splitting by the phosphorus atom and the triplet is due to the splitting by the methylene protons). Attempts to further study the methyl region by double irradiation experiments failed primarily because of the limited solubility of the compounds in solvents suitable for pmr spectra, instrumental limitations and the wide line widths encountered in these compounds.

While it must be remembered that three 'virtually coupled' phosphorus atoms now affect the pmr spectrum rather than two as in most reported cases, it is of interest to note that the *cis* $^2J_{PP}$ coupling constants in the analogous meridional compounds of rhodium[8,11] and iridium[11] are small (<25 Hz in most cases) and that only a sharp doublet is observed (phosphorus coupling) for the P_2 methyl substituted phosphines,[8,9,17,18] Strongly 'virtually coupled' systems with two mutually *trans* phosphines which exhibit a sharp 1:2:1 triplet (from two 'virtually coupled' phosphorus atoms) are reported to have very large $^2J_{PP}$ values for the platinum group metals.[24] Thus it would appear that *cis* $^2J_{PP}$ has increased somewhat in changing from a meridional complex to its facial isomer (see *ref.* 24 for a discussion of $^2J_{PP}$ values).

Although the advent of better instrumentation has somewhat decreased the importance of the choice of a solvent for ^{31}P studies, it should be noted that dichloroacetonitrile appears to be a much superior solvent for these and at least some other complexes which we have studied. Dichloroacetonitrile was found to be the best solvent of about forty common and not so common solvents examined.

REFERENCES

1 (a) Taken in part from the Ph.D. thesis of Larry C. Satek, University of Maryland, 1972; (b) Presented at the Fifth Middle Atlantic Regional Meeting, April 2, 1970, University of Delaware, Newark, Delaware. (c) supported by the National Science Foundation under Grant No. GP30703.
2. P. R. Brooks and B. L. Shaw, *J. Chem. Soc., A*, 1079 (1967).
3. J. Chatt, A. E. Field, and B. L. Shaw, *J. Chem. Soc.*, 3371 (1963).
4. G. M. Intille, *Inorg. Chem.*, 11, 695 (1972).
5. J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc., A*, 1674 (1969).
6. P. R. Brooks and B. L. Shaw, *Chem. Commun.*, 919 (1968) and references within.
7. S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, **6**, 1133 (1967).
8. S. O. Grim and R. A. Ference, *Inorg. Chim. Acta*, **4**, 277 (1970).
9. S. O. Grim and R. A. Ference, *J. Coord. Chem.*, **2**, 225 (1973).
10. B. D. Catskins and M. L. Good, *Inorg. Chem.*, **8**, 1095 (1969).
11. B. E. Mann, C. Masters, and B. L. Shaw, *J. C. S. Dalton*, 704 (1972).
12. 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.
13. P. R. McAllister, Ph.D. Thesis, University of Maryland, 1968.
14. L. S. Meriwether and J. R. Leto, *J. Amer. Chem. Soc.*, **83**, 3192 (1961).
15. W. McFarlane and R. F. M. White, *Chem. Commun.*, 744 (1969).
16. P_2 phosphines are those *trans* to chlorine atoms in meriodional $((R_3P)_3MCl_3$ complexes.
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. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1908 (1970).
21. J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *Inorg. Chem.*, **4**, 288 (1965).
22. P. K. Maples and C. S. Kraihanzel, *Chem. Commun.*, 922 (1968).
23. W. E. Sanclift and D. G. Hendricker, *Inorg. Chem.*, **7**, 1242 (1968).
24. E. G. Finer and R. K. Harris, *Progress in NMR Spectroscopy*, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, eds., Vol. 6, Pergamon Press, Oxford, 1971, pp. 61–118.