IV, proceeds by an inner-sphere mechanism. This conclusion is consistent with the one reached earlier about the mechanism of the $CrNCS^{2+}$–V^{2+} reaction. Since, as will be seen, there is good evidence that the rate of the $CrSCN^{2+}$–V^{2+} reaction is controlled by the rate of substitution on vanadium(II), the above reasoning requires that the "redox-controlled" rate for the $CrSCN^{2+}$–V^{2+} reaction not be much faster than the "substitution-controlled" rate. In any event, the similarity of the values of k_{NCS^-}/k_{SCN^-} for the vanadium(II) and chromium(II) reductions is quite striking.

There is evidence that the rates of a number of oxidation–reduction reactions involving vanadium(II) are primarily controlled by the rate of replacement of a water molecule coordinated to the vanadium(II).[11,16,22,23] The relevant data are summarized in Table V. It is apparent that the rate constants and activation parameters for the oxidation–reduction reactions are very similar to the corresponding parameters for the substitution of vanadium(II) by thiocyanate.

$$V(H_2O)_6^{2+} + SCN^- \longrightarrow (H_2O)_5VNCS^+ + H_2O$$

Some of the faster oxidation–reduction rates may be due to electrostatic effects, while steric effects may be important in some of the slower reactions.[23] The identification of the products of the oxidation–reduction reactions has shown that the reactions of vanadium(II) with $CrSCN^{2+}$, VO^{2+}, *cis*-$Co(en)_2(N_3)_2^+$, and $Co(NH_3)_5(C_2O_4)^+$ proceed mainly by inner-sphere mechanisms.

The rate law for the reaction of vanadium(II) with $CrSCN^{2+}$ contains a term which is first order in acid. This term is small, and very probably represents a medium effect. The absence of an inverse acid term in the rate law is not surprising, since the rate of reaction of $CrSCN^{2+}$ with vanadium(II) appears to be primarily determined by the rate of substitution on the vanadium(II), and under these conditions $Cr(OH)SCN^+$ would not react much more rapidly than $CrSCN^{2+}$ with vanadium(II). Such a term is found, for example, in the rate law for the reaction of $CrSCN^{2+}$ with chromium(II),[9] and of $CrNCS^{2+}$ with vanadium(II), reactions in which substitution on the reducing agents is not rate determining.

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Phosphorus-31 Nuclear Magnetic Resonance Studies of Coordination Compounds. I. The Stereochemistry of Some Complexes with Multidentate Ligands

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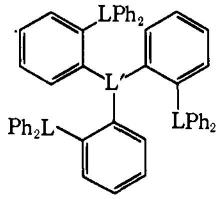
Abstract: Phosphorus-31 nmr has been used to determine the structures of some diamagnetic complexes containing the potentially quadridentate ligands $(o\text{-}Ph_2LC_6H_4)_3L'$ (L′ = L = P, QP; L′ = As, L = P, ASTP; L′ = Sb, L = P, SBTP; L′ = P, L = As, PTAS). The number, relative intensities, and chemical shifts of the resonances in the spectra of the five-coordinate complexes $[MCl(\text{ligand})]^+$ (M = Ni, Pd, or Pt, ligand = QP; M = Ni, ligand = ASTP, SBTP, or PTAS) and six-coordinate complexes $[M^{n+}X_2(\text{ligand})]^{(n-2)+}$ (M = Ru(II), X = Cl, ligand = QP, ASTP, or PTAS; M = Rh(III), X = Cl, ligand = QP; M = Fe(II), X = NCS, ligand = QP) confirm the structural assignments made on the basis of other physical measurements. The stereochemistry of the complex $[IrHCl(QP)][BPh_4]$ has been determined. In the spectra of the complexes $[M(CO)_3(QP)]$ (M = Cr or W), peaks in the chemical shift region associated with the free ligand signals have been assigned to uncoordinated phosphorus atoms.

Recent studies[2,3] have shown that phosphorus-31 nuclear magnetic resonance (^{31}P nmr) can be used for structural assignment in coordination compounds. We have used this technique to study complexes of the potentially quadridentate ligands shown in the facing column. The complexing properties of these ligands have been extensively investigated[4] and two main types of complex are known: $[M^{n+}X(\text{ligand})]^{(n-1+)}$ with trigonal-bipyramidal structure (**1**) and $[M^{n+}X_2(\text{ligand})]^{(n-2+)}$ with octahedral structure (**2**).



L′ = P, L = P, QP tris(*o*-diphenylphosphinophenyl)phosphine
L′ = As, L = P, ASTP tris(*o*-diphenylphosphinophenyl)arsine
L′ = Sb, L = P, SBTP tris(*o*-diphenylphosphinophenyl)stibine
L′ = P, L = As, PTAS tris(*o*-diphenylarsinophenyl)phosphine

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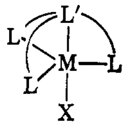
[2] S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Amer. Chem. Soc.*, 89, 5573 (1967), and references therein.

[3] S. O. Grim, D. A. Wheatland, and P. R. McAllister, *Inorg. Chem.*, 7, 161 (1968).

[4] J. G. Hartley, D. G. E. Kerfoot, and L. M. Venanzi, *Inorg. Chim. Acta*, 1, 145 (1967), and references therein.



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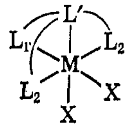

2

Complexes such as $[Cr(CO)_3(QP)]$, in which the phosphine is believed to act as a terdentate ligand, have also been obtained.[5] It was thought, therefore, that the above range of complexes would provide a test of the applicability of the ^{31}P nmr method to the stereochemical study of diamagnetic complexes.

Experimental Section

Physical Measurements. The ^{31}P nmr spectra were measured at 40.48 MHz and 23,490 G on a Japan Electron Optics Laboratory JNM-4H-100 spectrometer, using 5-mm o.d. tubes. In all cases, saturated dichloromethane solutions of the complexes were studied. The measured chemical shift for [NiCl(ASTP)]Cl, whose spectrum consists of a single, relatively sharp peak, was not concentration dependent over the range 0.1–0.6 mol of complex/liter of solvent, and the spectra of the other complexes were also assumed to be concentration independent.

The solubility of all the five-coordinate complexes, with the exception of [PtCl(QP)]Cl, was sufficient to allow the use of the slow passage absorption technique. The other complexes were examined under rapid or intermediate passage conditions.[6]

It was not feasible to use phosphorus trioxide, P_4O_6, as a calibrant either in an added capillary tube or in the annular region of a coaxial tube[7] because of the decrease in intensity of already weak signals. Chemical shifts, therefore, had to be measured using a sample tube–reference tube interchange method, with the latter containing P_4O_6. The sample peaks were calibrated by superimposition of side bands resulting from appropriate audiomodulation of the P_4O_6 main band. Peak positions and intensities were obtained on averaging several such spectra, using both increasing and decreasing field sweeps (essential for dispersion mode spectra). Coupling constants were measured by calibrating the chart paper with appropriate side bands from P_4O_6. Corrections for diamagnetic susceptibility differences between the sample and P_4O_6 were not applied.

The proton magnetic resonance spectrum of $[IrHCl(QP)][BPh_4]$ was obtained on the same instrument operating at 100 MHz.

Visible and ultraviolet spectra were measured on a Unicam SP 700 spectrophotometer, using dichloromethane solutions and 1-cm silica cells. Solutions were examined in the frequency range 10–40 kK and in the concentration range 10^{-3}–10^{-5} *M*.

Conductances were measured using a Cambridge conductivity bridge and a cell with black platinum electrodes. Approximately 10^{-3} *M* solutions in AnalaR nitrobenzene were used, and conductances were corrected to 20°.

Analyses. Nickel analyses were performed on a Unicam SP 90 atomic absorption spectrophotometer, with monochromator set at 232.0 mμ. Cyclohexanone solutions of the complexes were prepared containing about 20 ppm of nickel; at this concentration of nickel the instrument was found to be both sensitive and accurate. Calibration curves were constructed using solutions of bis(salicylaldoximato)nickel(II).

Phosphorus[8] was determined spectrophotometrically. Carbon and hydrogen were determined by Dr. A. Bernhardt, Mikroanalytisches Laboratorium im Max-Planck-Institut für Kohlenforschung, 433 Mülheim (Ruhr), West Germany, and by Mr. D. Chapple, Inorganic Chemistry Laboratory, Oxford.

Preparation of the Ligands. The tetratertiary phosphine, QP, was prepared by the method of Chiswell and Venanzi,[9] and PTAS by the method of Howell, *et al.*,[10] using the modified procedure of Cannon, *et al.*[11] The ligands ASTP and SBTP[12] were made by adding arsenic trichloride or antimony trichloride to the lithium derivative obtained from *o*-bromophenyldiphenylphosphine.

Preparation of the Complexes. All complexes were pumped at 135° (10^{-4} mm) for about 15 hr, unless stated otherwise.

[NiCl(QP)]Cl. Nickel chloride hexahydrate (0.54 g) and QP (1.96 g) were refluxed in ethanol (160 ml) for 3 hr, and the solution was evaporated to dryness. The complex was freed from excess ligand by dissolving the residue in the minimum amount of cold ethanol, filtering, and evaporating the solution to dryness. Nickel chloride (if present) was removed by extracting the residue with the minimum amount of dichloromethane and filtering. The pure product was obtained by addition of diisopropyl ether (50 ml) to this solution and removal of the dichloromethane by rotary evaporation.

[NiCl(ASTP)]Cl and [NiCl(PTAS)]Cl. These compounds were prepared and purified as for their QP analogs.

[NiCl(SBTP)]Cl. Nickel chloride hexahydrate (0.25 g) and SBTP (1.00 g) were refluxed in ethanol (70 ml) for 3 hr. No suitable solvent for recrystallization could be found. The complex was either too soluble (*e.g.*, in methanol, ethanol, chloroform, chlorobenzene, acetone, tetrahydrofuran, benzene, ethyl acetate), or, when dichloromethane was removed from the complex dissolved in a solvent mixture (*e.g.*, CH_2Cl_2–carbon tetrachloride, CH_2Cl_2–diethyl ether, or CH_2Cl_2–diisopropyl ether), a blue solid contaminated with ligand was obtained. The solid isolated by evaporation to dryness of a dichloromethane solution, purified as described for the QP analog, was, however, analytically pure.

[PdCl(QP)]Cl and [PtCl(QP)]Cl. These compounds were prepared by the method Hartley, *et al.*[13] They were recrystallized from dichloromethane–ethanol.

$[RhCl_2(QP)]Cl$. Bis(cycloocta-1,5-diene)-μ,μ'-dichlororhodium(I)[14] (0.45 g) and QP (1.49 g) were refluxed in ethanol (50 ml) for 2 hr. The red solid, [RhCl(QP)], was filtered off and suspended in dichloromethane (30 ml), and chlorine was passed through this suspension for 5 min. The resultant yellow solution was evaporated to dryness, and the residue was recrystallized from dichloromethane–ethanol and pumped at 110°.

Compounds $[Cr(CO)_3(QP)]$, $[W(CO)_3(QP)]$, and $[Cr(CO)_3(TP)]$ (TP is bis(*o*-diphenylphosphinophenyl)phenylphosphine) were prepared by the methods of Howell and Venanzi.[5] Compounds $[Fe(NCS)_2(QP)]$,[15] $[RuCl_2(ligand)]$[16] (ligand = QP, ASTP, or PTAS), and $[IrHCl(QP)][BPh_4]$[17] were prepared as indicated in the references.

Some physical properties of the new compounds studied are given in Tables I and II.

Results and Discussion

Free Ligands. The observed ^{31}P chemical shifts of the ligands are given in Table III. The chemical shift of QP is, within experimental error, the same in tetrahydrofuran and dichloromethane (the solvent used to study the complexes). Thus, the chemical shifts of ASTP and SBTP in dichloromethane are assumed to be the same as those found in tetrahydrofuran solution. The rapid passage dispersion spectrum of QP, in tetrahydrofuran and dichloromethane, shows only one peak, indicating that all four phosphorus atoms have chemical shift equivalence within the limits of error of a rapid passage experiment. As expected, the chemical shifts

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[17] D. G. E. Kerfoot, D.Phil. Thesis, Oxford University, England, 1967.

Table I. General Physical Data, Yields, and Analyses of the New Complexes

					Analytical data							
					Calcd, %				Found, %			
Complex	Color	Dec pt, °C	Λ_M[a]	Yield, %	C	H	Metal	P	C	H	Metal	P
[NiCl(QP)]Cl	Dark blue	317–322	23.5	80	68.68	4.48	6.2	13.1	68.45	4.67	6.3	12.9
[NiCl(ASTP)]Cl	Dark blue	293–298	21.8	89	65.62	4.28	5.9		65.79	4.40	5.9	
[NiCl(SBTP)]Cl	Blue-black	159–163	13.9	83	62.65	4.09	5.7	9.0	62.62	4.33	5.6	8.9
[NiCl(PTAS)]Cl	Dark blue	301–305	23.9	87	60.26	3.93	5.5		60.47	4.02	5.4	
[$RhCl_2$(QP)]Cl	Yellow	286–292	21.7	55	63.33	4.13		12.1	63.34	4.36		12.0

[a] Mhos cm^2 mol^{-1}; for 10^{-3} M nitrobenzene solutions at 20°.

Table II. Visible and Ultraviolet Spectra of the New Complexes in Dichloromethane Solution

Complex	E_{max}, kK	ϵ_{max}
[NiCl(QP)]Cl	36.3 sh[a]	20,400[b]
	32.2 sh	16,100[b]
	26.5 sh	3,000[b]
	17.1	4,550
[NiCl(ASTP)]Cl	36.9 sh	20,800[b]
	31.0 sh	13,400[b]
	16.3	4,450
[NiCl(SBTP)]Cl	35.9	20,300
	30.7 sh	11,400[b]
	27.4 sh	4,800[b]
	17.0	3,250
[NiCl(PTAS)]Cl	37.0 sh	16,400[b]
	32.0	14,850
	16.4	4,600
[$RhCl_2$(QP)]Cl	36.4 sh	24,730[b]
	28.3	19,770

[a] sh = shoulder. [b] Band height at point of inflection.

Table III. ^{31}P Chemical Shifts of the Free Ligands, with Respect to External P_4O_6

Ligand	Solvent	Chemical shift, ppm
QP	Tetrahydrofuran	+127.5[d]
QP	Dichloromethane	+127.7[e]
ASTP	Tetrahydrofuran[a]	+124.4[d]
SBTP	Tetrahydrofuran[a]	+119.0[d]
PTAS	Dichloromethane[b]	+130.5[d]
Ph_3P	Tetrahydrofuran	+118.3[c]
Ph_3P	Dichloromethane	+118.1[c]

[a] Insufficiently soluble in dichloromethane. [b] Insufficiently soluble in tetrahydrofuran. [c] ±0.1 ppm. [d] ±0.2 ppm. [e] ±0.5 ppm.

of the phosphorus atoms in the polydentate ligands have values which are close to those of triphenylphosphine, Ph_3P.

When the "central" phosphorus atom, L′, of QP is replaced by arsenic, as in ASTP, or by antimony, as in SBTP, the chemical shift of the "terminal" phosphorus atoms, L, steadily changes to low field. If, on the other hand, the terminal phosphorus atoms of QP are replaced by arsenic, as in PTAS, the central phosphorus shift changes to higher field. These relatively small changes are probably due to slight alterations in bond angles[18] around the phosphorus atoms concerned, caused by replacing one group Vb atom by another of different covalent radius; π-bonding effects on the ^{31}P chemical shifts of these aromatic phosphines should be negligible.[18]

Five-Coordinate Complexes. The ^{31}P nmr spectra of the QP complexes [MCl(QP)]Cl (M = Ni, Pd, or Pt) confirm that the cations have the trigonal-bipyramidal structure **1**. The slow passage absorption spectra of [NiCl(QP)]Cl and [PdCl(QP)]Cl are typical examples of AX_3 magnetic systems and contain a low-field peak, assigned to the central phosphorus atom, L′, and a high-field peak, of about three times the intensity, assigned to the three terminal phosphorus atoms, L, in structure **1**. In addition, the central phosphorus resonance of [NiCl(QP)]Cl is split into a quartet and the terminal phosphorus resonance into a doublet, with $|{}^2J({}^{31}P-{}^{31}P)| = 40 \pm 5$ Hz. Coupling between the central and equatorial phosphorus atoms of [PdCl(QP)]Cl is not resolved; the half-height line width of the high-field peak is 20 Hz.

The spectrum of [PtCl(QP)]Cl has been interpreted in terms of a 66.3% AX_3 + 33.7% AMX_3 system (^{195}Pt has natural abundance 33.7% and nuclear spin quantum number $I = {}^1/_2$). The complex [PtCl(QP)]Cl was insufficiently soluble in dichloromethane for $|{}^1J({}^{195}Pt-{}^{31}P_c)|$ to be observed but $|{}^1J({}^{195}Pt-{}^{31}P_t)|$ was found to be 2590 ± 10 Hz. Subscripts "c" and "t" refer to central and terminal phosphorus atoms, respectively. As with [PdCl(QP)]Cl, splitting of the high-field peak was not observed, even under slow passage absorption conditions (see Table IV).

The spectra of [NiCl(ASTP)]Cl and [NiCl(SBTP)]Cl both show only a single peak of chemical shift close to δ_t of [NiCl(QP)]Cl, as expected for the trigonal-bipyramidal structure, **1**, assigned to the complexes. The spectrum of [NiCl(PTAS)]Cl showed a single peak of shift close to δ_c for [NiCl(QP)]Cl, in agreement with the trigonal-bipyramidal coordination suggested by its visible and ultraviolet spectrum.

The visible and uv spectra of the new five-coordinate complexes (see Table II) are similar to that of [NiCl(QP)][BPh_4] discussed by Norgett, *et al.*[19,20]

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Table IV. ^{31}P Chemical Shifts, δ, of the Five-Coordinate Complexes, with Respect to External P_4O_6[a]

Complex	δ_c, ppm	δ_t, ppm
[NiCl(QP)]Cl	−2.9[b]	+78.3[c]
[PdCl(QP)]Cl	−1.3[d]	+78.3[c]
[PtCl(QP)]Cl	+21.0[d]	+87.2[d]
[NiCl(ASTP)]Cl	...	+75.7[c]
[NiCl(SBTP)]Cl	...	+78.0[c]
[NiCl(PTAS)]Cl	−5.7[d]	...

[a] Subscripts "c" and "t" refer to shifts of central and terminal phosphorus atoms, respectively, of the ligands. [b] ±0.4 ppm. [c] ±0.1 ppm. [d] ±0.2 ppm.

Table V. ^{31}P Chemical Shifts, δ, of the Six-Coordinate Complexes, with Respect to External P_4O_6[a]

Complex	δ_c, ppm	δ_t, ppm
$[RuCl_2(QP)]$	−10.1 (1)	+45.0 (1); +66.6 (2)
$[RuCl_2(ASTP)]$	...	+40.1 (1); +61.6 (2)
$[RuCl_2(PTAS)]$	−19.0	... ...
$[Fe(NCS)_2(QP)]$	−24.4 (1)	+34.5 (1); +48.8 (2)
$[RhCl_2(QP)]Cl$[b]	+1.9[c] (1)	+59.4[c] (1); +72.2[d] (2)
$[IrHCl(QP)][BPh_4]$[e]	+37.4[f] (1)	+93.7[c] (2); +105.1[g] (1)
$[Cr(CO)_3(QP)]$	−4.2 (1)	+26.3[c] (1); +31.0[c] (1); +127.8[c] (1)
$[Cr(CO)_3(TP)]$	+2.3 (1)	+28.5 (2)
$[W(CO)_3(QP)]$	+37.9 (1)	+63.5 (1); +70.2 (1); +128.5 (1)

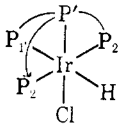
[a] Subscripts "c" and "t" refer to shifts of central and terminal phosphorus atoms, respectively, of the ligands. Chemical shifts are accurate to ±0.5 ppm (unless indicated otherwise), and figures in brackets after these values denote approximate relative peak intensities. [b] Each of the signals is a doublet with $|^1J(^{103}Rh-^{31}P)| = 95$, 115, and 80 ± 5 Hz for the peaks at +1.9, 59.4, and 72.2 ppm, respectively. [c] ±0.2 ppm. [d] ±0.3 ppm. [e] Hydride signal at τ 18.8 ± 0.1 ppm; $|^2J(^{31}P-^1H)| = 130 \pm 5$ Hz. [f] ±0.4 ppm. [g] Doublet with $|^2J(^{31}P-^1H)| = 150 \pm 20$ Hz.

Six-Coordinate Complexes. Because of insufficient solubility, the six-coordinate complexes were all studied under intermediate or rapid passage dispersion mode, which precluded resolution of any $^{31}P-^{31}P$ coupling *via* the metal.

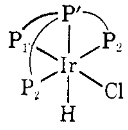
The six-coordinate complexes of the potentially quadridentate ligands, with all four donor atoms bonded to the metal, have the pseudo-octahedral structure 2. If the complexed ligand is QP, an AMX_2 ^{31}P nmr spectrum is expected. The spectrum of $[RuCl_2(QP)]$ is consistent with such a stereochemistry and shows three main peaks of approximate relative intensities 1:1:2. One of the low-intensity peaks is at much lower field than the other two peaks (see Table V). The chemical shift of this peak is relatively near to the shift of the single peak found in the spectrum of $[RuCl_2(PTAS)]$, which contains one central phosphorus atom. On the other hand, $[RuCl_2(ASTP)]$, with three terminal phosphorus atoms, has a spectrum containing two peaks of approximate intensity ratio 1:2, with chemical shifts close to those of the two upfield peaks in the spectrum of $[RuCl_2(QP)]$. Consequently, the lowest field peak in the $[RuCl_2(QP)]$ spectrum has been assigned to the central atom, L′, and the other low-intensity peak at higher field has been assigned to the terminal phosphorus atom, L_1, in 2.

The spectra of $[Fe(NCS)_2(QP)]$ and $[RhCl_2(QP)]Cl$ also contain three main signals of approximate relative intensities 1:1:2; the low-field peak in each spectrum has been assigned to the phosphorus atom, L′, by comparison with $[RuCl_2(QP)]$. Each of the signals for the rhodium complex is split into a doublet because of spin–spin coupling between ^{31}P and ^{103}Rh (100% natural abundance and spin $I = {}^1/_2$). The coupling constant $|^1J(^{103}Rh-^{31}P)|$ is least for mutually *trans*-phosphorus atoms.[21]

An interesting example of the use of the above assignments concerns the stereochemistry of $[IrHCl(QP)][BPh_4]$, which could have one of two possible structures



3a



3b

The hydride can be *trans* either to phosphorus P_1 or to P′. The proton magnetic resonance spectrum in the transition metal hydride region shows a weak doublet, due to coupling of the hydride with a *trans*-phosphorus atom[22,23] ($|^2J(^{31}P_{trans}-^1H)| = 130 \pm 5$ Hz), with fine structure due to coupling of the hydride with *cis*-phosphorus atoms. The ^{31}P nmr spectrum of $[IrHCl(QP)][BPh_4]$ is shown in Figure 1 and consists of three main peaks of approximate intensity ratio 1:2:1; the high-field peak is a doublet consistent with coupling of phosphorus to a *trans*-hydride. The coupling con-

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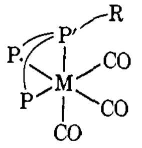
(23) A. P. Ginsberg, *Transition Metal Chem.*, 1, 112 (1965).

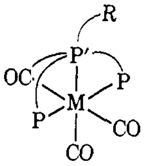
stant ($|{}^2J({}^{31}P_{trans}-{}^1H)| = 150 \pm 20$ Hz) cannot be obtained very accurately from the intermediate passage dispersion spectrum but it agrees, within experimental error, with the value obtained from the proton spectrum. Coupling of the hydride with *cis*-phosphorus nuclei cannot be resolved in the phosphorus spectrum.

By comparison with [RuCl$_2$(QP)], the low-field peak in Figure 1 has been assigned to phosphorus P′. If [IrHCl(QP)][BPh$_4$] had the structure shown in **3b**, this signal should be split into a doublet. The observed ^{31}P nmr spectrum is consistent with the hydride being *trans* to the phosphorus atom P$_1$ and the complex having the structure shown in **3a**.

Six-coordinate complexes are known in which the potentially quadridentate ligand QP is believed to act as a terdentate ligand.[5] Examples are the pseudo-octahedral complexes [M(CO)$_3$(QP)] (M = Cr or W), which could exist as the facial (*fac*) or mèridional (*mer*) isomers (**4**, R = *o*-Ph$_2$PC$_6$H$_5$) in solution. The phosphorus-31 nmr spectra of [M(CO)$_3$(QP)] contain four peaks each with approximate relative intensity 1:1:1:1 (Table V). The peaks at *ca.* +128 ppm are in the region associated with the free ligand signals and, in fact, are very close to the shifts of the phosphorus atoms of QP (see Table III). These signals, therefore, have been assigned to resonances of uncoordinated phosphorus atoms. By comparison with the octahedral complexes discussed above, the lowest field peak in each spectrum has been assigned to the central phosphorus atom, P′. The tungsten complex was insufficiently soluble for coupling between coordinated phosphorus atoms and ^{183}W (14.3% natural abundance, $I = {}^1/_2$) to be discerned.



4a



4b

R = *o*-Ph$_2$PC$_6$H$_5$ or Ph

The observation that the other two terminal phosphorus atoms in each compound are not magnetically equivalent could result from (a) a difference in stereochemical environment due to the presence of the bulky substituent *o*-Ph$_2$PC$_6$H$_5$ or (b) the presence of an isomeric mixture of **4a** and **4b**. If the latter were correct, one would conclude from the relative intensities of the two peaks under discussion that an approximately equimolecular mixture of the two isomers was present in each solution. Hypothesis a is more probable for the following reasons: (1) there is only one peak assignable to the central phosphorus atom in each compound (this atom should have a different chemical shift in **4a** and **4b**); (2) it is an unlikely coincidence that in both solutions of chromium and tungsten complexes there should be an equimolecular, isomeric mixture; (3) there are present only two resonances, of approximate relative intensities 1:2, in the spectrum of [Cr(CO)$_3$(TP)] (**4a** or **4b**, R = Ph), as might be expected when the *o*-Ph$_2$PC$_6$H$_5$ substituent is replaced by the smaller phenyl group.

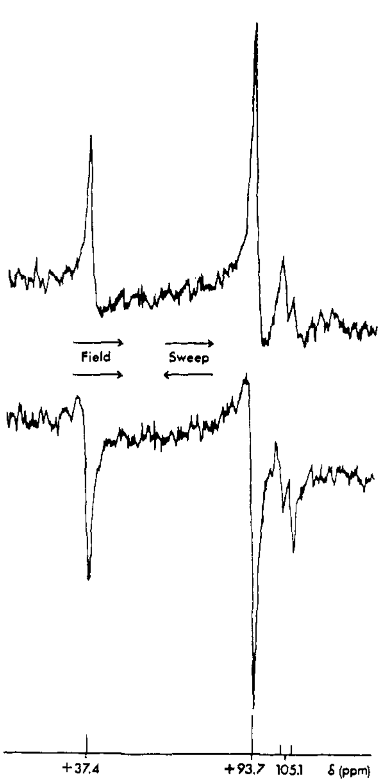


Figure 1. The ^{31}P nmr spectrum of [IrHCl(QP)][BPh$_4$]; intermediate passage dispersion mode.

Grim and Ference[21] used ^{31}P nmr to confirm the *mer* structure of some complexes [RhCl$_3$(R$_3$P)$_3$]. When the three coordinated phosphorus atoms are part of the multidentate ligands QP and TP, the resultant low symmetry of the complexes prevents elucidation of structures on the basis of nmr measurements.

The positions of the two peaks in the spectrum of [Cr(CO)$_3$(TP)] (Table V) confirm the assignment of the high-field peak in the spectrum of [Cr(CO)$_3$(QP)] to an uncoordinated phosphorus atom. Thus, phosphorus-31 nmr can be used to determine whether all of the phosphorus atoms of a phosphorus-containing multidentate ligand are actually bonded to the central metal atom. The possibility of rapid exchange between complexed and noncomplexed environments could be detected by low-temperature measurements.

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