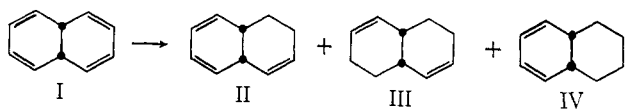


II showed the following signals in the nmr: δ 5.63 (6 H), 3.00 (1 H), 2.34 (1 H), 1.90 (2 H), and 1.58 (2 H) ppm. Among many peaks in the infrared the following are mentioned: 3050 (m), 3025 (s), 3015 (s), 1650 (w), 1575 (w), 1492–1480 (doublet, m), 1075 (m), and 1050 (m) cm^{-1} . The ultraviolet spectrum revealed λ_{max} 262 $\text{m}\mu$ (ϵ 4.38×10^3 ; pentane) with a shoulder at 269.5 $\text{m}\mu$ (ϵ 4.21×10^3). The parent mass was 132.² On catalytic hydrogenation II, as well as III and IV, gave only *cis*-decahydronaphthalene and may be assigned the structure *cis*-1,2,9,10-tetrahydronaphthalene.



III showed no absorption in the ultraviolet and an nmr spectrum consisting of signals at δ 5.53 (4 H, multiplet), 2.70 (2 H), 1.87 (4 H), and 1.64 (4 H) ppm. The infrared showed characteristic absorptions at 3015 (s), 1650 (w), 1450–1430 (doublet, m), 1050 (m), and 970 (m) cm^{-1} . The parent mass was at m/e 134. III is accordingly assigned the structure *cis*-1,2,5,6,9,10-hexahydronaphthalene.

The structure of IV (m/e 134; λ_{max} 264 $\text{m}\mu$ (ethanol); infrared absorption at 1650 cm^{-1}) is tentatively believed to be *cis*-5,6,7,8,9,10-hexahydronaphthalene. It is concluded from the relative quantities of the three products that the cyclohexadiene type of double bond undergoes 1,2-hydrogenation more readily than does the isolated cyclohexene type.

When I (110 mg) was heated with cyclohexene (740 mg) for 20 hr at 95°, cyclohexane (41 mg) was obtained in 57% of theory. The simultaneous formation of naphthalene, II, III, and IV points to an effective competition between I and cyclohexene as hydrogen acceptors. Determination of competition factors will be undertaken.

To determine the stereochemistry of the hydrogenation, the reaction of I (100 mg) with 1,2-dimethylcyclohexene³ (1.70 g) was effected at 150° for 48 hr. The resulting 1,2-dimethylcyclohexane, obtained in low yield (5.6 mg; 6.6%), was entirely the *cis* isomer (identified by infrared⁴) and was unaccompanied by *trans* isomer.

The analogy between this hydrogen transfer and that of diimide is particularly strong since both reactions appear to be stereospecifically *cis* hydrogenations.⁵ We have incidentally also reduced 1,2-dimethylcyclohexene with diimide and find only *cis*-1,2-dimethylcyclohexane.

As the driving force in the hydrogenation by diimide is very probably associated with the contribution of the heat of formation of nitrogen to the transition state,⁵ so the driving force in the transfer of hydrogen from *cis*-9,10-dihydronaphthalene may be dependent on the unique possibility of contributing a part of the full resonance energy of naphthalene (61 kcal/mole)⁶ to the transition state. This speculation would be considerably strengthened by further evidence in support of a

(2) We wish to thank D. J. Friedland, Yale University, for measurements of mass spectra.

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(5) E. J. Corey, D. J. Pasto, and W. L. Mock, *J. Am. Chem. Soc.*, **83**, 2957 (1961).

(6) J. L. Franklin, *ibid.*, **72**, 4278 (1950).

concerted transfer. At the moment only the *cis* stereospecificity points to this type of mechanism.

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Phosphorus-31 Chemical Shifts of Isostructural and Isoelectronic Trialkyl Phosphite Metal Complexes¹

Sir:

Recently it was established for the ligands $\text{P}(\text{OCH}_3)_3$, $\text{P}(\text{OCH}_2)_3\text{CR}$ (where $\text{R} = \text{C}_2\text{H}_5$ or *n*- C_3H_7), and $\text{P}(\text{OCH})_3(\text{CH}_2)_3$ ² that the series of complexes shown in Table I parallel one another in stoichiometry as well as in spectral and magnetic properties.^{3,4} Furthermore,

Table I. P^{31} Chemical Shifts of Trialkyl Phosphite (L) Complexes with Respect to 85% H_3PO_4 as External Standard

Compound	$\text{P}(\text{OCH}_3)_3$	$\text{P}(\text{OCH}_2)_3\text{CR}^a$	$\text{P}(\text{OCH})_3(\text{CH}_2)_3$
L	-141 ^b	-92 ^c (R = C_2H_5) -93 ^c (R = <i>n</i> - C_3H_7)	-137 ^d
$[\text{NiL}_5][\text{ClO}_4]_2$	-110 ^e	-108 ^f	-125 ^g
$[\text{AgL}_4][\text{ClO}_4]$	-132 ^e		
$[\text{AgL}_4][\text{NO}_3]$		-99 ^f	-134 ^d
$[\text{CuL}_4][\text{ClO}_4]$	-125 ^{e,h}
$[\text{CoL}_5][\text{ClO}_4]$		-138 ^f	-157 ^f
$[\text{CoL}_5][\text{NO}_3]$	-147 ^a		
$[\text{NiL}_4]$	-163 ⁱ	-128 ^k	-153 ^e

^a R = C_2H_5 in all cases except $[\text{CoL}_5][\text{ClO}_4]$ and $[\text{NiL}_4]$ where R = *n*- C_3H_7 . ^b Neat. ^c CH_3CN . ^d Dimethyl sulfoxide. ^e Acetone. ^f CH_2Cl_2 . ^g Dimethylformamide. ^h The P^{31} absorption was reported to consist of two overlapping four-line patterns due to $\text{Cu}^{63}\text{-P}^{31}$ and $\text{Cu}^{65}\text{-P}^{31}$ spin-spin coupling: R. W. King, T. J. Huttemann, and J. G. Verkade, *Chem. Commun.*, 561 (1965). Although only six of the eight lines were observed, we have since achieved sufficient resolution in the spectrum of the nitrate salt in acetone to identify all eight lines. ⁱ Insolubility prevented observation of the P^{31} signal. ^j C_6H_6 . ^k CHCl_3 .

the Dq values for these ligands in the $[\text{CoL}_6]^{+3}$ cation are similar.³ In view of the small differences in ligand properties of these phosphites, it was thought not unreasonable to expect parallels in any trends observed in the P^{31} chemical shifts of their complexes. We show here that correlation of metal oxidation states with the P^{31} resonances for the complexes is shown to be valid only for systems which are both isoelectronic and isostructural.

P^{31} chemical shifts for the $[\text{NiL}_5]^{+2}$, $[\text{CoL}_5]^{+3}$, and $[\text{CuL}_4]^{+2}$ complexes of all three phosphite ligands as well as those for the $[\text{NiL}_4]$ complexes of $\text{P}(\text{OCH}_2)_3\text{CR}$

(1) We thank the National Science Foundation for generous support of this work.

(2) 2,8,9-Trioxa-1-phosphaadamantane.

(3) K. J. Coskran, T. J. Huttemann, and J. G. Verkade, *Advances in Chemistry Series*, No. 62, American Chemical Society, Washington, D. C., 1967, p 590.

(4) D. G. Hendrick, R. E. McCarley, R. W. King, and J. G. Verkade, *Inorg. Chem.*, **5**, 639 (1966).

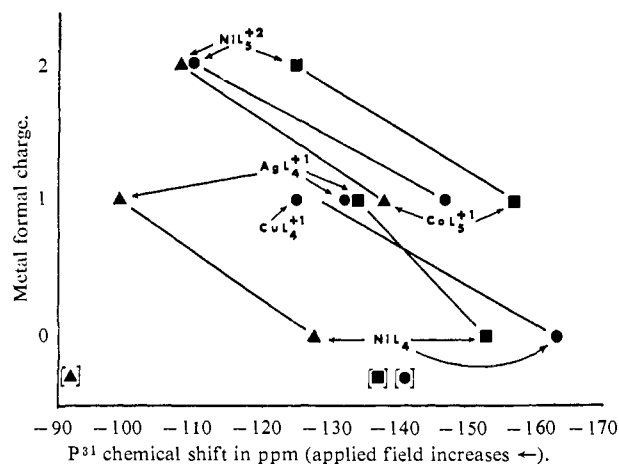


Figure 1. Plot of P^{31} chemical shift of complexes of $P(OCH_2)_3CR$ (▲), $P(OCH)_3(CH_2)_3$ (■), and $P(OCH_3)_3$ (●) against charge on the metal. The points in brackets represent the chemical shifts of the free ligands.

and $P(OCH)_3(CH_2)_3$ were not altered by the presence of excess ligand. In addition, the normal P^{31} chemical shifts of the uncomplexed phosphites were observed in solutions of the metal complexes and excess ligand. Thus chemical shift effects due to dissociation of the complexes and intermolecular ligand exchange could be considered negligible. Intramolecular ligand exchange, however, is not ruled out in any of the complexes since even the $[NiL_5]^+$ and $[CoL_5]^+$ systems exhibit only a single P^{31} resonance at room temperature in spite of the two chemically different coordination sites on a trigonal bipyramid.⁵

The P^{31} resonance of $[Ni(P(OCH_3)_3)_4]$ in acetone moved upfield from -162 ppm toward the ligand absorption upon addition of trimethyl phosphite. In spite of this indication of exchange, it is felt that -162 ppm is representative of the P^{31} resonance of undissociated $[Ni(P(OCH_3)_3)_4]$. Careful molecular weight studies in benzene at room temperature⁶ (in which solvent the P^{31} shift at -163 ppm was nearly the same) revealed no evidence of dissociation. For all the $[AgL_4]^+$ complexes the P^{31} resonances were observed to shift toward that of free ligand upon adding phosphite, and only resonances representative of a weighted average of the two components were observed in these solutions. Although dissociation to another species cannot be ruled out in these three cases, it will be assumed small for the purposes of this discussion. Therefore the P^{31} chemical shifts in the absence of excess ligand will be accepted as representative of undissociated $[AgL_4]^+$. Some justification for this assumption appears in the discussion which follows.

For the P^{31} shifts of several metal complexes of $P(OCH_3)_3$ and $P(OC_2H_5)_3$, Shupack and Wagner⁷ recently postulated that (1) the increasing upfield shift with respect to free ligand could be interpreted in terms of increased shielding of phosphorus by electron drift

(5) $[Ni(P(OCH)_3(CH_2)_3)_5](ClO_4)_2$ has been shown to be trigonal bipyramidal from an X-ray diffraction study: E. Riedel, J. G. Verkade, and R. A. Jacobson, submitted for publication. Arguments for the plausibility of the isostructural character of the $[CoL_5]^+$ and $[NiL_5]^+$ complexes appear in ref 3.

(6) D. G. Hendricker, R. E. McCarty, and J. G. Verkade, to be published.

(7) S. Shupack and B. Wagner, *Chem. Commun.*, 547 (1966).

from the alkoxy oxygens as the metal charge increased; (2) the downfield shift with respect to free ligand of zerovalent nickel complexes arose from the dominance of a temperature-independent paramagnetic contribution from $d_{\pi}-d_{\pi}$ back-bonding from the metal, the paramagnetic term becoming dominant in the absence of a metal charge. On the basis of our results we wish to point out several serious limitations on the above postulates in attempting to extend them to complexes of polycyclic phosphites or even other complexes of $P(OCH_3)_3$. (a) On the basis of postulate 1, the P^{31} shift for $[Co(P(OCH_3)_3)_5]NO_3$ would be expected at higher field than the free ligand rather than at lower field. It seems unlikely that $d_{\pi}-d_{\pi}$ bonding effects (postulate 2) would dominate the effect of a positive metal charge. (b) On the basis of postulate 1, it is unexpected that without exception all P^{31} shifts for complexes of $P(OCH_2)_3CR$ are found downfield from that of the free ligand. Not even a formally divalent metal charge seems capable of producing a net upfield shift. (c) The P^{31} shifts for $[AgL_4]ClO_4$ and $[NiL_5](ClO_4)_2$ (where $L = P(OCH_2)_3CR$) are reversed according to postulate 1. (d) Similarly, the P^{31} shifts for $[NiL_4]$ and $[CoL_5]NO_3$ (where $L = P(OCH_2)_3CR$) are reversed. (e) Contrary to postulate 1, the P^{31} resonance of $[CoL_5]^+$ moves downfield with respect to that of the free ligand $P(OCH)_3(CH_2)_3$.

A comparison of the free-ligand P^{31} resonances with those of their respective complexes in Figure 1 reveals that no apparent correlation exists between them. Evidently the changes in the phosphorus environments on coordination of these ligands are not constant nor do they act in the same direction.

From the positions of the points in Figure 1 of the trimethyl phosphite complexes (excluding that of our $[CoL_5]^+$ complex), it can be seen how an increasing metal charge might have been interpreted by Shupack and Wagner⁷ to correspond with a downfield movement of the P^{31} resonance. Although inclusion of the point for $[CoL_5]^+$ extends the range of P^{31} absorptions expected for monovalent complexes of $L = P(OCH_3)_3$, it does not destroy the trend. Clearly, however, the trend is broken for the pairs of slopes⁸ for the complexes of the polycyclic phosphites because of their larger separations. It is thus apparent that comparisons of P^{31} resonances for variously charged complexes can more meaningfully be made in isoelectronic-isostructural systems. In such complexes, all other variations which influence P^{31} shifts (e.g., changes in hybridization on phosphorus from one complex to another, ligand-ligand interactions, and magnetic anisotropies) are minimized. Thus for $L = P(OCH_3)_3$, $[CuL_4]^+$ and $[AgL_4]^+$ are seen to have similar chemical shifts,⁹ whereas that of $[NiL_4]$ appears further downfield. The same can be said for $[AgL_4]^+$ and $[NiL_4]$ where the ligand is $P(OCH_2)_3CR$ or $P(OCH)_3(CH_2)_3$. Similarly, the P^{31}

(8) Although the relationship between the P^{31} shift and metal charge in these systems is probably not linear, the lack of more than two points per isoelectronic-isostructural system allowed only the connection of these points by a line.

(9) The lack of dissociation of $[Cu(P(OCH_3)_3)_4]^+$ coupled with the reasonable assertion that its P^{31} resonance should be close to that of the undissociated silver(I) analog are the bases for the assumption that the P^{31} resonance observed for the silver(I) complex (which lies within 7 ppm of that of the copper(I) complex) is representative of at least nearly undissociated $[Ag(P(OCH_3)_3)_4]^+$. The same was assumed to be true of the $[AgL_4]^+$ complexes of the polycyclic phosphites.

shift of $[\text{NiL}_5]^{+2}$ is upfield of that of $[\text{CoL}_5]^+$ for each of the three ligands.

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Ligand Lability in Platinum(II) Complexes

Sir:

Ethylene-ethylene exchange in Zeise's salt, $\text{K}(\text{C}_2\text{H}_4\text{-PtCl}_3)$, has been shown¹ to occur in solution at temperatures as low as -75° . We wish to report that our nmr

ence in the magnitude of the *cis*- and *trans*-2-butene couplings is taken as further evidence of the steric effect of twisting the methyl groups away from, and the hydrogen atoms toward, the platinum atom in the *cis*-2-butene complexes.^{3,4} The olefinic hydrogen-platinum coupling in **1** is largest with all three olefins when $\text{Z} = \text{CN}$. These complexes are also the most labile and exhibit line broadening in the olefinic region. The chemical shift values (Table II) of the olefinic protons are in accord with those published earlier for a similar series.⁵

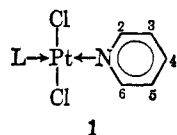
Our results indicate that in deuteriochloroform at room temperature the olefinic moieties of the pure complexes, **1**, are sufficiently strongly bonded to the metal to observe olefin-platinum coupling on the nmr

Table I. Coupling Constants^a in Some 1,3-Dichloro-2-olefin-4-(4-Z-pyridine)platinum(II) Complexes (**1**)

Z	$(\text{H}_a')_2\text{C}=\text{C}(\text{H}_a')_2$		$\text{I}^b =$			
	$J_{\text{Pt-H}_b}$	$J_{\text{Pt-H}_a}$	<i>trans</i> - $\text{H}_a'(\text{CH}_3)\text{C}=\text{C}(\text{CH}_3)\text{H}_a'$		<i>cis</i> - $\text{H}_a'(\text{CH}_3)\text{C}=\text{C}(\text{CH}_3)\text{H}_a'$	
			$J_{\text{Pt-H}_b}$	$J_{\text{Pt-H}_a}$	$J_{\text{Pt-H}_b}$	$J_{\text{Pt-H}_a}$
CH ₃	32.0 (3°)	60.5	32.8	60.3	33.5	68.1
H	36.0 (-14.5°)	60.5	33.6	62.4	34.5	69.0
COOCH ₃	36.0 (-14.5°)	61.7	33.4 (-24°)	62.3	34.6 (15°)	69.0
CN	36.5 (-51°)	62.6	34.0 (-25°)	63.2	34.0 (3°)	70.4

^a Most of the coupling constants between platinum and the pyridine protons were measured at lower than ambient (29–35°) temperatures; when this was the case, the temperature is indicated in parentheses. The constants are in cycles per second. The internal reference is CHCl_3 ; the external is tetramethylsilane. All spectra were taken in CDCl_3 . ^b All the ethylene and *cis*-2-butene complexes are known. The *trans*-2-butene complexes are new; all gave satisfactory analyses.

studies of the deuteriochloroform solutions of the complexes **1** (L = ethylene, *cis*- or *trans*-2-butene) show that



even in the absence of any excess ligand, the pyridine as well as the olefin readily depart from the coordination sphere of platinum. Although platinum-hydrogen coupling occurs between the metal and the 2,6 protons of pyridine as well as between the metal and olefinic protons, both couplings are sensitive to temperature and to the electronic character of the olefin and the pyridine.

Table I shows that when ethylene is coordinated to platinum no platinum-pyridine coupling occurs at room temperature; the maximum temperature at which such coupling is observed is 3°. Replacing ethylene by 2-butene stabilizes pyridine, since coupling is now observed at considerably higher temperatures.

The effect of the basicity of the pyridine is reflected in the temperature dependence of the coupling: the weaker the pyridine base, the more labile its complex with the metal. Thus it is necessary to cool the 4-cyanopyridine complex **1** (L = C_2H_4) to -50° before coupling is observed.

The magnitude of the olefinic-platinum coupling is in the range expected when the *trans* ligand is a relatively strong electron donor.² The rather large differ-

Table II. Chemical Shifts in the 1,3-Dichloro-2-olefin-4-(4-Z-pyridine)platinum(II) Complexes

Ligand	Z	Olefinic chemical shifts, ppm ^a		Aromatic chemical shifts, ppm		
		CH ₃	H _{a'}	H _a	H _b	
<i>cis</i> -2-Butene	OCH ₃	1.77	5.60	6.88	8.67	
	H	1.78	5.66	7.42	8.83	7.84 ^b
	CN	1.81	5.76	7.72	9.19 ^c	
<i>trans</i> -2-Butene	OCH ₃	1.82	5.39	7.67	8.63	
	H	1.81	5.44	7.37	8.79	7.82 ^b
	CN	1.89	5.58	7.73	9.15	

^a All spectra were run at 100 Mc in DCCl_3 using CHCl_3 as the internal reference. The temperature was the ambient temperature of the machine, $\sim 34^\circ$. ^b This is the value for the proton in the 4 position. ^c Since the complexed 4-cyanopyridine is not coupled with the metal at ambient temperature, the chemical shifts of the aromatic protons represent either the time-averaged values due to exchange or a loosely coordinated pyridine. At -49° , H_a has shifted to 7.77 ppm and H_b to 9.06 ppm.

time scale. On the other hand, the pyridine moieties are not strongly bonded to the metal at room temperature and are not coordinated to the metal in the conventional sense. Such behavior is consistent with the well-known large *trans*-labilizing effect of olefins in square-planar complexes.⁶ The nmr data are characteristic of a classical exchange mechanism. In the present case,

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