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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Metal–Phosphorus Stretching Frequencies of Some Tetrakis(bicyclic phosphite) Complexes of Nickel(0), Palladium(0), Platinum(0), Copper(I), and Silver(I)

BY RICHARD L. KEITER AND J. G. VERKADE

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A recently reported far-infrared investigation of tetrakis(triethyl phosphite)metal complexes wherein M = Ni, Pd, and Pt[1] prompts us to describe the results we have obtained with the bicyclic phosphite species $(CH_3C(CH_2O)_3P)_4M$ and $((CH_2)_3(CHO)_3P)_4M$ in which M = Ni, Pd, Pt, Cu^+, and Ag^+. Three bands were assigned by Myers, Basolo, and Nakamoto to M–P stretching modes for each of the triethyl phosphite complexes. The two bands in the 340–290-cm^{-1} region were assigned to the M–P stretching frequency of the split F_2 species and one band at 220–190 cm^{-1} was ascribed to the A_1 mode. The splitting of the F_2 species and the appearance of the unallowed A_1 were attributed to deviation of the complexes from T_d symmetry. Inasmuch as the bicyclic phosphites $CH_3C(CH_2O)_3P$ and $(CH_2)_3(CHO)_3P$ are constrained and therefore highly symmetrical, spectra of these complexes are expected to be somewhat simpler and thus more amenable to interpretation. Recently we assigned the M–P stretching frequency in $(CH_3C(CH_2O)_3P)_4Ni$ at 157 cm^{-1},[2] and since this value is significantly lower than those reported by Myers, *et al.*, for the triethyl phosphite analog,[1] a broader far-infrared study is presented here.

Experimental Section

Reagents.—The ligands $CH_3C(CH_2O)_3P$ and $(CH_2)_3(CHO)_3P$ have been described previously.[3] Triethyl phosphite was purchased from J. T. Baker Chemical Co. and used without further purification. The copper(I) and silver(I) bicyclic phosphite complexes were prepared following the method reported earlier.[4] Although we previously reported a preparation of the tetrakis(bicyclic phosphite)nickel(0) complexes involving the displacement of CO from $Ni(CO)_4$ by the appropriate bicyclic phosphite,[5,6] it was found more convenient to synthesize them in the manner described by Vinal and Reynolds.[7] The yields with both bicyclic phosphites were nearly quantitative.

Anal. Calcd for $C_{20}H_{36}O_{12}P_4Ni$: C, 36.87; H, 5.57; P, 19.02. Found: C, 37.15; H, 5.60; P, 18.91. Calcd for $C_{24}H_{36}O_{12}P_4Ni$: C, 41.23; H, 5.19; P, 17.72. Found: C, 40.91; H, 5.38; P, 17.51.

$(CH_3C(CH_2O)_3P)_4M$ and $((CH_2)_3(CHO)_3P)_4M$ (M = Pd or Pt).—The starting materials for these complexes were $((C_6H_5)_3P)_4Pd$ and its platinum analog which were prepared by the method reported by Malatesta and Cariello.[8] The colorless bicyclic phosphite complexes were precipitated in nearly quantitative yields by dissolving 40 mmol of the appropriate phosphite in 75 ml of ethanol in which was suspended 8 mmol of the appropriate starting complex. Completion of the heterogeneous reaction was signaled by conversion of the yellow starting complex to the colorless product after stirring for several hours at room temperature. Filtration and washing of the products with ethanol yielded complexes of sufficient purity for this study. The near-infrared spectra were found to be devoid of phenyl proton vibrations which suggested that complete substitution of the triphenylphosphine ligands had taken place. The palladium complex of $CH_3C(CH_2O)_3P$ was also prepared following the method which Vinal and Reynolds[7] described for $((C_2H_5O)_3P)_4Ni$ to provide additional assurance that none of the assigned bands in the far-infrared region could be associated with undisplaced triphenylphosphine. The platinum and nickel complexes appear to be quite stable in air while the palladium compounds show evidence of air oxidation within several hours.

Anal. Calcd for $C_{20}H_{36}O_{12}P_4Pd$: C, 34.37; H, 5.19; P, 17.72. Found: C, 34.15; H, 5.10; P, 17.50. Calcd for $C_{20}H_{36}O_{12}P_4Pt$: C, 30.50; H, 4.60; P, 15.73. Found: C, 30.29; H, 4.71; P, 15.49. Calcd for $C_{24}H_{36}O_{12}P_4Pd$: C, 38.74; H, 4.85; P, 16.58. Found: C, 36.68; H, 4.90; P, 16.35. Calcd for $C_{24}H_{36}O_{12}P_4Pt$: C, 34.50; H, 4.34; P, 14.82. Found: C, 34.43; H, 4.26; P, 14.60.

Spectra.—Proton nmr spectra were obtained on a Varian A-60 spectrometer on saturated benzene solutions in which the complexes were slightly soluble. Tetramethylsilane was used as an internal standard. Integration of all three spectra gave the expected 2:1 ratio for the CH_2 to CH_3 proton absorptions which appeared, respectively, at 4.00 and 0.45 ppm in the nickel, 3.82 and 0.27 ppm in the palladium, and 4.02 and 0.40 ppm in the platinum complex. The CH_3 proton peak was sharp while the CH_2 band was broader with several unresolved shoulders. The proton spectrum of $((CH_2)_3(CHO)_3P)_4Ni$ showed broad doublets for H_{ax} (1.74 ppm), H_{eq} (2.84 ppm), with $^2J_{HH} = 12.9$ Hz, and a broad single resonance for H_{CH} (4.37 ppm). A similar spectrum was exhibited by the platinum analog wherein these parameters were 1.75 ppm, 2.70 ppm, 12.2 Hz, and 4.70 ppm, respectively, while the palladium compound decomposed in benzene solution.

Far-infrared spectra were obtained with a Beckman Model 11 grating spectrometer. The $CH_3C(CH_2O)_3P$ and $(CH_2)_3(CHO)_3P$ complexes were too insoluble for recording spectra in solution and so Nujol mulls were placed between two polyethylene plates each 1 mm in thickness which were sparated from one another by a gasket constructed from a third plate of equal thickness. All palladium complexes were mulled in a nitrogen-filled glove bag. Twenty per cent benzene solutions of $(C_2H_5O)_3P$ were measured in 1-mm polyethylene cells while spectra of $CH_3C(CH_2O)_3P$ and $(CH_2)_3(CHO)_3P$ were recorded in fused polyethylene. The spectra in the region studied are shown in Figures 1–3.

Results and Discussion

The ligand $CH_3C(CH_2O)_3P$ gives rise to a reasonably

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(1) V. G. Myers, F. Basolo, and K. Nakamoto, *Inorg. Chem.*, **8**, 1204 (1969).

(2) A. C. Vandenbroucke, D. G. Hendricker, R. E. McCarley, and J. G. Verkade, *ibid.*, **7**, 1825 (1968).

(3) J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *ibid.*, **4**, 83 (1965).

(4) J. G. Verkade and T. S. Piper, *ibid.*, **1**, 453 (1962).

(5) J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *ibid.*, **4**, 228 (1965).

(6) D. G. Hendricker, R. E. McCarley, R. W. King, and J. G. Verkade, *ibid.*, **5**, 639 (1966).

(7) R. S. Vinal and L. T. Reynolds, *ibid.*, **3**, 1062 (1964).

(8) L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958); *J. Inorg. Nucl. Chem.*, **8**, 561 (1958).

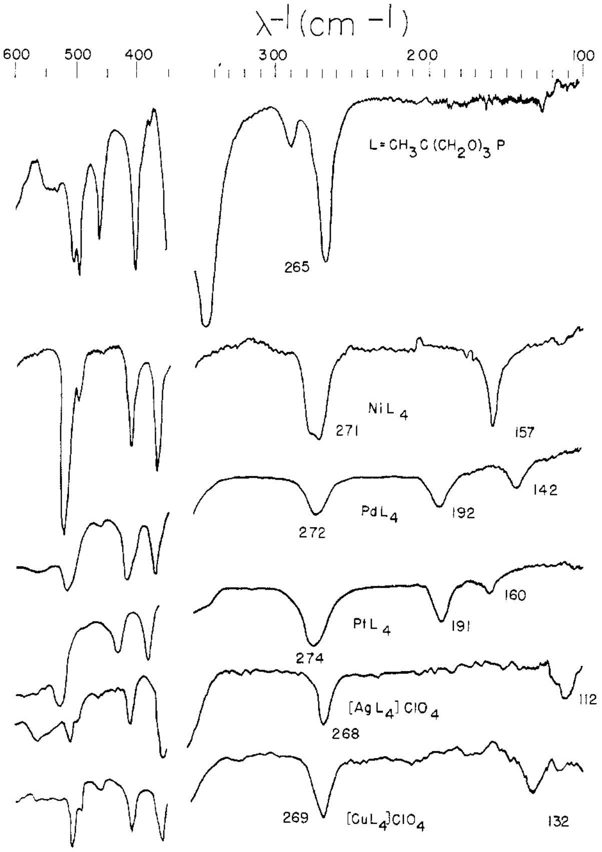

Figure 1.—Infrared spectra of $CH_3C(CH_2O)_3P$ (fused polyethylene disk) and its complexes (Nujol mulls).

sharp band at 265 cm^{-1} with no other significant absorptions being observed down to 70 cm^{-1} [2] (Figure 1). It should be noted that each of the three complexes of this ligand also exhibits a band in this region at 274, 272, and 271 cm^{-1} for the Pt(0), Pd(0), and Ni(0) complexes, respectively. The ligand $(CH_2)_3(CHO)_3P$ shows a strong band at 321 cm^{-1}, and a band in this region is also found in the Pt(0), Pd(0), and Ni(0) complexes at 338, 333, and 349 cm^{-1}, respectively (Figure 2). Although the $(C_2H_5O)_3P$ spectrum of a neat sample reported by Myers, *et al.*,[1] showed no absorption in the region of 300 cm^{-1}, we find that a benzene solution and a Nujol mull of this ligand exhibit a broad but reproducible absorption at about 330 cm^{-1} (Figure 3). On the basis of the appearance of similar bands in all three ligands and their respective complexes, we suggest that at least one of the two bands assigned to the split F_2 metal–phosphorus stretch in the $(C_2H_5O)_3P$ complexes in the 340–240-cm^{-1} region[1] may possibly be a ligand mode. At least in the spectra of the bicyclic ligands and their complexes, we conclude that the band in the 270–355-cm^{-1} region is very likely associated with a ligand bending mode.

For the two nickel(0) complexes and the copper(I) and silver(I) bicyclic phosphite complexes, the remaining band in the far-infrared region (110–165 cm^{-1}) is best ascribed to the asymmetric M–P stretch expected for T_d systems. The simplicity of these spectra allowed us to conclude that the complexes were not distorted from tetrahedral. Supporting evidence for the undistorted tetrahedralism of the nickel(0), copper(I), and silver(I) bicyclic phosphite complexes comes from a recent X-ray diffraction study of $[(CH_3C(CH_2O)_3P)_4Ag]ClO_4$[9] in which it was found that the average P–Ag–P angle is 109.25 ± 0.4°. We were unable to locate the weak band at 210 cm^{-1} reported by

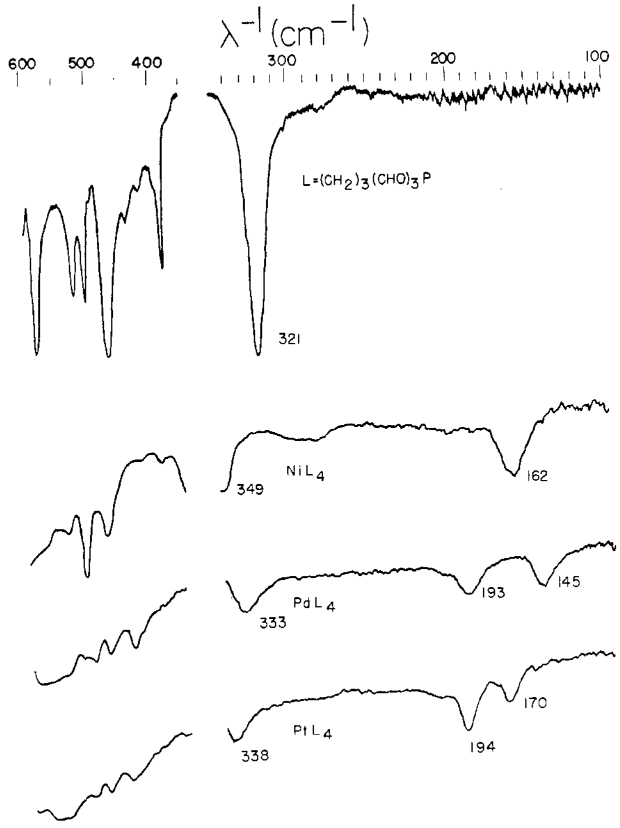

Figure 2.—Infrared spectra of $(CH_2)_3(CHO)_3P$ (fused polyethylene disk) and its complexes (Nujol mulls).

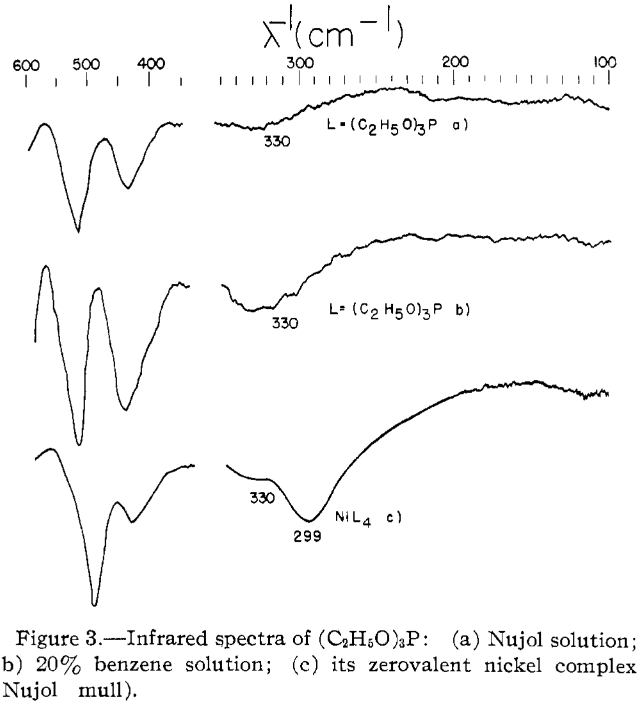

Figure 3.—Infrared spectra of $(C_2H_5O)_3P$: (a) Nujol solution; (b) 20% benzene solution; (c) its zerovalent nickel complex (Nujol mull).

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[9] J. Ugro and R. A. Jacobson, to be submitted for publication.

TABLE I

TENTATIVE FAR-INFRARED BAND ASSIGNMENTS (cm^{-1}) OF PHOSPHITES AND THEIR COMPLEXES

Compound	Ligand mode	Shifted ligand mode or F_2 species	νM–P
$CH_3C(CH_2O)_3P$	265		
$(CH_3C(CH_2O)_3P)_4Ni$	271		157
$(CH_3C(CH_2O)_3P)_4Pd$	272	192	142
$(CH_3C(CH_2O)_3P)_4Pt$	274	191	160
$[(CH_3C(CH_2O)_3P)_4Ag]ClO_4$	268		112
$[(CH_3C(CH_2O)_3P)_4Cu]ClO_4$	269		132
$(CH_2)_3(CHO)_3P$	321		
$((CH_2)_3(CHO)_3P)_4Ni$	349		162
$((CH_2)_3(CHO)_3P)_4Pd$	333	193	145
$((CH_2)_3(CHO)_3P)_4Pt$	338	194	170
$(C_2H_5O)_3P$	330		
$((C_2H_5O)_3P)_4Ni$	330		299

Myers, *et al.*,[1] for the complex $((C_2H_5O)_3P)_4Ni$, though we did observe the bands at 299 and 330 cm^{-1} (Figure 3c) in essential agreement with the two absorptions described by these workers at 305 and 335 cm^{-1}. Our observation on this complex may be indicative of a single M–P vibration at 299 cm^{-1} if the 330-cm^{-1} band can be assigned to the ligand mode we observed at 330 cm^{-1} in free $(C_2H_5O)_3P$ (see Figure 3). Although this conclusion would be consistent with that reached for our bicyclic phosphite–nickel(0) complexes, we regard it only as a very tentative possibility inasmuch as it rests on the presently moot question of the existence of the weak 210-cm^{-1} band reported by Myers, *et al.*[1] Furthermore it leads to an unexpectedly large difference between the metal–phosphorus frequencies in the nickel(0) polycyclic phosphites (157, 162 cm^{-1}) and the analogous triethyl phosphite complex (299 cm^{-1}). Further investigations are necessary to test the validity of these assignments.

The assignment of the absorption in the 142–170-cm^{-1} region in the four platinum(0) and palladium(0) complexes to an M–P mode is made somewhat difficult by the presence of a band in the 191–194-cm^{-1} range. It is surprising that this latter absorption is so constant from the palladium to the platinum complex (1 cm^{-1}) while the M–P mode varies as much as 18 and 25 cm^{-1} in the $CH_3C(CH_2O)_3P$ and $(CH_2)_3(CHO)_3P$ complexes, respectively. Although this band may be a ligand mode which has moved to lower energy upon coordination, an F_2 species of an M–P mode arising out of a distortion from T_d symmetry cannot be ruled out. If distortion occurs, however, the second member of the split F_2 species as described by Myers, *et al.*,[1] for the $(C_2H_5O)_3P$ complexes is not apparent. The coincidence of the missing F_2 member with the ligand band in the 270–338-cm^{-1} range for both ligands would be fortuitous and somewhat unlikely in view of the extremely large splitting of 80–140 cm^{-1} which would then be the case for this mode. It should be recognized, however, that there is some evidence for suggesting[8] that three of the M–P bonds may be different from the fourth in Pt(0) complexes of this type. The powder patterns of the $CH_3C(CH_2O)_3PNi^0$ and -Pt^0 complexes were not identical and so isomorphism arguments cannot be used to favor the conclusion that these compounds have identical geometries. Single-crystal studies are planned hopefully to shed light on this problem. Our provisional assignments are summarized in Table I.

Taking into account the changing mass of the metal, the progression of the M–P mode in the 140–170-cm^{-1} range to increasing energy in the order $Pd < Ni < Pt$ suggests that the bond order is greatest for platinum if the trend in M–P stretching force constants parallels their associated frequencies. The M–P stretching frequency in $[(CH_3C(CH_2O)_3P)_4Cu]ClO_4$ and the silver(I) analog appears at a distinctly lower energy than in the nickel(0) and palladium(0) complexes, respectively, in spite of the nearly identical masses involved in the third- and fourth-row metal pairs. Moreover the presence of a positive charge on the silver and copper complexes might have been expected to increase rather than decrease the M–P stretching frequency because of an increase in the polarity of the M–P bond. It is tentatively suggested that the weak σ basicity of phosphites may result in a subordination of this effect to a substantial weakening of metal to phosphorus π bonding from the zerovalent to the monovalent d^{10} complexes. The decrease in M–P from the copper(I) to the silver(I) complex parallels that observed for the nickel(0) to the palladium(0) compounds.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
AND THE JAMES FRANCK INSTITUTE,
THE UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS 60637

The Enthalpy of the Solid Decomposition Reaction $Cs_3NiCl_5(s) = CsNiCl_3(s) + 2CsCl(s)$

BY G. N. PAPATHEODOROU AND O. J. KLEPPA

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An investigation by Iberson, Gut, and Gruen[1] of the nickel(II) chloride–cesium chloride phase diagram has shown that this system exhibits two congruently melting compounds, the blue Cs_3NiCl_5 (mp 547°) and the orange-yellow $CsNiCl_3$ (mp 768°). In the former compound Ni^{2+} is in tetrahedral coordination; in the latter it is in octahedral coordination. At 417° a solid-state transformation of Cs_3NiCl_5 results in a decomposition according to the equation

$$Cs_3NiCl_5(s) = 2CsCl(s) + CsNiCl_3(s) \qquad (\Delta H^D) \qquad (1)$$

Cs_3NiCl_5 is stable above 417°, and the mixture of $2CsCl + CsNiCl_3$ below 417°. We wish to report

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[1] E. Iberson, R. Gut, and D. M. Gruen, *J. Phys. Chem.*, **66**, 65 (1962).