quinuclidine–borane (mp 159–161°) was obtained from 2.2 g of $LiBH_4$ and 9.2 g of quinuclidine hydrochloride. *Anal.* Calcd for $C_7H_{16}NB$: H (hydridic), 2.42. Found: H (hydridic), 2.42.

Kinetic Measurements.—Temperatures at which rate studies were carried out were maintained within ±0.04° by use of a Wilkins-Anderson constant-temperature bath. At t_0, a weighed sample (usually about 40–80 mg) of amine–borane was treated with an appropriate volume of solvent which had been equilibrated at the appropriate temperature, and the rate of disappearance of amine–borane was then followed by iodometric determination of soluble hydride at various intervals of time. Usually large batches of solvent were prepared and separate samples of a given batch (about 100 ml) were used for studies of the rates of hydrolyses of both amine–boranes at the same time. Initial concentrations of amine–borane ranged from about 0.004 to 0.008 *M*. Hydrogen ion was always present in large excess (0.09–0.41 *M*). For a given run, a "pseudo-first-order" rate constant was obtained from the slope of the line obtained by plotting the logarithm of the amine–borane concentration against time. The second-order rate constant, defined as

$$k_2 = \frac{-\mathrm{d}[\mathrm{AB}]}{\mathrm{d}t} \Big/ [\mathrm{AB}][\mathrm{H_3O^+}]$$

where [AB] is the concentration of amine-borane, was obtained by dividing the pseudo-first-order constants by the value of $[H_3O^+]$ for that particular run.

Acknowledgments.—This research was supported by The Robert A. Welch Foundation and the Texas Christian University Research Foundation. The authors wish to acknowledge Dr. Donald Noyce of The University of California, Berkeley, Calif., for helpful discussions.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201,
AND ILLINOIS INSTITUTE OF TECHNOLOGY,
CHICAGO, ILLINOIS 60616

Far-Infrared Spectra of Tetrakis(triethyl phosphite) Complexes of Nickel(0), Palladium(0), and Platinum(0)

BY VICTOR G. MYERS, FRED BASOLO, AND KAZUO NAKAMOTO

Received November 20, 1968

Recently, a number of investigations have been made on far-infrared spectra of metal complexes containing various phosphines.[1–12] Table I summarizes some metal–phosphorus stretching frequencies assigned by these investigators. It is seen that these frequencies scatter over a wide frequency region from 460 to 90 cm^{-1}. Several investigators[10,12] have suggested that this scattering of frequencies may be due to the differences in the nature (1) of the metals (oxidation state, electronic configuration, etc.), (2) of the phosphine ligands PR_3, where R is CH_3, C_2H_5, or C_6H_5, and (3) in the structure of the complex (stereochemistry, coordination number, etc). If this is the case, a meaningful comparison of metal–phosphorus stretching frequencies can only be made for a series of metal complexes in which the three factors mentioned above are kept constant. However, such a series is very rare. This paper reports the far-infrared spectra and band assignments for a series of compounds of the type $M[P(OC_2H_5)_3]_4$ (M = Ni(0), Pd(0), or Pt(0)), all of which presumably have tetrahedral or nearly tetrahedral structures.

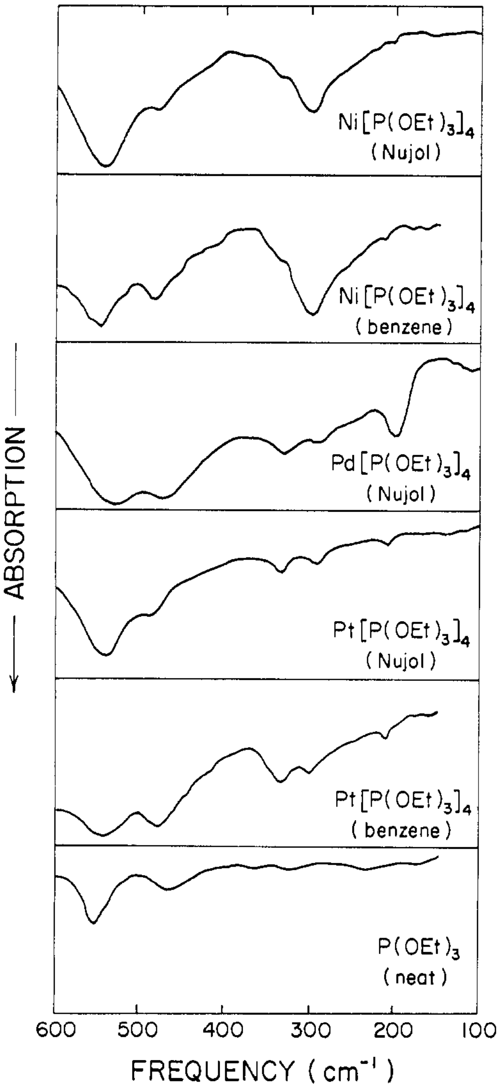

Figure 1.—Infrared spectra of tetrakis(triethyl phosphite) complexes of Ni(0), Pd(0), and Pt(0) obtained in Nujol mull or in benzene solution.

Experimental Section

Samples of the white tetrakis(triethyl phosphite) complexes of nickel(0), palladium(0), and platinum(0) used in the present spectroscopic investigation were gifts from Dr. M. Meier, who

---

(1) V. Albano, P. L. Bellon, and V. Scatturin, *Chem. Commun.*, 507 (1966).

(2) P. C. Goggin and R. J. Goodfellow, *J. Chem. Soc.*, *A*, 1462 (1966).

(3) D. M. Adams and P. J. Chandler, *Chem. Commun.*, 69 (1966).

(4) R. J. Goodfellow, P. L. Goggin, and L. M. Venanzi, *J. Chem. Soc.*, *A*, 1897 (1967).

(5) L. A. Woodward and J. R. Hall, *Spectrochim. Acta*, **16**, 654 (1960).

(6) W. F. Edgell and M. P. Dunkle, *Inorg. Chem.*, **4**, 1629 (1965).

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

(8) J. Bradbury, K. P. Forest, R. H. Nuttall, and D. W. A. Sharp, *Spectrochim. Acta*, **23A**, 2701 (1967).

(9) G. D. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963).

(10) A. A. Chalmers, J. Lewis, and R. Whyman, *ibid.*, *A*, 1817 (1967).

(11) M. A. Bennett, R. J. H. Clark, and A. D. J. Goodwin, *Inorg. Chem.*, **6**, 1625 (1967).

(12) G. B. Deacon and J. H. S. Green, *Chem. Commun.*, 629 (1966).

TABLE I

METAL–PHOSPHORUS STRETCHING FREQUENCIES (CM^{-1})

Metal and oxidn state	Compound	M–P str freq, cm^{-1}	Ref
Pt(0)	$Pt(P(C_6H_5)_3)_3$	422	1
Pt(II)	*cis*- and *trans*-$Pt(P(C_2H_5)_3)_2X_2$ ($X^- = Cl^-, Br^-, I^-, NCS^-$)	442–409	2, 3
	$Pt_2Cl_4L_2$ ($L = P(CH_3)_3, P(C_2H_5)_3, P(C_6H_5)_3$)	456–393	4
Pd(II)	$Pd_2Cl_4L_2$ ($L = P(CH_3)_3, P(C_2H_5)_3, P(C_6H_5)_3$)	450–382	4
	trans-$Pd(P(C_2H_5)_3)_2X_2$ ($X^- = Cl^-, Br^-, I^-$)	412–410	2
Ni(0)	$Ni(PF_3)_4$	219, 195	5
	$Ni(CO)_3(P(C_6H_5)_3)$	192	6
	$Ni(P(OCH_2)_3CCH_3)_4$	157	7
Ni(II)	*trans*-$Ni(P(C_2H_5)_3)_2X_2$ ($X^- = Cl^-, Br^-$)	415–412	2
	$Ni(P(C_6H_5)_3)_2Cl_2$	189–166	8
	$Ni(P(C_6H_5)_3)Cl_3^-$	177	8
Au(I)	$Au(PR_3)X$, $Au(PR_3)X_3^{2-}$ (R = alkyl)	388–347	9
Cr(0), Mo(0), W(0)	$M(CO)_x(P(C_6H_5)_3)_y$ ($x = 3$–5; $y = 6 - x$)	230–173	10
Cr(III)	$Cr(NCS)_4(P(CH_3)_3)_2^-$	275	11
	$Cr(NCS)_4(P(C_2H_5)_3)_2^-$	304	11
Co(II), Zn(II)	$M(P(C_6H_5)_3)_2X_2$, $M(P(C_6H_5)_3)X_3^-$ ($X^- = Cl^-, Br^-$)	190–128	8
Zn(II), Cd(II), Hg(II)	$M(P(C_6H_5)_3)_2X_2$ ($X^- = Cl^-, Br^-, I^-$)	166–98	12

TABLE II

INFRARED SPECTRA[a] OF TRIETHYL PHOSPHITE COMPLEXES IN THE REGION 100–600 CM^{-1}

$Ni[P(OC_2H_5)_3]_4$		$Pd[P(OC_2H_5)_3]_4$	$Pt[P(OC_2H_5)_3]_4$		$P(OC_2H_5)_3$	
Nujol mull	Benzene soln	Nujol mull	Nujol mull	Benzene soln	Neat	Probable assignment
210 w	226 w	200 m	215 w	212 w		ν(M–P), sym
305 s	302 s	290 w	290 m	300 m		ν(M–P), asym
335 m, sh	335 m, sh	335 m	332 m	335 m		
480 s, sh	484 s, sh	475 s	490 s, sh	480 s	470 m	$\delta(P–O–C_2H_5)$
540 s	546 s	535	540 s	540 s	545 sh	
					555 s	

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; ν, stretching; δ, bending; M, metal.

prepared them according to literature methods.[13,14] Details of the syntheses and identification of the compounds used were reported earlier.[15] Although all of the compounds were stored either under vacuum or in a nitrogen atmosphere, Nujol mulls of the nickel and platinum complexes could be prepared in the air. Rapid decomposition in air of the palladium complex required that its mull be prepared in a nitrogen-filled glove bag. Triethyl phosphite was used as received from Eastman Organic Chemicals.

The infrared spectra from 100 to 600 cm^{-1} were obtained on a Beckman Model 11 grating spectrophotometer. The Nujol mulls and neat liquid $P(OC_2H_5)_3$ were placed between polyethylene plates. Spectra of benzene solutions were obtained with a cell constructed from two polyethylene plates fused to a third plate with its center removed. A spectrum of benzene in this region showed no significant absorption. Concentrations of the benzene solutions of $Ni[P(OC_2H_5)_3]_4$ and $Pt[P(OC_2H_5)_3]_4$ observed in the far-infrared region were 0.13 and 0.15 g/ml, respectively.

Results and Discussion

Figure 1 shows the infrared spectra of tetrakis(triethyl phosphite) complexes of Ni(0), Pd(0), and Pt(0) obtained in Nujol mull or in benzene solution. The spectra are essentially the same in both physical states. Table II lists the observed frequencies. The strong bands at 560–470 cm^{-1} of the metal complexes are due to the ligand since triethyl phosphite itself absorbs in the same region. They are probably due to the P–O–C_2H_5 bending modes because a number of organophosphorus compounds containing the P–O–R (R = alkyl or phenyl) groups exhibit their P–O–R bending modes in this region.[16,17]

All three metal complexes studied exhibit two bands at 340–290 cm^{-1} and one band at 220–190 cm^{-1}. Since the free ligand does not show any absorption in these regions, it is reasonable to assign them to the vibrations due to the MP_4 skeleton (M = metal). The calculations summarized below show that it is most reasonable to assign the former two bands to the M–P stretching modes of the F_2 species which is split into two components and the latter band to the M–P stretching mode of the A_1 species which is allowed in the infrared spectrum due to deviation from perfect T_d symmetry.

The fact that all three complexes reveal M–P stretching bands in almost the same regions is somewhat surprising, since previous investigations (Table I) show a marked dependency of the M–P stretching frequencies on the nature of the metals. The frequency of an infrared-active vibration is a function of the masses of individual atoms involved and of the force constants determined by the electronic nature of the chemical bonds. Since Pt is the heaviest and Ni is the lightest in this series, the present results suggest that the increasing order of the M–P stretching force constants would be Ni(0) < Pd(0) < Pt(0).

---

(13) R. S. Vinal and L. T. Reynolds, *Inorg. Chem.*, **3**, 1062 (1964).

(14) L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958).

(15) M. Meier, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, in press.

(16) F. S. Mortimer, *Spectrochim. Acta*, **9**, 270 (1957).

(17) J. R. Ferraro, D. F. Peppard, and G. W. Mason, *ibid.*, **19**, 811 (1963).

In order to make rough estimates of the M–P stretching force constants, we have calculated the frequencies of the tetrahedral MR_4 ($R = P(OC_2H_5)_3$) molecules using the Urey–Bradley force field.[18] Assuming that H (bending force constant) is 0.05 mdyn/Å and F (repulsive force constant) is 0.4 mdyn/Å, all of the calculated frequencies can be fitted to those observed within an error of 25 cm^{-1} if K (the M–P stretching force constant) is taken to be 1.7, 2.7, and 3.7 mdyn/Å for Ni(0), Pd(0), and Pt(0), respectively. The R–M–R bending bands must be below 100 cm^{-1} since they are calculated to be 90–80 cm^{-1}. Evidently, the value of K depends upon that of F. Therefore, we have calculated K values by changing F. The latter value is expected to be relatively constant among the metals studied. For a fixed F value we have always found that the order of the K values is Ni(0) < Pd(0) < Pt(0) and that these values are separated by about 1.0 mdyn/Å from each other.

The order of the M–P stretching force constants obtained can be interpreted in terms of increasing π- or σ- (or both) bond order of the M–P bonds in the order Ni(0) < Pd(0) < Pt(0). It is interesting to note that the Ni(0)–P stretching frequencies of $Ni[P(OC_2H_5)_3]_4$ assigned in this work (335–305 and 210 cm^{-1}) are much higher than that reported for $Ni[P(OCH_2)_3CCH_3]_4$ (157 cm^{-1}).[7] The nature of Ni–P bonds in these two compounds is expected to be similar. Also, the total masses of these two phosphine ligands are similar. Thus, the Ni–P stretching frequencies are expected to be similar as long as we approximate their normal vibrations by using a simple MR_4-type model. It is probable that the 157-cm^{-1} band of $Ni[P(OCH_2)_3CCH_3]_4$ corresponds to the 210 cm^{-1} of $Ni[P(OC_2H_5)_3]_4$ and that a band corresponding to the 335–305 cm^{-1} of the latter is obscured by the presence of other bands in the former compound. Even so, the Ni–P stretching frequencies are different between these two compounds. This result may suggest that a more complete calculation including all of the atoms of the ligands is necessary to account for the Ni–P stretching frequencies of metal phosphine complexes containing different ligands.

Acknowledgment.—This work was supported in part by the U. S. Atomic Energy Commission under Grant No. At(11-1)-1087.

(18) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245 (1949).

CONTRIBUTION FROM THE
ISTITUTO DI CHIMICA GENERALE ED INORGANICA,
UNIVERSITY OF MILAN, MILAN, ITALY

Synthesis of Hexadecacarbonylhexacobalt

BY PAOLO CHINI

Received January 2, 1969

Considerable confusion has existed regarding the neutral carbonyls in the cobalt subgroup. Cobalt is known to give $Co_2(CO)_8$ and $Co_4(CO)_{12}$, and rhodium is stated to give $Rh_2(CO)_8$, $Rh_4(CO)_{12}$, and $Rh_6(CO)_{16}$, while for iridium both $Ir_2(CO)_8$ and $Ir_4(CO)_{12}$ have been reported.[1] We now report the preparation of $Co_6(CO)_{16}$[2] which completes the series of the cobalt compounds. Later some information will be given about the isolation of $Ir_6(CO)_{16}$,[3] and some evidence will be adduced against the existence of the hypothetical $Rh_2(CO)_8$ and $Ir_2(CO)_8$.[3,4]

Experimental Section

Analyses have been carried out as reported in a previous paper.[5] $K_2[Co_6(CO)_{15}]$ and $K_4[Co_6(CO)_{14}]$ have been prepared according to the literature.[5,6] Infrared spectra have been recorded on a Perkin-Elmer 621 spectrophotometer.

Synthesis of $Co_6(CO)_{16}$.—A solution of $HgCl_2$ (6 g) and NaCl (6 g) in water (25 ml) was rapidly added to an aqueous solution (25 ml) of $K_2[Co_6(CO)_{15}]$ (4 g). A fine red-brown precipitate was formed, filtered off, washed with water, and vacuum dried over P_2O_5 for 24 hr. The infrared spectrum of this solid was consistent with that of a mixture (about 1:2) of $Co_4(CO)_{12}$ and $Co_6(CO)_{16}$.

The dry solid was washed five times with toluene (20 ml) until the toluene was only slightly brown and then was extracted with isopentane. During this extraction the temperature was controlled using a heating bath at 55°, and an atmosphere of carbon monoxide was maintained over the boiling isopentane, but on cooling the carbon monoxide was replaced by nitrogen. This prevented decomposition to cobalt metal during the boiling and formation of $Co_4(CO)_{12}$ during the cooling.

The first isopentane extract (12 hr) containing $Co_4(CO)_{12}$ mixed with $Co_6(CO)_{16}$ was discarded; then, after 48 hr of extraction, black crystals of $Co_6(CO)_{16}$ were obtained (0.305 g). *Anal.* Calcd for $Co_6(CO)_{16}$: C, 23.97; Co, 44.10. Found: C, 23.84; Co, 44.08. In the C═O stretching region of the infrared spectrum there are bands at 2113 w, 2061 vs, 2057 sh, 2026 w, 2020 w, 2018 w, 1806 w, 1772 vs cm^{-1} (Nujol mull). The same product was obtained starting from $Na_4[Co_6(CO)_{14}]$ or using iron trichloride as the oxidizing agent.

Reaction between $Co_6(CO)_{16}$ and Pyridine.—Pyridine (4 ml) and $Co_6(CO)_{16}$ (0.1096 g) were allowed to react together under high vacuum at room temperature for 15 min. Pumping out with a Toepler pump gave 0.705 cm^3 of gas (1.4%). The infrared spectrum of the solution showed only the band of the $Co(CO)_4^-$ anion at 1890 cm^{-1}; some metallic cobalt was also present.

Results

Oxidation of a water solution containing the pentadecacarbonylhexacobaltate(2−) or the tetradecacarbonylhexacobaltate(4−) anion with excess of a mild reagent such as iron trichloride or sodium tetrachloromercurate precipitates a mixture of $Co_4(CO)_{12}$ and $Co_6(CO)_{16}$.

The isolation of the hexadecacarbonylhexacobalt offers special difficulties due to its low solubility, low thermal stability, and high reactivity. The best results have been obtained by fractional extraction with isopentane. The hexadecacarbonylhexacobalt has been isolated as black, well-formed crystals (brown in mull). In nitrogen it decomposes at 110–120°; under vacuum (0.001 Torr), at 70–80° without sublimation. In air

(1) F. Calderazzo, R. Ercoli, and G. Natta in "Organic Syntheses *Via* Metal Carbonyls," Vol. I, I. Wender and P. Pino, Ed., Interscience Publishers, New York, N. Y., 1968.

(2) P. Chini, *Chem. Commun.*, 440 (1967).

(3) L. Malatesta, G. Caglio, and P. Chini, work in progress.

(4) P. Chini and S. Martinengo, *Inorg. Chim. Acta*, in press.

(5) P. Chini and V. Albano, *J. Organometal. Chem.* (Amsterdam), **15**, 433 (1968).

(6) P. Chini, V. Albano, and S. Martinengo, *ibid.*, in press.