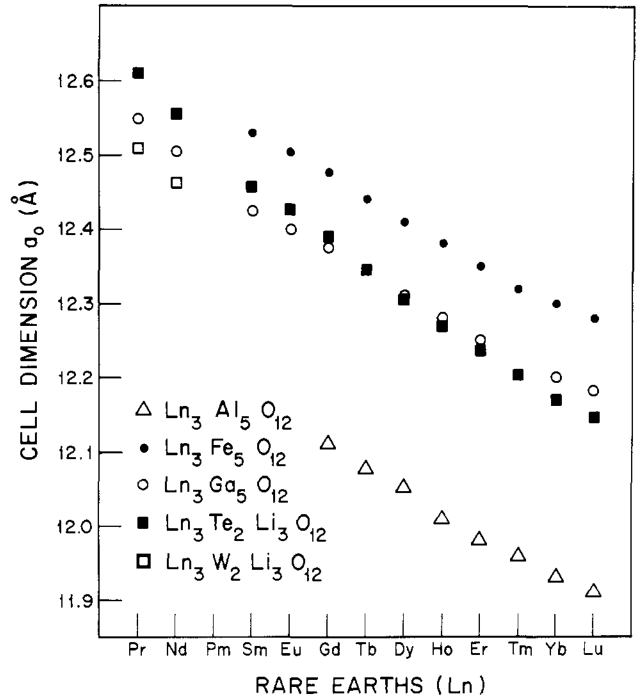

Figure 1.—Lattice constants of rare earth garnets.

octahedral interstices by moving out of the center of symmetry. The octahedral-site coordination has been discussed by Zemann,[11] who pointed out that garnets with very nearly regular octahedra should be possible. This suggests that the TeO_6^{6-} octahedra in the tellurate garnets are regular and that the relative stability of regular octahedra is the reason that there is a much more extended series of rare earth garnets with Te^{6+} ions than with W^{6+} ions.

Acknowledgments.—The advice and assistance of J. B. Goodenough, A. Ferretti, J. M. Longo, E. B. Owens, Mary C. Finn, and A. J. Strauss are gratefully acknowledged.

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[11] J. Zemann, *Beitr. Mineral. Petrog.*, **8**, 180 (1962).

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Solvent Displacement of Ligands from Carbonyl Complexes of Platinum (II)

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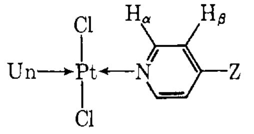
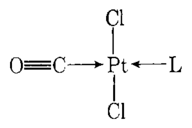
Earlier work in this laboratory has shown that the nmr spectra of pyridine complexes of structure **1** may not show the expected $^{195}Pt-H_\alpha$ spin coupling because of rapid exchange of the pyridine ligand with solvent molecules until the exchange rate is slowed by low temperatures.[1,2]



1 (Un = unsaturated ligand)



2

(a) L = 4-Z-PyO
(b) L = 4-Z-Py
(c) L = 4-Z-An

The temperature at which such coupling is observed depends upon the solvent and the nature of Un and Z. Thus, for example, when Z = CN and Un is varied in the series: ethylene, *trans*-2-butene, *cis*-2-butene, and carbon monoxide, the temperatures at which coupling is observed in chloroform solution are respectively: -51, -25, 3, and 30°. This order of ligands may thus be construed to be the order of *trans*-labilizing ability: ethylene >> *trans*-2-butene > *cis*-2-butene > CO. When Un is held constant, the temperature for coupling is a function of the nature of Z: the strongest electron-withdrawing substituents require the lowest temperature for coupling to be observed. Finally, it has also been shown that when the nmr spectrum of any particular complex **1** is taken in several solvents, the solutions made from coordinating solvents such as acetone must be cooled to lower temperatures to observe coupling than when solvents such as chloroform are employed. In the present study, we examined the infrared spectra of a series of carbonyl complexes **2** in order to determine whether the labilizing effects of solvent determined by nmr spectra could also be demonstrated by the infrared spectra.

Experimental Section

The complexes **2a** and **2b** were prepared by the displacement of ethylene by carbon monoxide from the corresponding complexes **1** (Un = ethylene) by a procedure similar to that previously reported.[3,4] The ethylene complex, which was prepared from Zeise's salt and the appropriate pyridine, was dissolved in 10 ml of dry $CHCl_3$ and CO bubbled through the yellow solution until most of the original color had disappeared. The volume of the solution was reduced by evaporation and hexane added with cooling. The precipitated complex was filtered, washed with hexane, and dried. The product was then redissolved in dry chloroform and the above precipitation repeated to assure pure complexes.

The aniline carbonyl complexes **2c** were prepared by the reaction of the appropriate aniline with the carbonyl analog of Zeise's salt, $[(CO)PtCl_3]K$, in acetone. After the precipitated KCl was removed, the solution was concentrated and hexane added to induce precipitation of the product.

Most of the complexes have been previously reported.[3,4] All infrared spectra were determined with a Perkin-Elmer Model 337 grating spectrophotometer with expanded scale and polystyrene calibration using 0.05-mm KBr cells unless otherwise noted. The spectra were determined in spectral grade acetone, chloroform, and acetonitrile, dried over Linde 4A molecular seives.

Results and Discussion

The carbonyl stretching frequencies of complexes with structure **2** are listed in Table I for the three

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[1] P. D. Kaplan, P. Schmidt, and M. Orchin, *J. Amer. Chem. Soc.*, **89**, 4537 (1967).

[2] P. D. Kaplan, P. Schmidt, and M. Orchin, *ibid.*, **91**, 85 (1969).

[3] W. H. Clement and M. Orchin, *J. Organometal. Chem.*, **3**, 98 (1965).

[4] A. R. Brause, M. Rycheck, and M. Orchin, *J. Amer. Chem. Soc.*, **89**, 6500 (1967).

TABLE I

STRETCHING FREQUENCIES, $\nu_{C\equiv O}$ (CM^{-1}) OF COMPLEXES $LPt(Cl_2)CO$

Ligand	$CHCl_3$	Acetone		Acetonitrile	
4-Z-pyridine					
Z = NO_2	2147[a]	2134	2087	2136	2095
CN	2140[a]	2133	2087	2135	2095
CO_2CH_3	2139[a]	2128	2087	2133	2096
$COCH_3$	2135[a]	2128	2087	2132	2096
H[b]	2133[a]	2128	2087 w	2131 w	2096
CH_3	2132[a]	2126	2087 w	2128 w	2096
OCH_3	2129[a]	2123	2087 w	2128 w	2096
4-Z-Pyridine N-oxide					
Z = NO_2	2124	. . .	2087	. . .	2100
H	2122	2106	2087	2114	2100
$OCH_2C_6H_5$	2118	2104	2085	2108	2099
CH_3	2117	2108	2088		
OCH_3	2116	2107	2087	2110	2100
4-Z-Aniline					
Z = Cl[c,d]	2131	2122	2085		
H[b]	2132	2122	2085		
CH_3[b]	2132	2122	2085		
OCH_3[c,e]	2130	2123	2086		

[a] Ref 4. [b] R. J. Irving and E. A. Magnusson, *J. Chem. Soc.*, 2018 (1957). [c] These are new complexes; they gave satisfactory analyses. [d] Mp 205° (dec). [e] Mp 175° (dec).

series of compounds where L is a series of 4-Z-substituted pyridines **2a**, a series of 4-Z-substituted pyridine N-oxides **2b**, and a series of 4-Z-substituted anilines **2c**. If we examine first the results in chloroform solution we note the presence of one carbonyl band as expected, and further that in the pyridine series (and to a much smaller extent in the N-oxide series) the stretching frequency increases as the electron-attracting ability of the 4-substituent increases. Although there is some overlap, as a group the order of decreasing frequencies as a function of L is: Py ≅ An > PyO. In a first approximation it might be expected that the more electronic charge brought into the positive metal atom by L, the lower the $\nu_{C\equiv O}$, since charge relief can be achieved by enhanced population of the antibonding orbitals of the C≡O. Within the pyridine series this appears to be the case but the order of basicity of the three ligands L does not parallel their effect on $\nu_{C\equiv O}$. It is clear that the lack of correlation must be due to factors such as competitive back-bonding with L and the nucleophilic power of L as distinguished from its base strength in protic solvents.

There are several noteworthy features of the spectra listed in Table I. In acetone (and acetonitrile) solution, two carbon monoxide carbonyl bands appear. The high-frequency band differs in each series of L's in the same way as $\nu_{C\equiv O}$ in the chloroform solution: Py ≅ An > PyO. Within the pyridine series, the bands parallel those found in the chloroform solution. In the series **2b** and **2c** the character of the Z substituent has little or no effect on the spectra in acetone solution. Perhaps the most significant facts about the spectra taken in acetone solution are that in each instance a second low-frequency band appears and this band is essentially the same (2086 ± 2 cm^{-1}) for each of the 16 complexes investigated. It is reasonable to assume that the appearance of the same species in each instance must be responsible for this low-frequency band. Such a complex is a solvent-coordinated complex $SPtCl_2(CO)$ (S = acetone), in which the solvent has displaced L in a substantial portion of the molecules. It will be noted further from Table I that acetonitrile has the same effect as acetone. Here a common low-frequency band of 2097 ± 3 cm^{-1} is observed, undoubtedly due to $SPtCl_2(CO)$ (S = acetonitrile). It is to be expected that this common low-frequency band would be in a different position from the common band found in acetone solutions.

The relative intensities of the two carbonyl bands observed in acetone solution are of considerable interest. The relative intensity differs, depending in each series on the character of the substituent Z. The bands found for the pyridine series **2a** are shown in Figure 1. The low-frequency band ascribed to $SPtCl_2(CO)$ is most intense when Z is NO_2 and decreases in intensity with decreasing electron-withdrawing power of Z. This behavior is expected, since the Pt–N bond should be easier to cleave by solvent when Z is most electron-withdrawing. Studies of the bond strength between 4-Z-pyridine and copper reveal large changes as a function of the Z substituent; the weaker the base strength of the pyridine, the weaker the bond.[5,6]

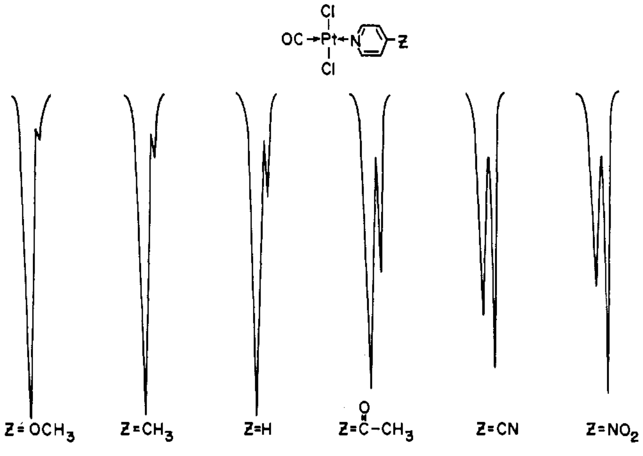

Figure 1.—The carbonyl bands of (4-Z-Py)Pt(CO)Cl_2 in acetone solution.

In the pyridine N-oxide series **2b** there is also a similar variation in the intensities of the low-frequency band as a function of Z and again in this series the low-frequency band (solvent complex) is more intense. As a matter of fact, with the strongest electron-withdrawing group **2b**, Z = NO_2, only the low-frequency band is observed. This may reflect a weaker coordinating ability of the pyridine N-oxide; other complexes with this ligand are known to dissociate in solvents of high coordinating ability.[7] Although it is of course

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(5) P. T. T. Wong and D. G. Brewer, *Can. J. Chem.*, **46**, 131 (1968).

(6) P. T. T. Wong and D. G. Brewer, *ibid.*, **46**, 139 (1968).

(7) D. W. Herlocker, R. S. Drago, and V. I. Meek, *Inorg. Chem.*, **5**, 2009 (1966).

theoretically possible to determine equilibrium constants from intensity measurements, we find the intensity perplexingly sensitive to experimental conditions (*vide infra*) and also we have not been able to isolate solvent-coordinated species; accordingly, such studies have not been pursued as yet.

Although our data are readily explained in terms of the formation of a solvent-coordinated species SPtCl$_2$(CO) with a lower frequency $\nu_{C\equiv O}$, the formation of a dimer and resulting *trans* to *cis* isomerization cannot be completely ruled out. It is known that strong *trans*-directing groups facilitate dimer formation[8] and such a dimer could be the precursor to a *cis* isomer.[9] However, the platinum carbonyl dimer (PtCl$_2$CO)$_2$ has been reported to have $\nu_{C\equiv O}$ at 2152 cm^{-1} in mull[10] and such a high-frequency band has not been observed in our solution work.

Finally, certain difficulties with respect to the determination of spectra of these complexes were encountered and should be mentioned. When the complexes were mulled with halocarbon oil, the resulting spectra were erratic. The extent of mulling and grinding seemed to affect the spectra. The spectra showed broad and split bands in many cases. Solution spectra of the pyridine complexes taken in KBr cells and NaCl cells differed. Although the values of $\nu_{C\equiv O}$ and the effect of Z were similar in each type of cell, the relative intensities of the two carbonyl bands were affected, the low-frequency band increasing and the high-frequency band decreasing in intensity in changing from NaCl to KBr cells. The KBr pellet technique also gave erratic results possibly because of bromide incorporation into the complex.[11]

Acknowledgment.—We are pleased to acknowledge the assistance of Thomas Atkins and partial support from the Petroleum Research Fund, National Science Foundation, and Standard Oil of Ohio. We also wish to thank Engelhard Industries for a generous supply of platinum.

[8] S. J. Lokken and D. S. Martin, Jr., *Inorg. Chem.*, **2**, 562 (1963).

[9] J. Chatt, N. Johnson, and B. Shaw, *J. Chem. Soc.*, 1662 (1964).

[10] R. J. Irving and E. A. Magnusson, *ibid.*, 1860 (1956).

[11] J. Pradilla-Sorzano and J. P. Fackler, Jr., *J. Mol. Spectrosc.*, **22**, 80 (1967).

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The Reactions of Triethylaluminum with Some Hydrazinophosphorus Compounds

BY STANLEY F. SPANGENBERG AND HARRY H. SISLER

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The reactions of organoaluminum compounds with some hydrazines,[1,2] biphosphines,[3] and aminophosphines[3] have resulted in formation of adducts in which the aluminum atom is believed to be pentacoordinate by virtue of its attachment to two adjacent electron donor centers. The various hydrazinophosphines afford a variety of possibilities for such "pentacoordination," since such compounds contain adjacent nitrogen atoms as well as phosphorus and nitrogen atoms in adjacent positions. We were, therefore, interested in examining the products of the reactions of aluminum triethyl with 2,3,5,6,7,8-hexamethyl-2,3,5,6,7,8-hexaaza-1,4-diphosphabicyclo[2.2.2]octane, with 2,3,5,6-tetramethyl-2,3,5,6-tetraaza-1,4-diphenyl-1,4-diphosphacyclohexane, and with 1,2-bis(diphenylphosphino)-1,2-dimethylhydrazine. These products have been prepared and studied, and the results are reported below.

Experimental Section

Materials.—Toluene, hexane, benzene, and petroleum ether (bp 20–40°) were obtained as reagent grade materials and were dried and stored over calcium hydride. Triethylaluminum was obtained from the Ethyl Corp. and was distilled under nitrogen at 66° (0.4 mm). Phosphorus trichloride, obtained from the J. T. Baker Chemical Co., was used as received. Diphenylchlorophosphine and phenyldichlorophosphine were obtained from the Victor Chemical Co. These reagents were distilled under nitrogen and fractions boiling at 212–214° (760 mm) and 110° (0.5 mm), respectively, were kept for use. 1,2-Dimethylhydrazine dihydrochloride, obtained from the Aldrich Chemical Co. was used as obtained. Dimethylamine was obtained from the Matheson Co. Inc. Tris(dimethylamino)phosphine was prepared by the reaction of dimethylamine with phosphorus trichloride according to standard procedure.[4] The 2,3,5,6,7,8-hexamethyl-2,3,5,6,7,8-hexaaza-1,4-diphosphabicyclo[2.2.2]octane, P[(CH$_3$)NN(CH$_3$)]$_3$P, was synthesized by the method of Payne, Nöth, and Henniger.[5]

General Methods.—Triethylaluminum, phosphines, and hydrazinophosphorus compounds were handled in an atmosphere of nitrogen. A Vacuum Atmospheres Model HE-43 inert-atmosphere box equipped with a Model HE-93B Dri-Train or a typical high-vacuum line was used for manipulation and storage of all reagents. Infrared spectra were obtained using a Beckman IR-10 spectrophotometer. The proton magnetic resonance spectra were recorded using a Varian A-60A nmr spectrometer. Tetramethylsilane was used as an internal reference when it was possible and as an external reference in all other cases. The phosphorus nuclear magnetic resonance spectra were obtained using a Varian high-resolution spectrometer, Model V-4300-2, equipped with a field homogeneity control, magnet insulation, and field stabilizer. These spectra were recorded at 19.3 Mc using 85% phosphoric acid as an external reference. Fine splitting was not observed on some of the ^{31}P spectra since the sample tubes could not be spun. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn. and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Preparation of 1,2-Bis(diphenylphosphino)-1,2-dimethylhydrazine.—The (C$_6$H$_5$)$_2$P(CH$_3$)NN(CH$_3$)P(C$_6$H$_5$)$_2$ was prepared as follows. 1,2-Dimethylhydrazine (2.58 g, 0.0431 mol) was added to a solution of diphenylchlorophosphine (19.1 g, 0.107 mol) in 200 ml of benzene. The solution was stirred as the hydrazine was added. The resulting mixture was allowed to stand for 12 hr. The mixture was then filtered and the solvent was removed under vacuum to yield 16.8 g of a clear liquid. This liquid was crystallized by dissolving it in boiling hexane and allowing the solution to cool. The resulting white crystals were filtered; after drying, they melted at 82–84°. The yield of

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[1] D. F. Clemens, W. S. Brey, and H. H. Sisler, *Inorg. Chem.*, **2**, 1251 (1963).

[2] R. P. Nielsen and H. H. Sisler, *J. Chem. Soc.*, 3819 (1962).

[3] D. F. Clemens, H. H. Sisler, and W. S. Brey, Jr., *Inorg. Chem.*, **5**, 527 (1966).

[4] A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80**, 1107 (1958).

[5] D. S. Payne, H. Nöth, and G. Henniger, *Chem. Commun.*, **1**, 327 (1965).