stop further donation; the back-donation reduces this dipole and thus the over-all bond strength depends very largely upon the degree of back-donation that is possible. The extent of back-donation depends upon the availability of electrons at iridium and the chloro complex would be expected to form a weaker bond with oxygen than the iodo complex. In the formation of the bond to iridium, electrons are removed from an O–O bonding orbital and the back-donation is to a molecular orbital very similar to the lowest antibonding orbital in the "prepared" valence state of oxygen. Thus the more strongly the O_2 group is bound to iridium, the longer is the expected O–O distance. In this way, we rationalize the observed effects.

Infrared absorptions due to the O_2 group attached to a metal have been reported for a wide range of compounds. In general, the only band observed is in the region 840–900 cm^{-1}; such bands have been assigned to the O–O stretch. The positions of this absorption for some compounds of the general formula $IrX(O_2)(CO)(P(C_6H_5)_3)_2$ are 858 cm^{-1} (X = Cl), 862 cm^{-1} (X = Br, I), and 855 cm^{-1} ($X = N_3$). The facile assignment of this absorption as an O–O stretch does not explain why a difference of 0.2 A in O–O bond length between the oxygenated chloro and iodo compounds only results in a change of 4 cm^{-1} in the position of the absorption. Normally the position of an absorption should vary greatly with the bond length, *i.e.*, bond strength. For the system $Ir–O_2$ (C_{2v} symmetry), three infrared-active modes are expected: two symmetric and one antisymmetric. In this system, the absorption due to the antisymmetric mode is expected to occur at a wavelength lower than has been investigated. Of the two symmetric modes, we believe that the observed band corresponds to that mode analogous to the ν_1 mode in H_2O. The displacement coordinates of the oxygen atoms in this mode can be resolved into components along and perpendicular to the O–O bond. Because of the greater strength of the bond in the chloro compound, the displacement along the O–O bond should be less there than in the iodo compound. Because the O_2 group is more tightly bonded to iridium in the iodo compound the displacement normal to the O–O bond should be less there than in the chloro compound. Thus it seems probable that these changes in the displacements counterbalance one another and lead to essentially the same over-all displacement and hence the same observed frequency. The usual relations between bond strength and stretching frequencies strictly apply only to diatomic gaseous molecules, and the present case is an example where extension of these relations to polyatomic molecules is not successful.

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Stereochemistry of Organophosphorus Complexes of Transition Metals

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Syntheses for 20 new complexes of the type $[M(CO)_4L_2]$ and $[M'X_2L_2]$ where M = Cr, Mo, or W; M′ = Pd or Pt; X = Cl or I; and L = $P(CH_3)_3$, $P(CH_2Cl)_3$, $P(CH_2O)_3CCH_3$, $P(N(CH_3)_2)_3$, $P(OCH_2)_3CC_2H_5$, and $P(OCH_2)_3C(CH_2)_4CH_3$ are described. An improved method is presented for the preparation of the dichloro Pt and Pd(II) complexes from the corresponding dichlorobis(benzonitrile)metal(II) compound in cases where the ligand or derived complex is easily solvolyzed. Both near- and far-infrared measurements are interpreted in terms of the *cis* and *trans* geometry of all of the complexes. Metal–phosphorus stretching frequencies from 220 to 214 cm^{-1} were assigned in three of the carbonyl complexes. The required number of metal–chlorine modes could be identified in all of the Pt and Pd(II) complexes: 329–362 cm^{-1} in the *trans* compounds and 289–334 cm^{-1} in the *cis*. Metal–iodine modes in the Pt and Pd(II) systems could be assigned with reasonable certainty in only two of the *trans* (151, 158 cm^{-1}) and one of the *cis* (157, 150 cm^{-1}) compounds because their intensities were generally low.

A number of examples of $P^{31}–P^{31}$ spin–spin coupling in various complexes containing two phosphorus nuclei have been reported.[1–5] In order to gain some insight into the nature of this interaction and its relation to the phosphorus–metal bond, a new experimental approach has been developed involving the study of $P^{31}–P^{31}$ spin–spin coupling constants in disubstituted complexes as a function of ligand strength and coordination geometry.[6] To enlarge the scope of our study, the preparation of new disubstituted complexes containing various phosphorus ligands was undertaken.

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TABLE I

ANALYTICAL DATA

Compound	% C		% H		% Q	
	Calcd	Found	Calcd	Found	Calcd	Found
cis- and *trans*-$[Cr(CO)_4(P(CH_3)_3)_2]$	38.00	38.11	5.73	5.89	19.60	19.46[a]
cis-$[Mo(CO)_4(P(CH_3)_3)_2]$	33.33	32.34	5.00	4.84	17.22	16.57[a]
cis-$[Mo(CO)_4(P(CH_2Cl)_3)_2]$	21.20	21.42	2.12	2.21	37.50	37.38[b]
cis-$[W(CO)_4(P(CH_3)_3)_2]$	26.82	27.07	4.02	3.97	13.82	13.91[a]
trans-$[PdCl_2(P(CH_2Cl)_3)_2]$	13.23	13.49	2.22	2.33	52.10	52.90[b]
trans-$[PdI_2(P(CH_2Cl)_3)_2]$	9.91	9.83	1.66	1.73	14.59	14.53[d]
cis-$[PdCl_2(P(CH_2O)_3CCH_3)_2]$	25.38	25.35	3.84	3.65	14.95	14.99[b]
trans-$[PdI_2(P(CH_2O)_3CCH_3)_2]$	18.35	18.54	2.77	3.01	38.78	38.54[c]
trans-$[PdCl_2(P(N(CH_3)_2)_3)_2]$	28.63	29.01	7.21	7.20	14.10	14.23[b]
trans-$[PdI_2(P(N(CH_3)_2)_3)_2]$	20.99	20.67	5.29	5.39	36.99	36.75[c]
cis-$[PdCl_2(P(OCH_3)_3)_2]$	16.94	17.05	4.26	4.14	16.69	16.80[b]
cis-$[PdI_2(P(OCH_3)_3)_2]$	11.86	12.02	2.98	3.04	41.71	41.56[c]
cis-$[PdCl_2(P(OCH_2)_3CC_5H_{11})_2]$	36.90	37.12	5.86	6.00	12.22	12.05[b]
trans-$[PdI_2(P(OCH_2)_3CC_5H_{11})_2]$	28.18	28.07	4.46	4.55	33.02	32.78[c]
					13.85	13.58[d]
cis-$[PtCl_2(P(OCH_2)_3CC_2H_5)_2]$	24.40	25.82	3.73	3.95	12.03	11.60[b]
cis-$[PtI_2(P(OCH_2)_3CC_2H_5)_2]$	18.63	18.41	2.87	2.88	32.82	32.61[c]
cis-$[PtCl_2(P(OCH_2)_3CC_5H_{11})_2]$	32.06	32.18	5.09	5.11	10.51	10.79[b]
cis-$[PtI_2(P(OCH_2)_3CC_5H_{11})_2]$	25.22	25.49	4.00	4.05	29.60	29.41[c]
cis- and *trans*-$(PtCl_2(P(N(CH_3)_2)_3)_2]$	24.30	24.30	6.13	6.05	11.95	12.05[b]
trans-$[PtCl_2(P(N(CH_3)_2)_3)_2]$	24.30	24.05	6.13	6.28	11.95	12.07[b]
trans-$[PtI_2(P(N(CH_3)_2)_3)_2]$	18.60	18.87	4.68	4.76	32.78	32.48[c]

[a] Q = P. [b] Q = Cl. [c] Q = I. [d] Q = Pd.

We report here the preparation of some disubstituted octahedral group VI carbonyl complexes of trimethyl- and tris(chloromethyl)phosphine and some disubstituted square-planar palladium(II) and platinum(II) complexes with tris(chloromethyl)phosphine, tris(dimethylamino)phosphine, trimethyl phosphite, and the bicyclic phosphorus ligands $P(OCH_2)_3CC_2H_5$ (A), $P(OCH_2)_3C(CH_2)_4CH_3$ (A′), and $P(CH_2O)_3CH_3$ (B). A discussion of the P^{31}–P^{31} spin–spin coupling constants extracted from the H^1 nmr spectra of these and similar known complexes appears elsewhere.[6]

The hexacarbonyls of chromium, molybdenum, and tungsten form an extensive series of disubstituted complexes with phosphorus ligands which can exist in *cis* or *trans* forms.[7] Poilblanc and Bigorgne formed *cis*- and *trans*-$[Mo(CO)_4(P(CH_3)_3)_2]$ in solution by reaction of the hexacarbonyl and trimethylphosphine but did not characterize them further.[8] We have been able to isolate the *cis* isomers of the bis(trimethylphosphine) complexes of all three of the group VI metals as well as the *trans* isomers in the case of chromium from the appropriate bicyclo[2.2.1]heptadienemetal tetracarbonyls. In addition the *cis*-bis(tris(chloromethyl)phosphine)tetracarbonylmolybdenum(0) compound was also prepared.

Palladium(II) and platinum(II) form well-defined square-planar complexes of the type $[MX_2(L)_2]$ (M = Pd, Pt; X = anionic ligand; L = trialkylphosphine or trialkyl phosphite) which can exist as *cis* or *trans* isomers.[7,9,10] Similar complexes reported here with the ligands tris(chloromethyl)phosphine, tris(dimethylamino)phosphine, the bicyclic phosphine B, trimethyl phosphite, and the bicyclic phosphites A and A′ extend this series. An improved method is reported for the preparation of these platinum or palladium(II) complexes in cases where the ligand or derived complex is easily solvolyzed.

An interesting route has been reported to the formation of $[PdCl_2(P(OCH_3)_3)_2]$[9] and $[PtCl_2(P(OCH_3)_3)_2]$[10] in which methyl alcohol is allowed to react with the ligand in the appropriate dichlorobis(phosphorus trichloride)metal(II) complex. As reported herein, this method also can be used to make *cis*- and *trans*-$[PtCl_2(P(N(CH_3)_2)_3)_2]$.

Both near- and far-infrared data have been interpreted to determine the isomeric configuration of the new complexes as well as of the bis(trimethyl phosphite) complexes of palladium(II) and platinum(II) reported earlier.[9,10]

Experimental Section

Research quantities of tetrakis(hydroxymethyl)phosphonium chloride ($P(CH_2OH)_4Cl$) were obtained as a gift from Hooker Chemical Corp. and recrystallized from 1-propanol. Benzene was dried by the sodium–benzophenone–ketyl method. All other organic solvents were dried over Linde Molecular Sieve No. 3A. Other reagents were used without further purification. Infrared spectra of the group VI carbonyl complexes in the carbonyl region were obtained in cyclohexane solution and recorded on a Perkin-Elmer Model 21 double-beam spectrometer using sodium chloride optics. Far-infrared spectra, in the region 750–50 cm^{-1}, were obtained as Nujol mulls supported on polyethylene plates and were recorded on a Beckman IR-11 spectrometer. Values reported are correct to ±2 cm^{-1}. Melting points were taken in sealed capillaries and are uncorrected. The microanalyses in Table I were performed by Galbraith Laboratories Inc., Knoxville, Tenn.

Preparation of Organophosphorus Ligands.—Previously described methods were used to prepare trimethylphosphine,[11] tris-

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(chloromethyl)phosphine,[12] tris(dimethylamino)phosphine,[13] $P(OCH_2)_3CC_2H_5$ (A),[14] $P(OCH_2)_3C(CH_2)_4CH_3$ (A′),[15,16] and $P(CH_2O)_3CCH_3$ (B).[17] All yields of complexes are based on the metals.

Group VI Carbonyl Complexes.—All operations were carried out under dry nitrogen. The bicyclo[2.2.1]heptadienetetracarbonyl complexes of chromium,[17] molybdenum,[18] and tungsten[19] were synthesized according to methods given in the literature.

Bis(trimethylphosphine)tetracarbonylchromium(0), $[Cr(CO)_4(P(CH_3)_3)_2]$.—One-half milliliter (*ca.* 6.6 mmoles) of trimethylphosphine was condensed onto a suspension of 0.50 g (1.95 mmoles) of freshly sublimed bicyclo[2.2.1]heptadienetetracarbonylchromium(0) in 10 ml of cyclohexane at −196°. After agitation for 2 days at 25° the solvent was removed under reduced pressure to give a pale yellow solid. Recrystallization from pentane gave a mixture of colorless and pale yellow prisms (0.40 g), the infrared spectrum of which in the carbonyl region showed the product to be a mixture of *cis* and *trans* isomers. An attempt at mechanical separation was only partially successful but sufficient to identify the colorless form as the *cis* and the yellow form as the *trans* isomer. Both isomers decompose slowly in air and readily in organic solvents.

***cis*-Bis(trimethylphosphine)tetracarbonylmolybdenum(0), $[Mo(CO)_4(P(CH_3)_3)_2]$.**—One-half milliliter (*ca.* 6.6 mmoles) of trimethylphosphine was condensed onto a suspension of 0.75 g (2.50 mmoles) of bicyclo[2.2.1]heptadienetetracarbonylmolybdenum(0) in 10 ml of cyclohexane at −196°. On warming the mixture to room temperature and agitating, a colorless crystalline product formed which after filtration was recrystallized from pentane to give colorless needles, mp 95–96°, in 47% yield.

***cis*-Bis(trimethylphosphine)tetracarbonyltungsten(0), $[W(CO)_4(P(CH_3)_3)_2]$.**—This complex was prepared in a manner analogous to the corresponding molybdenum one but using bicyclo[2.2.1]heptadienetungsten(0). It was obtained as pale yellow needles, mp 106–107°, in 55% yield.

***cis*-Bis(tris(chloromethyl)phosphine)tetracarbonylmolybdenum(0), $[Mo(CO)_4(P(CH_2Cl)_3)_2]$.**—A stirred solution of 0.40 g (1.33 mmoles) of bicyclo[2.2.1]heptadienemolybdenum(0) in 10 ml of pentane was treated at room temperature with 0.38 g (3.00 mmoles) of tris(chloromethyl)phosphine to give a colorless precipitate. After 5 min the product was filtered and recrystallized from pentane to give colorless needles, mp 81–83°, in 81% yield.

Palladium Complexes.—Standard methods were used to prepare sodium tetrachloropalladate(II)[20] and bis(benzonitrile)palladium(II).[21]

***trans*-Dichlorobis(tris(chloromethyl)phosphine)palladium(II), $[PdCl_2(P(CH_2Cl)_3)_2]$.**—To a stirred solution of 0.80 g (2.72 mmoles) of sodium tetrachloropalladate(II) in 15 ml of ethanol was added 0.73 ml (5.44 mmoles) of tris(chloromethyl)phosphine. A yellow solid formed immediately. After the reaction mixture was heated until boiling and cooled, the solvent was removed under reduced pressure. The chloroform-soluble extract was filtered and evaporated to dryness under reduced pressure to give a yellow solid which when recrystallized from methanol gave yellow prisms, mp 170–172° dec, in 83% yield.

***trans*-Diiodobis(tris(chloromethyl)phosphine)palladium(II), $[PdI_2(P(CH_2Cl)_3)_2]$.**—A large excss of sodium iodide was added to a stirred solution of 0.50 g of *trans*-dichlorobis(tris(chloromethyl)phosphine)palladium(II) in 15 ml of acetone. After 15 min the solvent was removed under reduced pressure. The dichloromethane-soluble extract was filtered and evaporated to dryness under reduced pressure to give an orange-red solid which when recrystallized from ethanol gave orange-red prisms, mp 159–160°, in 91% yield.

***cis*-Dichlorobis(A′)palladium(II), $[PdCl_2(P(OCH_2)_3C(CH_2)_4CH_3)_2]$.**—One gram (5.74 mmoles) of anhydrous dichloropalladium(II) was dissolved in a minimum of concentrated hydrochloric acid and then evaporated to dryness. The solid residue was dissolved in 25 ml of ethanol, 2.30 g (11.5 mmoles) of A′ added, and the solution shaken for 12 hr. The solid was filtered and recrystallized from acetonitrile to give pale yellow prisms in 43% yield.

***trans*-Diiodobis(A′)palladium(II), $[PdI_2(P(OCH_2)_3C(CH_2)_4CH_3)_2]$.**—A suspension of 0.60 g (1.02 mmoles) of dichlorobis(A′)palladium(II) in 20 ml of acetone was treated with 1.0 g (6.7 mmoles) of sodium iodide and the mixture shaken for 4 hr at room temperature. Evaporation of the solvent gave a solid residue which was washed several times with water followed by diethyl ether. The compound was dried under vacuum at room temperature and recrystallized from acetonitrile to give red prisms in 63% yield.

Palladium Complexes *via* Dichlorobis(benzonitrile)palladium(II).—A typical example of a methathetical reaction involving an organophosphorus ligand and the benzonitrile complex is given in detail. The next three preparations were thus carried out in a similar fashion.

***trans*-Dichlorobis(tris(dimethylamino)phosphine)palladium(II), $[PdCl_2(P(N(CH_3)_2)_3)_2]$.**—To a stirred suspension of 0.965 g (2.50 mmoles) of *trans*-dichlorobis(benzonitrile)palladium(II) in 15 ml of dry benzene was quickly added 0.85 ml (5.25 mmoles) of tris(dimethylamino)phosphine. The solution immediately changed from dark red to pale yellow, and a yellow crystalline precipitate formed. After 30 min, 10 ml of pentane was added to the solution to cause further precipitation. The solid was filtered and washed three times with pentane then recrystallized from benzene to give orange-yellow prisms, dec pt above 120°, in 83% yield.

***cis*-Dichlorobis(trimethyl phosphite)palladium(II), $[PdCl_2(P(OCH_3)_3)_2]$.**—This complex was recrystallized from a dichloromethane–*n*-hexane mixture to give colorless prisms, mp 128–129° dec, in 96% yield.

***cis*-Dichlorobis(B)palladium(II), $[PdCl_2(P(CH_2O)_3CCH_3)_2]$.**—This compound was recrystallized from acetonitrile to give pale yellow needles, dec pt above 135°, in 79% yield.

Diiodopalladium(II) Complexes.—The three diiodo derivatives of the above three complexes were prepared by metathesis with sodium iodide on the dichloro complexes as described for *trans*-diiodobis(tris(chloromethyl)phosphine)palladium(II) except in the case of the tris(dimethylamino)phosphine complex in which the complex was extracted with benzene.

***trans*-Diiodobis(tris(dimethylamino)phosphine)palladium(II), $[PdI_2(P(N(CH_3)_2)_3)_2]$.**—This complex recrystallized from a benzene–*n*-hexane mixture to give red prisms in 91% yield.

***cis*-Diiodobis(trimethyl phosphite)palladium(II), $[PdI_2(P(OCH_3)_3)_2]$.**—This compound recrystallized from a benzene–*n*-hexane mixture to give orange prisms, mp 115–116° dec, in 52% yield.

***cis*-Diiodobis(B)palladium(II), $[PdI_2(P(CH_2O)_3CCH_3)_2]$.**—This complex recrystallized from a dichloromethane–*n*-hexane mixture to give orange prisms in 63% yield.

Platinum Complexes.—Standard methods were used to prepare potassium tetrachloroplatinate(II),[22] *cis*-dichlorobis(benzonitrile)platinum(II),[23] dichlorobis(trichlorophosphine)platinum(II),[10] and *cis*-dichloro- and *cis*-diiodobis(trimethyl phosphite)platinum(II).[10]

***cis*- and *trans*-Dichlorobis(tris(dimethylamino)phosphine)plati-**

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num(II), $[PtCl_2(P(N(CH_3)_2)_3)_2]$. Four milliliters (60.5 mmoles) of dimethylamine was condensed onto a suspension of 2.0 g (3.70 mmoles) of $[PtCl_2(PCl_3)_2]$ in 5 ml of toluene at −196°. The mixture was allowed to warm to room temperature and was then agitated for 1 hr to give a pale yellow suspension. Pentane was added and the solution filtered. The solid was washed with pentane and extracted with hot benzene. Evaporation almost to dryness at reduced pressure followed by the addition of *n*-hexane gave a pale yellow solid which when recrystallized from a benzene–*n*-hexane mixture gave a mixture of colorless and yellow microprisms in 51% yield. Attempts to separate the mixture by recrystallization failed. The *trans* isomer could be obtained pure by chromatography using a silica column and eluting with benzene, but the *cis* isomer remained at the top of the column and rapidly decomposed.

***trans*-Dichlorobis(tris(dimethylamino)phosphine)platinum(II), $[PtCl_2(P(N(CH_3)_2)_3)_2]$.**—One milliliter (6.15 mmoles) of tris(dimethylamino)phosphine was added to a stirred suspension of 1.20 g (2.54 mmoles) of $[PtCl_2(C_6H_5CN)_2]$ in 10 ml of benzene. After 4 hr the pale yellow solid was filtered and washed several times with pentane. Recrystallization of the solid from benzene gave lemon yellow prisms, dec pt above 182°, in 77% yield.

***trans*-Diiodobis(tris(dimethylamino)phosphine)platinum(II), $[PtI_2(P(N(CH_3)_2)_3)_2]$.**—This complex was prepared in an analogous manner to that of the corresponding palladium complex and recrystallization from benzene gave orange prisms, dec pt above 150°, in 53% yield.

***cis*-Dichlorobis(A)platinum(II), $[PtCl_2(P(OCH_2)_3CC_2H_5)_2]$.**—To a solution of 0.94 g (2.40 mmoles) of potassium tetrachloroplatinate(II) in 25 ml of water was added 0.91 g (5.62 mmoles) of A in 15 ml of ethanol. The solution was warmed on a steam bath for 0.5 hr. After cooling, the mixture was filtered to give a colorless solid which was dried under vacuum at room temperature. The product was recrystallized from acetonitrile to give colorless prisms in 53% yield.

***cis*-Diiodobis(A)platinum(II), $[PtI_2(P(OCH_2)_3CC_2H_5)_2$.**—This was prepared in an analogous manner to that of *trans*-$[PdI_2(A')_2]$. The complex was recrystallized from acetonitrile to give pale yellow prisms in 45% yield.

***cis*-Dichlorobis(A′)platinum(II), $[PtCl_2(P(OCH_2)_3C(CH_2)_4CH_3)_2]$.**—This was prepared as was the analogous complex of ligand A and was obtained in 51% yield.

***cis*-Diiodobis(A′)platinum(II), $[PtI_2(P(OCH_2)_3C(CH_2)_4CH_3)_2]$.**—This was prepared as was the complex of ligand A and was obtained as pale yellow prisms in 40% yield.

Discussion

While *trans*-$[PdCl_2(P(CH_2Cl)_3)_2]$, *cis*-$[PdCl_2(A')_2]$, *cis*-$[PtCl_2(A)_2]$, and *cis*-$[PtCl_2(A')_2]$ were made from the appropriate tetrahalometalate ion in aqueous ethanol, *trans*-$[PdCl_2(P(N(CH_3)_2)_3)_2]$, *cis*-$[PdCl_2(B)_2]$, *cis*-$[PdCl_2(P(OCH_3)_3)_2]$, and *trans*-$[PtCl_2(P(N(CH_3)_2)_3)_2]$ were found to form smoothly and in excellent yields from the appropriate dichlorobis(benzonitrile)metal(II) complex in benzene. The latter method is advantageous where the ligand or its complexes are easily solvolyzed since the inert solvent, benzene, can be employed. Moreover, this procedure eliminates the necessity of using the hygroscopic complex $[PdCl_2(PCl_3)_2]$ or its platinum(II) analog which are not very versatile in terms of the variety of ligands which can be formed by reaction in their coordination sphere. Attempts to prepare the palladium(II) complexes synthesized from the benzonitrile complex *via* the tetrahalopalladate(II) ions produced only intractable oils and solids.

It should be noted that the metathesis of the benzonitrile palladium(II) complex has been carried out previously with olefins [24,25] and allenes.[26] More recently, while our work was in progress, Burmeister[27] synthesized palladium(II) complexes by this method with thiourea, 2,3,5,6-tetraphenylpyridine, and diphenylphosphinoethane. Although the bis(benzonitrile)palladium(II) and -platinum(II) complexes are *trans* and *cis*, respectively,[28,29] the configuration of the metathetical product depends upon the substituting ligand in a manner which at present is not clear.

The disubstituted tertiary phosphine carbonyl complexes were assigned configurations primarily from the number of carbonyl stretching absorptions observed for their cyclohexane solutions. The *cis* complexes showed the typical[8,30] four absorptions, and the *trans*, only one as shown in Table II. Further evidence for the *cis* configuration of $[Mo(CO)_4(P(CH_3)_3)_2]$, $[W(CO)_4(P(CH_3)_3)_2]$, and $[Mo(CO)_4(P(CH_2Cl)_3)_2]$ is given by their far-infrared spectra in the region 700–340 cm^{-1}. Apart from phosphine ligand absorptions, the metal–carbon stretching, metal–phosphorus stretching, and metal–carbon–oxygen bending modes occur in this region.[31–33] The nonphosphorus ligand bands can be readily distinguished by comparison with the far-infrared spectra of the corresponding dichloropalladium(II) complexes. For group VI metal complexes of D_{4h} symmetry it has been shown that only one metal–phosphorus stretching, one metal–carbon stretching, and two metal–carbon–oxygen bending modes should appear in the infrared region. In contrast, the *cis* isomer (C_{2v} symmetry) should exhibit four metal–carbon stretching (ν(M–C)), six metal–carbon–oxygen bending (δ(M–C–O)), and two metal–phosphorus stretching (ν(M–P)) infrared-active modes.[31–33] In bis(tertiary phosphine) complexes of this type, δ(M–C–O) and ν (M–C) occur in the range 610–360 cm^{-1} [8, 32] with the δ(M–C–O) at highest and ν(M–C) at lowest frequencies. Owing to extensive coupling, the observed infrared bands cannot be given unique assignments and at best can be described as arising primarily from a bending or stretching mode. For this reason both δ(M–C–O) and ν(M–C) are presented together in Table III along with values as-

TABLE II

CARBONYL STRETCHING FREQUENCIES OF GROUP VI COMPLEXES

Compound	γ(CO), cm^{-1}
cis-$[Cr(CO)_4(P(CH_3)_3)_2]$	2000 m, 1890 sh, 1876 s, 1858 sh
trans-$[Cr(CO)_4(P(CH_3)_3)_2]$	1876 s
cis-$[Mo(CO)_4(P(CH_3)_3)_2]$	2024 m, 1930 sh, 1901 s, 1879 sh
cis-$[Mo(CO)_4(P(CH_2Cl)_3)_2]$	2032 m, 1952 sh, 1932 s, 1928 sh
cis-$[W(CO)_4(P(CH_3)_3)_2]$	2012 m, 1912 s, 1893 s, 1865 sh

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TABLE III

FAR-INFRARED SPECTRA OF GROUP VI METAL COMPLEXES

Compound	δ(M–C–O), γ(M–C), cm^{-1}	γ(M–P), cm^{-1}
cis-$[\mathrm{Mo(CO)_4(P(CH_3)_3)_2}]$	616 s, 590 sh, 584s, 553 sh, 488 m, 455 w, 440 m, 410 s, 395 s	214 m^b
cis-$[\mathrm{Mo(CO)_4(P(C_2H_5)_3)_2}]^a$	608 s, 586 s, 575 s, 428 m, 413 m, 404 m, 392 s	
trans-$[\mathrm{Mo(CO)_4(P(C_2H_5)_3)_2}]^a$	631 s, 573 s, 405 s	
cis-$[\mathrm{Mo(CO)_4(P(CH_2Cl)_3)_2}]$	603 s, 581 s, 565 sh, 542 m, 480 m, 448 m, 426 sh, 402 m, 382 s	200 m^b
cis-$[\mathrm{W(CO)_4(P(CH_3)_3)_2}]$	601 s, 582 s, 568 s, 540 sh, 493 m, 457 m, 418 m, 395 s	205 s, 189 sh

^{a} See ref 8. ^{b} Broad.

signed for *cis*- and *trans*-$[\mathrm{Mo(CO)_4(P(CH_2CH_3)_3)_2}]$[8] for comparison. In zerovalent carbonyl complexes with substituted organophosphorus ligands ν(M–P) values have been assigned in the range 140–260 cm^{-1},[31,34] and on this basis we have assigned ν(M–P) in these complexes to isolated medium–strong intensity peaks at approximately 200 cm^{-1}.

TABLE IV

FAR-INFRARED SPECTRA OF Pd(II) AND Pt(II) COMPLEXES

Compound	ν(M–X), cm^{-1}	750–350 cm^{-1}	350–140 cm^{-1}
trans-$[\mathrm{PdCl_2(P(CH_2Cl)_3)_2}]$	362 s	670 s, 652 sh, 383 s	340 s, 243 s, 204 s, 174 s
trans-$[\mathrm{PdI_2(P(CH_2Cl)_3)_2}]$	158 s	662 s, 655 sh, 375 s	338 s, 273 m, 265 m, 234 m, 204 m
cis-$[\mathrm{PdCl_2(P(CH_2O)_3CCH_3)_2}]$	334 sh, 323 m	702 s, 682 s, 662 s, 655 s, 549 w, 527 s, 512 s, 435 s	294 s, 266 s, 205 m, 193 m, 164 m, 162 w, 144 m
trans-$[\mathrm{PdI_2(P(CH_2O)_3CCH_3)_2}]$	151 s	700 m, 660 s, 500 s, 437 s	290 vs, 273 vs, 260 sh, 198 m, 165 m, 139 m
trans-$[\mathrm{PdCl_2(P(N(CH_3)_2)_3)_2}]$	357 m	692 s, 652 s, 510 s, 450 sh, 440 m	344 m,^{a} 311 m^a
cis-$[\mathrm{PdCl_2(P(OCH_3)_3)_2}]$	326 m, 307 m	553 s, 535 s, 447 s, 400 s	295 sh, 274 m, 260 sh, 239 sh, 211 w, 160 w^a
cis-$[\mathrm{PdI_2(P(OCH_3)_3)_2}]$		553 s, 537 s, 437 m, 400 s	310 m,^{a} 284 s, 252 s, 182 w, 140 m
cis-$[\mathrm{PdCl_2(P(OCH_2)_3CC_5H_{11})_2}]$	332 vs, 305 vs	675 s, 584 m, 570 s, 490 w, 414 m, 385 w, 363 m	264 m, 228 w, 207 w, 187 m, 153 w
trans-$[\mathrm{PdI_2(P(OCH_2)_3CC_5H_{11})_2}]$		673 s, 563 s, 517 s, 383 m, 363 m	325 w, 267 m, 259 sh, 176 w, 135 w
trans-$[\mathrm{PtCl_2(P(N(CH_3)_2)_3)_2}]$	329 s	692 s, 651 s, 511 s, 455 sh, 442 s	313 sh, 276 m,^{a} 170 m^a
trans-$[\mathrm{PtI_2(P(N(CH_3)_2)_3)_2}]$		685 s, 651 s, 510 s, 465 w, 438 m	320 m, 202 w^a
cis-$[\mathrm{PtCl_2(P(OCH_3)_3)_2}]$	310 s, 289 s^b	558 s, 537 s, 450 s, 402 s	256 sh, 237 sh, 224 w, 150 m^a
cis-$[\mathrm{PtI_2(P(OCH_3)_3)_2}]$		562 s, 543 s, 449 m, 385 m	322 w, 289 s, 266 w, 218 w, 148 m^a
cis-$[\mathrm{PtCl_2(P(OCH_2)_3CC_2H_5)_2}]$	334 vs, 308 vs	660 s, 643 s, 549 sh, 541 m, 494 m, 427 s, 393 m, 369 m	280 w,^{a} 230 m, 197 w,^{a} 178 w,^{a} 166 w^a
cis-$[\mathrm{PtI_2(P(OCH_2)_3CC_2H_5)_2}]$	157 m, 150 m	664 s, 647 s, 533 m, 522 m, 493 m, 421 s, 377 sh, 369 s	268 m, 225 w, 210 w, 188 m,^{a} 170 w
cis-$[\mathrm{PtCl_2(P(OCH_2)_3CC_5H_{11})_2}]$	329 vs, 303 vs	676 s, 593 s, 576 s, 492 m, 422 s, 388 m, 367 s	270 m, 209 w, 193 m, 162 w^a
cis-$[\mathrm{PtI_2(P(OCH_2)_3CC_5H_{11})_2}]$		675 s, 591 s, 575 s, 494 w, 421 s, 385 m, 365 m	328 w, 267 m, 216 w,^{a} 188 w,^{a} 162 w^a

^{a} Broad. ^{b} Most intense peaks in a broad band from 315 to 270 cm^{-1}.

The insolubility of most of the complexes of palladium and platinum(II) in solvents with low dielectric constants prohibited the determination of their dipole moments. An attempt was made with *trans*-$[\mathrm{PdCl_2(P(N(CH_3)_2)_3)_2}]$ in benzene solution but during the determination a small amount of pale yellow solid precipitated out of solution and the calculated value for the dipole moment was 2.1 D. This suggests that some isomerization took place to give the *cis* isomer. The solubility of the complexes in benzene was used as an indication of their stereochemistry. Thus $[\mathrm{PdCl_2(P(OCH_3)_3)_2}]$, assigned the *cis* configuration, was insoluble in benzene in contrast to $[\mathrm{PdCl_2(P(CH_2Cl)_3)_2}]$, assigned the *trans* configuration, which showed appreciable solubility in benzene. The majority of the complexes were insoluble in benzene. Supporting albeit inconclusive evidence for the configuration of the complexes is given by their color. Complexes of palladium(II) chloride are generally colorless or pale yellow when *cis* whereas the *trans* isomers are orange and yellow.[7] All of our chloro complexes apart from those of tris(dimethylamino)phosphine and tris(chloromethyl)phosphine were colorless or pale yellow. In a similar manner the colors of the diiodo complexes were used to indicate their stereochemistry.

The configurations of these complexes were primarily determined from their far-infrared spectral data shown in Table IV. In square-planar complexes with the *cis* (C_{2v} symmetry) configuration, both the symmetric and antisymmetric metal–halogen stretching modes are infrared active whereas in the *trans* isomers (D_{2h} symmetry) only the antisymmetric stretching mode is infrared active. It has been shown that the metal–chlorine stretching frequencies generally appear as strong absorptions in the region 360–270 cm^{-1} for platinum(II) and palladium(II) complexes[35–39] while the

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metal–iodine stretching modes appear at much lower frequencies in the range 191–167 cm^{-1}.[38,40,41] In general, for our dichloro complexes, the metal–chlorine absorptions were readily apparent, but, to confirm these assignments, comparison was made with the corresponding diiodo complexes. As there was little change in the portion of the spectrum due to the phosphorus ligands between the dichloro and diiodo complexes, the metal–chlorine absorptions were identified without difficulty.

The antisymmetric metal–chlorine stretching mode for the palladium(II) and platinum(II) complexes falls between 362 and 289 cm^{-1}. These values for the *trans*-[$PdCl_2(P(N(CH_3)_2)_3)_2$] and *trans*-[$PdCl_2(P(CH_2Cl)_3)_2$] (362 and 357 cm^{-1}, respectively) are similar to those found in *trans*-[$PdCl_2L_2$] where L = diethyl sulfide (358 cm^{-1}) and triethylphosphine (355 cm^{-1}).[36] The only *trans*-dichloroplatinum(II) complex we obtained, the tris(dimethylamino)phosphine derivative, exhibited the metal–chlorine stretching frequency at 329 cm^{-1}. The substantial decrease of 33 cm^{-1} in this frequency from the palladium(II) analog is paralleled by similar decreases from *trans*-[$PdCl_2(S(CH_2CH_3)_2)_2$] and *trans*-[$PdCl_2(P(CH_2CH_3)_3)_2$] to their platinum analogs of 16 and 15 cm^{-1}, respectively.[35]

Both the symmetric and antisymmetric modes could be identified in all of the *cis* platinum(II) and palladium(II) complexes, the former modes appearing between 334 and 289 cm^{-1} and the latter being between 11 and 27 cm^{-1} lower. It is interesting to note the constancy in both metal–halogen frequencies in the *cis*-dichloropalladium(II) complexes of phosphites A′ (332, 305 cm^{-1}), trimethyl phosphite (326, 307 cm^{-1}), and phosphine B (334, 323 cm^{-1}) and that the values are similar to those assigned in *cis*-[$PdCl_2(NH_3)_2$] (327, 306 cm^{-1}).[41] We have tentatively assigned the two ν(Pd–Cl) modes in *cis*-[$PdCl_2(B)_2$] to absorptions at 334 and 323 cm^{-1} by comparisons with the spectra of the *trans*-diiodo complex. These values are somewhat difficult to explain when compared with those of *cis*-[$PdCl_2(P(CH_3)_3)_2$] (294, 282, 270 cm^{-1}).[36] Although Coates and Parkin ascribed all three of the bands in the latter complex to Pd–Cl stretching modes, comparison with the free-ligand spectrum is in accord with assignment of the band at 294 cm^{-1} to a ligand band leaving the bands at 282 and 270 cm^{-1} to account for the Pd–Cl stretching modes. If these assignments in both compounds are correct, it is not clear why they occur in different regions of the spectrum for such similar ligands.

In the case of the *cis*-dichloroplatinum(II) complexes of A and A′, the metal–chlorine stretching modes are similar to those for the corresponding palladium complexes, but there is a marked drop in the frequencies of these two bands (*ca.* 20 for the higher and 25 cm^{-1} for the lower) for *cis*-[$PtCl_2(P(OCH_3)_3)_2$]. These values for the latter complex (310, 289 cm^{-1}) correspond more closely to those of *cis*-[$PtCl_2(P(CH_2CH_3)_3)_2$] (303, 280 cm^{-1}).[35]

Unfortunately the intensities of the metal–iodine stretching vibrations are low and we were only able to locate these bands with fair certainty in a limited number of cases. An aid in determining the isomeric configuration of these complexes was the number of bands ascribable to the ligand vibrations in the 700–400-cm^{-1} region. In all cases the number of these bands was the same in corresponding diiodo and dichloro complexes (suggesting similar geometries) except for the palladium(II) complexes of A′ and B where diiodo compounds showed fewer bands. Combined with the other evidence already discussed, the disparity in the number of these bands for the latter complexes indicates that the dichloropalladium(II) complexes of A′ and B are *cis* while the diiodo analogs are *trans*.

It was not always possible to locate the metal–iodine absorptions in the diiodo complexes; however, strong peaks which were absent in the dichloro complexes were assigned to this vibration in *trans*-[$PdI_2(P(CH_2Cl)_3)_2$] at 158 cm^{-1} and in *trans*-[$PdI_2(B)_2$] at 151 cm^{-1}. In only one *cis*-diiodo complex, namely, *cis*-[$PtI_2(A)_2$], was it possible to locate two absorptions due to the symmetric (157 cm^{-1}) and antisymmetric (150 cm^{-1}) metal–iodine stretching modes.

Although the number of metal–phosphorus absorptions would have been a valuable guide to the stereochemistry of these complexes, we are not presently able to make such assignments with confidence. A detailed investigation directed toward assigning this mode in these and related complexes is in progress.

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