$\bar{D}(AI_n)] = 16 \pm 3$ kcal, where A = Al, Si, Ge, Sn, Pb, As.[28,29]

It is concluded that a covalent model involving d^2s hybrid orbitals on the lanthanide provides a better basis for understanding the thermochemical atomization energies of the lanthanide trihalides than does the ionic model. However, more work, both theoretical and experimental, is obviously needed. With respect to the latter, a redetermination of the enthalpy of sublimation of europium would seem to have high priority, followed closely by enthalpies of formation and sublimation of the bromides as well as determination of missing values for the other halides. Hopefully, atomic and molecular spectroscopic studies will provide additional clarification.

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Tungsten Carbonyl Complexes as Ligands

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Phosphorus–phosphorus coupling through a metal atom in complexes containing two chemically nonequivalent phosphorus atoms may be measured directly from the ^{31}P spectrum of the complex.[3,4] If the phosphorus atoms are chemically equivalent, however, this direct approach is not possible although the value of the coupling constant can often be obtained from the ^1H spectrum of the complex by band shape analysis, by use of double resonance techniques, and in some instances by observation of weak-intensity ($\chi = 1$) wing peaks.[5-9] Values of $^2J_{PP}$ reported for cis square planar complexes of platinum(II), $(R_3P)_2PtCl_2$, have all been obtained by computer simulation techniques and this method has been shown to be somewhat unreliable.[5] In this study we have utilized the unique ligand, $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$, to obtain $^2J_{PP}$ for the chemically equivalent phosphorus nuclei in the complex *cis*-$[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2PtCl_2$.

In addition, the ligating properties of $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ have been further examined by isolating and characterizing the complexes $[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2Hg_2Cl_4$ and $(OC)_5WP(C_6H_5)_2CH_2CH_2P(O)(C_6H_5)_2$.

Experimental Section

Phosphorus-31 nmr spectra were recorded with a Varian XL-100 spectrometer equipped with Fourier transform and a pulsed deuterium lock. The samples were examined in 12-mm tubes and 2.5 ml of $CDCl_3$ was used for solvent and lock. Phosphoric acid (85%) in a 1.0-mm capillary was suspended in the sample as an external reference. Coupling constants are accurate to ±0.1 Hz. Infrared spectra in the carbonyl region were recorded with a Perkin-Elmer 337 infrared spectrometer. These spectra were expanded with an E. H. Sargent recorder and are considered accurate to ± 2 cm^{-1}. Polystyrene was used as a frequency standard and chloroform was used as a solvent for each measurement. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparations. The ligand, $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$, was prepared as previously described.[10]

***cis*-$[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2PtCl_2$ and $(OC)_5WP(C_6H_5)_2CH_2CH_2P(O)(C_6H_5)_2$.** To 50 ml of ethanol were added $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ (1.03 g, 0.00143 mol) and K_2PtCl_4 (0.3 g, 0.0007 mol). The reaction mixture was stirred for 2 days at 35° after which time all traces of the red K_2PtCl_4 had disappeared. The fine white precipitate which resulted was washed with water and recrystallized from a 50% methanol–dichloromethane solution to give 0.3 g of white crystals which were found to decompose at 191–194°. *Anal.* Calcd for $C_{62}H_{48}O_{10}P_4W_2PtCl_2$: C, 43.53; H, 2.83; P, 7.24; Cl, 4.15. Found: C, 43.18; H, 2.70; P, 7.14; Cl, 4.30. The filtrate was taken to dryness and to the residue was added 20 ml of water. The water mixture was extracted with 10 ml of dichloromethane. To the dichloromethane was added an equal volume of methanol. The solution was heated on a steam bath until the volume was halved. Upon sitting for 12 hr, 0.2 g of the oxide complex, $(OC)_5WP(C_6H_5)_2CH_2CH_2P(O)(C_6H_5)_2$, precipitated. The compound was found to decompose at 170–175°. *Anal.* Calcd for $C_{31}H_{24}P_2O_6W$: C, 50.43; H, 3.28; P, 8.39. Found: C, 50.15; H, 3.26; P, 8.22.

$[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2Hg_2Cl_4$. To 50 ml of absolute ethanol were added $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ (0.50 g, 0.0069 mol) and $HgCl_2$ (0.19 g, 0.00070 mol). The solution became cloudy immediately. The mixture was stirred for 18 hr. Upon filtering the mixture 0.52 g of white crystals were collected. These were recrystallized with a 50% methanol–dichloromethane solution to give 0.41 g of the mercury–tungsten complex. The complex was found to decompose at 183–185°. *Anal.* Calcd for $C_{62}H_{48}P_4Hg_2W_2Cl_4O_{10}$: C, 37.46; H, 2.43; P, 6.23; Cl, 7.13. Found: C, 37.08; H, 2.50; P, 6.15; Cl, 6.97.

Results and Discussion

The structure of $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ has been previously established with ^{31}P nmr and its ligating tendencies have been demonstrated with the preparation of the quaternized product $(OC)_5WP(C_6H_5)_2CH_2CH_2P^+(C_6H_5)_2C_4H_9[PF_6^-]$ and the bimetallic product $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2W(CO)_5$.[10,11] In various organic

Table I. Phosphorus-31 Nmr Data[a]

Compd	$^1J_{W-P}$	δ_{W-P}	δ_P	$^2J_{PP}$	$^3J_{PP}$	$^1J_{Pt-P}$	$^1J_{Hg-P}$
$(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$	240.0	−11.4	13.7		37.2		
$(OC)_5WP(C_6H_5)_2CH_2CH_2P^+(C_6H_5)_2C_4H_9\,[PF_6^-]$	243.2	−15.2	−27.8		47.6		
$(OC)_5WP(C_6H_5)_2CH_2CH_2P(O)(C_6H_5)_2$	241.5	−13.3	−31.6		48.8		
$[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2Hg_2Cl_4$	243.4	−14.3	−34.6		47.2		7362
cis-$[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2PtCl_2$	240.3	−13.0	−6.8	14.3	43.6	3642	

[a] Chemical shifts are reported in ppm with respect to 85% H_3PO_4 with a positive value taken as upfield from the acid.

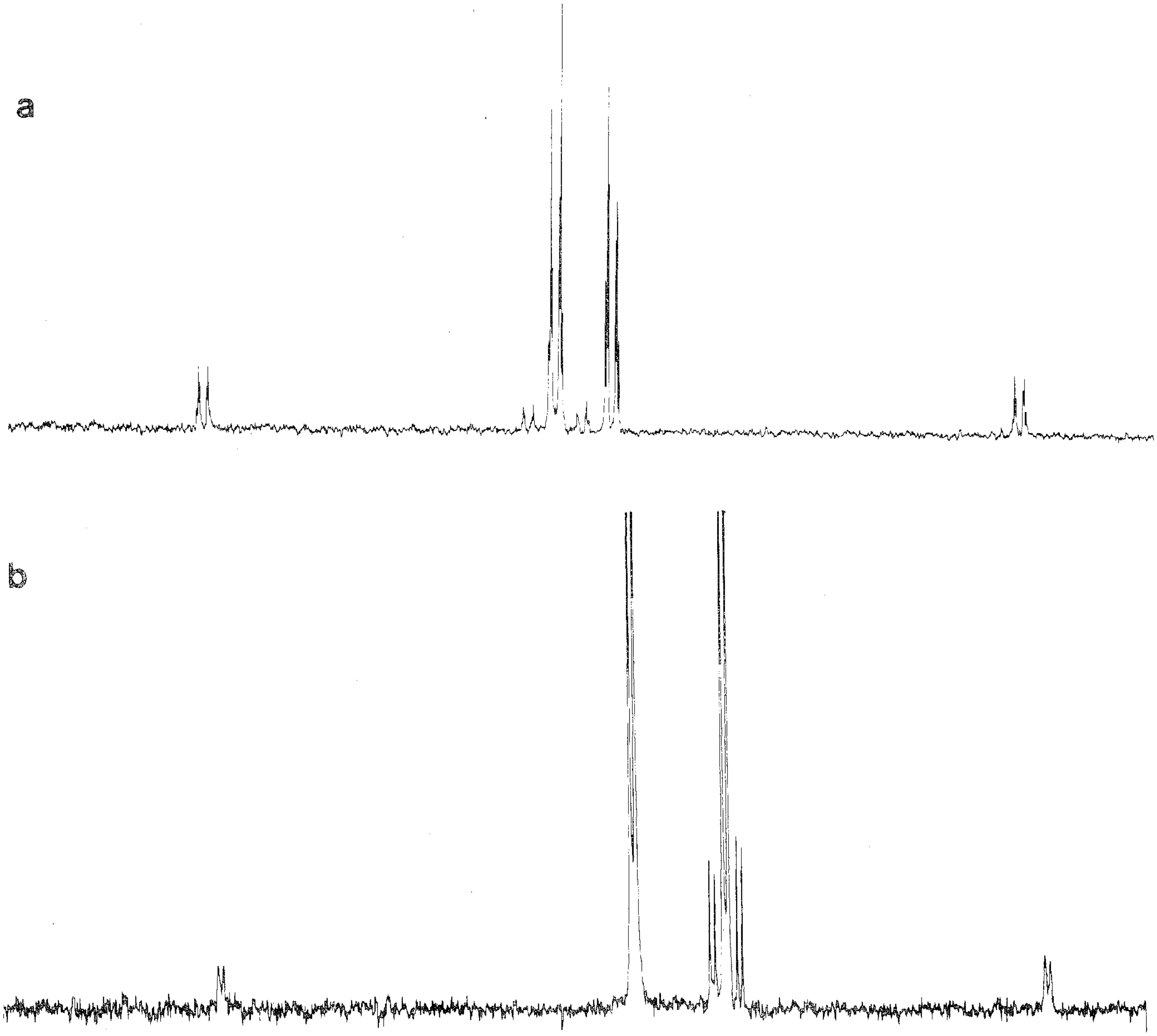


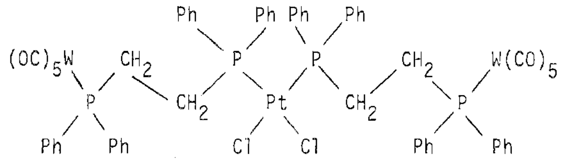
Figure 1. (a) ^{31}P-nmr spectrum of *cis*-$[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2PtCl_2$. (b) ^{31}P-nmr spectrum of $[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2Hg_2Cl_4$.

solvents at ambient temperature $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ is quite stable, showing no tendency for the free phosphine to displace a carbonyl group. The displacement reaction does proceed at elevated temperatures and its rate has been reported for those conditions.[12]

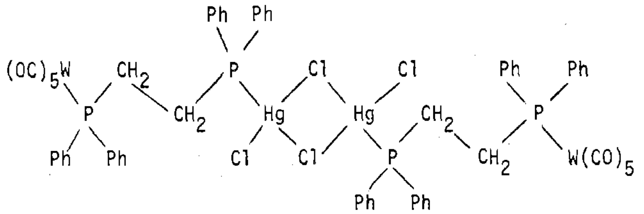
Solutions of *cis*-$[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2PtCl_2$ and of $[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2Hg_2Cl_4$ appear to be quite stable in solution as shown by the invariance of ^{31}P nmr and infrared spectra with time. No evidence for ligand exchange was noted.

Carbonyl stretching frequencies of both the mercury and platinum complexes were identical, within experimental error, to that of the starting carbonyl complex ligand. This result is not surprising since it has been shown previously that quaternizing the uncoordinated phosphorus atom of $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ does not lead to a change in the carbonyl stretching frequencies.[10]

Phosphorus-31 nmr data for the complexes are reported in Table I. The spectra of



and



are shown in Figure 1.

The ${}^1J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ value of 3642.3 Hz establishes the structure of $[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2PtCl_2$ to be cis rather than trans. The magnitude of the coupling compares well with that previously recorded for *cis*-$[(C_6H_5)_2(C_2H_5)P]_2PtCl_2$ (3640 Hz).[13] Square planar platinum(II) complexes of the trans configuration characteristically have coupling constants which are much smaller in magnitude than those of the cis configuration. For example, the value for *trans*-$[(C_2H_5)_2(C_6H_5)_2P]_2PtCl_2$ is 2482 Hz.[13]

For the purpose of determining the magnitude of ${}^2J_{PP}$ the platinum complex may be treated as an AA'XX' system. Spin systems of the type $AA'X_nX'_n$ have been discussed in detail by Harris.[7] For the platinum complex one can observe both the A and X parts in the ${}^{31}P$ spectrum. It is reasonable to assume that $J_{XX'}$ is zero since these nuclei are so far removed from each other. Both the X and A parts of the XX'AA' spectrum have three pairs of lines centered about $\nu_{(X)}$ and $\nu_{(A)}$, respectively (see Figure 1). Half of the total intensity lies in doublets with separations $N = |J_{AX} + J_{AX'}|$ and $N = |J_{AX} + J_{A'X}|$. The remaining intensity is divided between one pair of inner lines and one pair of outer lines for each part of the two-part spectrum. The quantity N was measured to be 43.6 Hz. From the separation of inner lines and outer lines ${}^2J_{PP}$ was determined to be 14.3 Hz. The absolute value of ${}^5J_{PP}$ was calculated to be smaller than experimental error.

The ${}^{31}P$ spectrum of the mercury complex is first order (see Figure 1). The magnitude of ${}^1J_{^{199}\mathrm{Hg}-^{31}\mathrm{P}}$ establishes the dimeric nature of the mercury complex. The dimers, $[(C_4H_9)_3P]_2Hg_2Cl_4$ and $[(C_4H_9)_2(C_6H_5)P]_2Hg_2Cl_4$, are reported to have mercury–phosphorus coupling constants of 7446 and 7514 Hz, respectively, while the monomers $[(C_4H_9)_3P]_2HgCl_2$ and $[(C_4H_9)_2(C_6H_5)P]_2HgCl_2$ have couplings of 5078 and 5035 Hz, respectively.[14]

In complexes of the type $R_3PW(CO)_5$ it is well established that the tungsten–phosphorus coupling constants increase as the electronegativities of the substituents on phosphorus increase.[15,16] It is apparent from the values of the tungsten–phosphorus coupling constants that the electronegativities of the substituents $CH_2CH_2P(C_6H_5)_2$, $CH_2CH_2P(O)(C_6H_5)_2$, $CH_2CH_2P(C_6H_5)_2Hg$, $CH_2CH_2P(C_6H_5)_2Pt$, and $CH_2CH_2P^+(C_6H_5)_2C_4H_9$ are all very similar.

The formation of the oxide, $(OC)_5WP(C_6H_5)_2CH_2CH_2P(O)(C_6H_5)_2$, as a minor product during the platinum complex synthesis was unexpected (see Experimental Section) and apparently is catalyzed by the presence of Pt(II). The P=O stretching occurs as a doublet (1168 and 1195 cm^{-1} in Nujol) and appears to be very much like the oxide spectra reported by Ercolani.[17] For the oxide one observes two separate ${}^{31}P$ resonances appearing as doublets, both downfield from 85% phosphoric acid, and one is flanked by tungsten–phosphorus satellites. The resonance at −13.3 ppm, assigned to the phosphorus attached to tungsten, agrees well with −11.4 ppm found for $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)$ and −15.2 ppm for $(OC)_5WP(C_6H_5)_2CH_2CH_2P^+(C_6H_5)_2C_4H_9[PF_6]^-$. The chemical shift at −31.6 ppm is assigned to phosphorus coordinated to oxygen, consistent with that reported for $(C_6H_5)_2(O)P(CH_2)_5P(O)(C_6H_5)_2$ (−31.8 ppm).[18]

In conclusion the ligand $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ has been shown to react with K_2PtCl_4 and $HgCl_2$ to yield stable, soluble complexes of high molecular weight. The ligand also provides a unique method of determining phosphorus–phosphorus coupling constants of chemically equivalent phosphorus nuclei.

Registry No. $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$, 35324-76-6; $(OC)_5WP(C_6H_5)_2CH_2CH_2P^+(C_6H_5)_2C_4H_9[PF_6^-]$, 39248-09-4; $(OC)_5WP(C_6H_5)_2CH_2CH_2P(O)(C_6H_5)_2$, 52843-30-8; $[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2Hg_2Cl_4$, 52843-29-5; *cis*-$[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2PtCl_2$, 52873-47-9; ${}^{31}P$, 7723-14-0.

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Rapid Oxygen Exchange between $[Mo(O)(OH)(CN)_4]^{4-}$ and Water

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For many years there has been confusion regarding the composition and structure of the species present in solution when $K_4[Mo(O)_2(CN)_4]$ is dissolved in water.[1-4] In particular, questions regarding the acid–base behavior of the ion and the coordination number (basic structures I or II) have not been completely settled. Recently the solid structures of two of these ions have been determined[5] ($[Mo(O)(OH)(CN)_4]^{3-}$ and $[Mo(O)(OH_2)(CN)_4]^{2-}$) by X-ray techniques. We had intended to use ${}^{18}O$ measurements to obtain information about the coordination number of these substances in solution and to study the kinetics of isotopic oxygen exchange as a function of solution composition. However, as will be shown, the isotopic water exchange under obtainable conditions is too rapid to allow structural or kinetic information to be obtained.

Results and Discussion

The treatment of $K_3[Mo(O)_2(CN)_4]$ with ${}^{18}O$-enriched water at 85–90° for 10 min and the subsequent isolation of the ion as anhydrous $K_3[Mo(O)(OH)(CN)_4]$ resulted in the complex ion having an ${}^{18}O$ content equal to that of the final