

TRANSITION METAL COMPLEXES OF HEXAPHENYLCARBODIPHOSPHORANE

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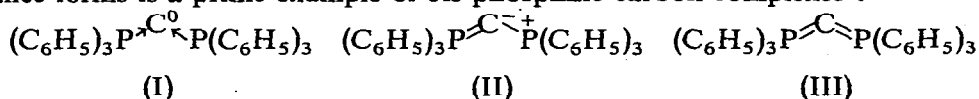
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SUMMARY

The displacement of tetrahydrofuran (THF) from $W(CO)_5(THF)$ with hexaphenylcarbodiphosphorane yields a compound with a carbon-metal bond $(CO)_5W-C[P(C_6H_5)_3]_2$. The *in situ* photolysis of tungsten hexacarbonyl and hexaphenylcarbodiphosphorane, however, yields a product $(CO)_5W^-C\equiv C-^+P(C_6H_5)_3$. Ethylenebis(triphenylphosphine)platinum and hexaphenylcarbodiphosphorane in benzene yield a platinum containing heterocycle $[(C_6H_5)_3P]_2Pt-C[=P(C_6H_5)_3]-P(C_6H_5)_3$.

Phosphorus ylides exhibit a broad spectrum of chemical reactivity with a variety of organic compounds and yet their potential chemistry as coordinated ligands to transition metal complexes has been scantily explored. Thus triphenylphosphoniumcyclopentadienide forms very stable complexes with certain metal carbonyls¹, methylenetriphenylphosphorane and ethylenetriphenylphosphorane coordinate to vanadium² and molybdenum³ carbonyls, respectively. Furthermore, recent studies have shown that phosphorus ylides form stable derivatives with platinum complexes and other heavy metal atoms⁴⁻⁶.

The scope of phosphorus ylide structure and reactivity is broadened by considering them as coordinatively unsaturated complexes of carbon. In particular, the bis-ylide hexaphenylcarbodiphosphorane⁷ which is illustrated below in three major resonance forms is a prime example of bis-phosphine carbon complexes⁸.



Although each resonance form is strictly a formalism, the structures suggest that a special kind of reactivity can be expected for this molecule. The first formal structure(I) implies that the carbodiphosphorane is a coordinatively unsaturated carbon complex with a formally zero-valent central atom stabilized by phosphine groups. In this way it resembles the coordinatively unsaturated low-valent transition metal phosphine complexes such as $[(C_6H_5)_3P]_3Pt \leftarrow P(C_6H_5)_3$. The second resonance form of the carbodiphosphorane(II) is similar to the familiar Wittig reagent and the third structure implies a molecule with heterocumulene chemistry.

This paper begins the exploration of a relationship between the chemistry of hexaphenylcarbodiphosphorane, a phosphorus-carbon coordinatively unsaturated complex, and low-valent transition metal derivatives.

RESULTS

Tungsten hexacarbonyl and hexaphenylcarbodiphosphorane

The interaction of hexaphenylcarbodiphosphorane with $W(CO)_6(THF)_2$, in a 1/1 molar ratio in THF yielded a bright yellow-orange solid which was extremely sensitive to moisture in THF solution. The solid was soluble in THF or dichloromethane, moderately soluble in ether and benzene, and insoluble in pentane. Fig. 1A shows the infrared spectrum of the complex in THF solution with bands at 2050 w, 1914s and 1882m cm^{-1} in the carbonyl stretching region. No bands attributed to tungsten hexacarbonyl were observed in the pure complex. When the solution remained in the infrared cell for 5 min, bands at 2039 w, 1941 s and 1851 m cm^{-1} increased in intensity. Repeated scanning in the range 2100–1700 cm^{-1} showed that the band at 2050 cm^{-1} merged to the band at 2039 cm^{-1} . The band at 1914 cm^{-1} was replaced by the 1941 cm^{-1} band and the peak at 1882 cm^{-1} was replaced by one at 1851 cm^{-1} , as shown in Fig. 1. The infrared spectrum of the complex in dichloroethane solution showed three bands in the carbonyl stretching region at 2048w, 1913s and 1861m cm^{-1} . The spectrum in dichloroethane had to be recorded immediately after preparation because another band at 1978 cm^{-1} , which was identified as tungsten hexacarbonyl, grew in intensity as the spectrum was repeatedly scanned. The tungsten hexacarbonyl, which was not originally present in the complex, could be isolated from the dichloroethane solution after removal of the solvent under nitrogen. Evidently the complex is slowly decomposed by halocarbon solvents.

When a similar interaction was performed with the carbodiphosphorane and $W(CO)_6(THF)_2$ in a 1/2 molar ratio, respectively, the bright yellow-orange solid which was isolated showed an infrared spectrum (THF solvent) identical to that obtained from the product of the 1/1 molar ratio interaction.

The addition of gaseous HCl to the orange THF solution of the complex gave a green solution from which tungsten hexacarbonyl was the only identifiable product. All of the infrared bands in the carbonyl stretching region for the complex were gone. However, if the infrared spectrum was recorded immediately after passing gaseous HCl into a solution of the complex, three new bands were observed at 2064w, 1922s and 1867 m cm^{-1} . As these peaks disappeared they were replaced by a band at 1978 cm^{-1} for tungsten hexacarbonyl.

The addition of dilute anhydrous HCl/THF to a dilute THF solution of the complex produced immediately a white precipitate and a yellow supernatant liquid which slowly became green. Infrared spectra of the yellow liquid were recorded after each addition of HCl/THF solution. The bands at 2050, 1914, 1882 cm^{-1} gradually disappeared and new bands appeared at 2064, 1922, and 1867 cm^{-1} . With additional HCl/THF, remnants of the most intense bands present in the original THF solution disappeared and the infrared spectrum in the carbonyl stretching region became featureless except for a peak at 1978 cm^{-1} which was tungsten hexacarbonyl.

The white precipitate was identified as methylenebis(triphenylphosphonium chloride) by its m.p., infrared spectrum and 1H NMR spectrum compared with an

authentic sample²⁴. The precipitate accounted for 96% of the ligand present in the complex.

The ³¹P NMR spectrum of the complex at 40.5 MHz in dichloroethane solution displayed only one peak at -20.7 ppm with respect to external H₃PO₄. One broad peak at -21.8 ppm was observed for the complex in THF solution. No other peaks were observed in the ³¹P NMR spectrum. If any free carbodiphosphorane had been present in solution, a peak at +5.0 ppm would have been observed.

The ¹H NMR spectrum of the complex in C₆D₆ showed two multiplets in the aromatic region at 60 MHz in the ratio of 2/3. These correspond to the *ortho* and *meta*+*para* protons of the triphenylphosphine group, respectively.

A 70 eV mass spectrum of the tungsten pentacarbonyl carbodiphosphorane complex showed a base peak of P(C₆H₅)₃⁺ (*m/e* 262) and W(CO)[C=P(C₆H₅)₃]⁺

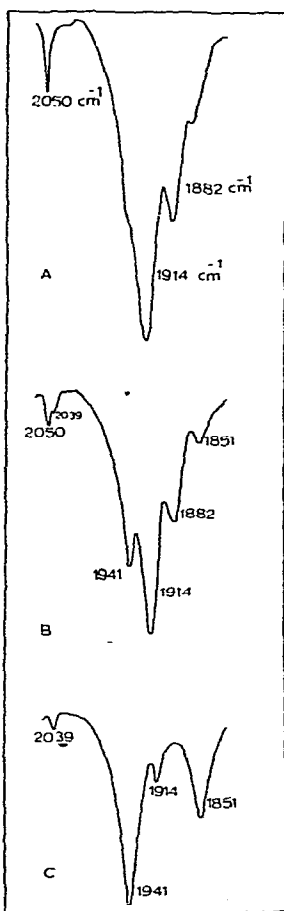


Fig. 1. Infrared spectra in the carbonyl stretching region of the product from the interaction of W(CO)₅-(THF) and [(C₆H₅)₃P]₂C in THF.

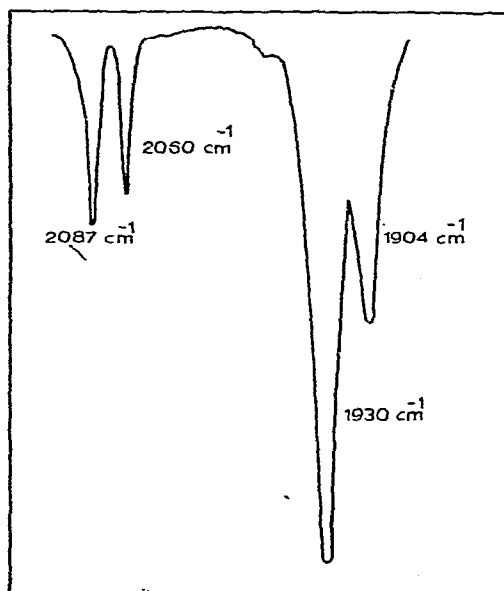


Fig. 2. Infrared spectrum in the carbonyl stretching region of product from the photolysis of W(CO)₆ and [(C₆H₅)₃P]₂C in THF.

(m/e 486) as the highest fragment ion. The presence of a parent ion could not be determined.

The interaction of hexaphenylcarbodiphosphorane with tungsten hexacarbonyl in boiling THF yielded no identifiable product. However, photolysis of a THF solution of tungsten hexacarbonyl and hexaphenylcarbodiphosphorane yielded 5–10% of a bright yellow crystalline substance. The mass spectrum at 70 eV showed the parent ion $W(CO)_5C_2P(C_6H_5)_3^{\ddagger}$ (m/e 610) and $P(C_6H_5)_3^{\ddagger}$ (m/e 262) as the base peak. An infrared spectrum in the carbonyl stretching region is shown in Fig. 2 with bands at 2087, 2060, 1930, 1904 cm^{-1} .

Hexaphenylcarbodiphosphorane and ethylenebis(triphenylphosphine)platinum

The interaction of hexaphenylcarbodiphosphorane and ethylenebis(triphenylphosphine) platinum in benzene at 25° gave a yellow-orange solution and evolution of ethylene gas. Removal of excess benzene yielded a yellow-orange solid, m.p. 72–76°. The complex was characterized by decomposition with anhydrous hydrogen chloride in benzene. A white precipitate of methylenebis(triphenylphosphonium chloride) and *trans*-hydridochlorobis(triphenylphosphine)platinum(II) was obtained. There was no evidence for free triphenylphosphine in the solution.

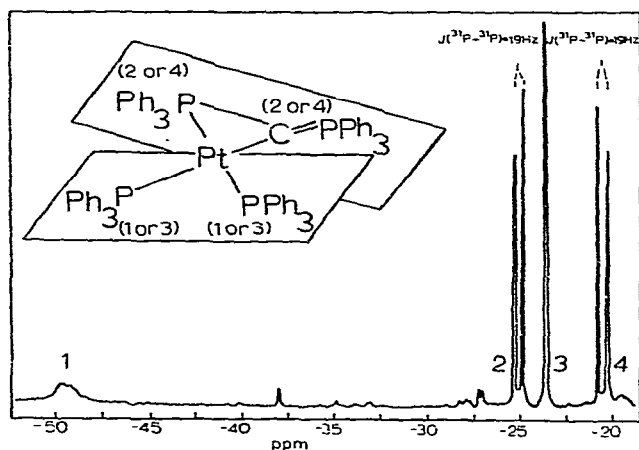


Fig. 3. The 40.5 MHz ^{31}P NMR spectrum in toluene of the product obtained from the interaction of ethylenebis(triphenylphosphine)platinum and hexaphenylcarbodiphosphorane. The spectrum was scanned for 11 min by Fourier techniques.

A pulse Fourier transform ^{31}P NMR spectrum of the complex in toluene (1 *M* concentration) is shown in Fig. 3 with a 2500 Hz spectral width. The spectrum shows four peaks labelled 1, 2, 3, 4, which are of equal area. The natural abundance of ^{195}Pt has been considered and the absorptions represent four magnetically different phosphorus atoms. Peak 1 occurs at δ -49.5 ppm, followed by a set of doublets δ -25.1 ppm for 2, a singlet 3, δ -23.0 ppm, and a pair of doublets 4, δ -20.1 ppm. The pair of doublets (2, 4) in Fig. 3 are assigned to the AB pattern of non-equivalent carbodiphosphorane phosphorus atoms.

Fig. 4 with a 10000 Hz spectral width illustrates satellite peaks for ^{195}Pt ($I = \frac{1}{2}$, 33.7%) to ^{31}P coupling which occur only for peak 1. The coupling constant $J(^{31}P-$

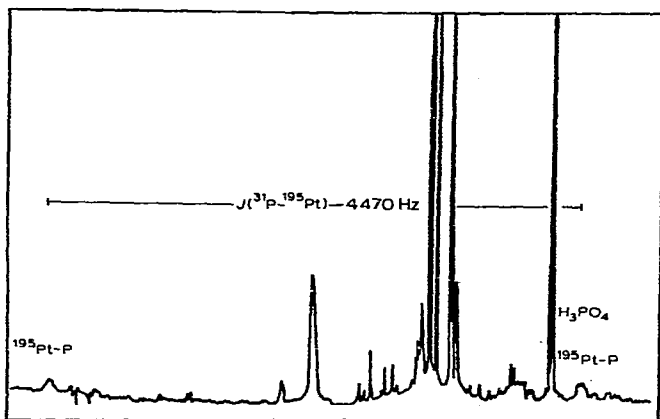


Fig. 4. The 40.5 MHz ^{31}P NMR spectrum in toluene of the product obtained from the interaction of ethylenebis(triphenylphosphine)platinum and hexaphenylcarbodiphosphorane. The spectrum was scanned for 13 h by Fourier techniques.

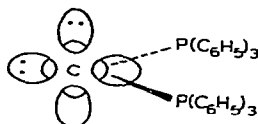
^{195}Pt) of 4470 Hz and the ^{31}P chemical shift of -49.5 ppm is consistent with recent NMR data on zero-valent platinum complexes^{10,11}. This clearly indicates that one triphenylphosphine group is strongly bound to the platinum atom.

DISCUSSION

Tungsten hexacarbonyl and hexaphenylcarbodiphosphorane

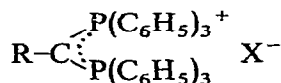
The recent X-ray crystal structure study of hexaphenylcarbodiphosphorane showed that the molecule was bent¹². A maximum P-C-P angle of 144° and a minimum of 131° was observed. Hence the cumulenic bond in (III) does not represent the best bonding description for the molecule. Either form (I) or (II) with partially filled p orbitals on the central carbon atom describes a more appropriate formulation.

The availability of filled p orbitals on the carbodiphosphorane presents ample opportunity for coordination to Group VI transition metal pentacarbonyl complexes.



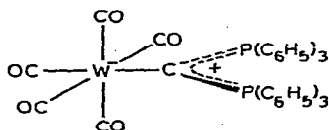
This type of coordination is analogous to other pentacarbonyl complexes of Group VI with anionic (CN^- , $\text{C}\equiv\text{C}-\text{R}^-$, H^- , Br^-) and neutral ligands [CH_3CN , $(\text{C}_6\text{H}_5)_3\text{P}$].

In the area of carbodiphosphorane chemistry, ^{31}P NMR spectra offer the most conclusive evidence for the nature of the coordinated ligands. Most carbodiphosphorane inner salts of the form



show only one ^{31}P NMR peak at approximately -20 ppm with respect to external

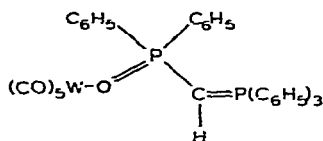
$\text{H}_3\text{PO}_4^{24}$. The observation of one ^{31}P NMR absorption for the tungsten pentacarbonyl complex confirms the equivalency of the phosphorus nuclei and suggests the best formulation for the complex as described below:



This represents a mesomeric structure which emphasizes the equivalency of the triphenylphosphine groups and the coordinatively unsaturated carbon atom. Although such a structure is consistent with ^{31}P NMR and infrared data, it is not clear that the complex is a carbene-bound carbon system such as those synthesized by Fischer¹³. All carbene complexes of Group VI transition metal carbonyl compounds have a vacant p orbital on the carbon atom, whereas the carbon atom in the carbodiphosphorane ligand has a filled p orbital.

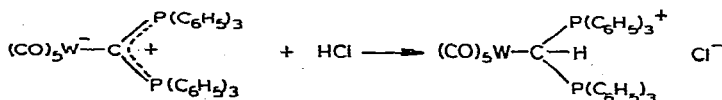
Monosubstituted metal carbonyls of the type $\text{M}(\text{CO})_5\text{L}$ with $\text{M} = \text{Mo}, \text{Cr}, \text{W}$ belong to the idealized C_{4v} molecular point group with three infrared active CO stretching frequencies ($2A_1 + E$). The observed stretching frequencies of the hexaphenylcarbodiphosphorane-tungsten pentacarbonyl adduct correspond favorably with frequencies from anionic ligands coordinated to tungsten pentacarbonyl: CN (ν 2098, 2056, 1961, 1914, 1879 cm^{-1})¹⁴; $-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$ (ν 2043, 1908, 1851 cm^{-1})¹⁵; Cl (ν 2061, 1904, 1869 cm^{-1})¹⁶. The approximate CO stretching force constants (A_1^2 2050, E 1914, A_1^1 1882) $k_1 = 14.42$, $k_2 = 15.47$ and $k_3 = 0.33$ $\text{mdyn}/\text{\AA}$ were calculated using the Cotton-Kraihanzel method¹⁷. According to Graham's formulation¹⁸, these values suggest that the carbodiphosphorane is a good σ -donor molecule in $\text{M}(\text{CO})_5$ complexes.

Shortly after dissolving $(\text{CO})_5\text{WC}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ in THF and placing it in the infrared cell, the bands at 2050, 1914, and 1882 cm^{-1} began to disappear and were replaced by bands at 2039, 1941 and 1851 cm^{-1} . This result may indicate the reaction of adventitious moisture. Indeed, results of an X-ray structural determination show that the complex responsible for these new bands has the following form¹⁹. Although the conversion of hexaphenylcarbodiphosphorane to the pentaphenylcarbodiphos-



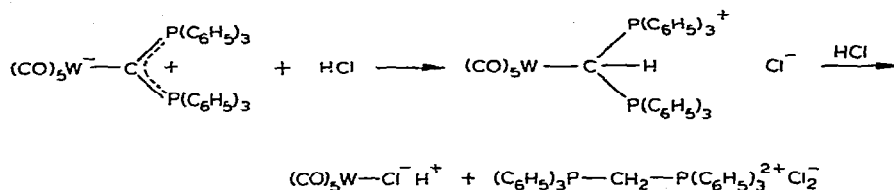
phorane oxide in water is slow⁷, coordination to the transition metal markedly enhances this transformation.

All attempts to isolate a metal carbonyl carbodiphosphorane product after introduction of anhydrous HCl/THF were unsuccessful.

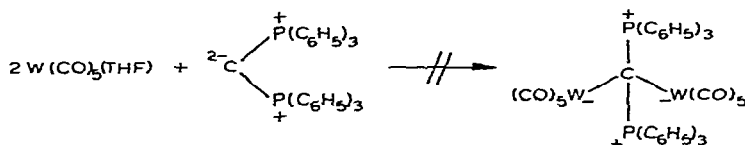


Experiments were performed to synthesize the protonated complex from $\text{H-C}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}^-$ and $\text{W}(\text{CO})_5(\text{THF})$, but they were not successful.

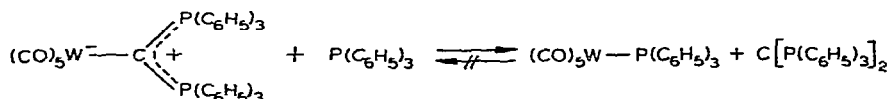
The isolation of methylenebis(triphenylphosphonium chloride) suggests the following reaction course for the complex with HCl :



Tungsten pentacarbonyl chloride has bands at 2064, 1922 and 1867 cm^{-1} in the carbonyl stretching region¹⁶. Although two coordination sites were available on the central carbon atom, only one tungsten pentacarbonyl moiety coordinates to the carbodiphosphorane.

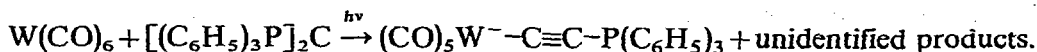


The carbodiphosphorane ligand was displaced from tungsten pentacarbonyl by triphenylphosphine to yield (triphenylphosphine)pentacarbonyltungsten which was identified by its infrared spectrum. The reverse reaction was not observed:



Since the preferred synthetic approach to $\text{M}(\text{CO})_5\text{L}$ compounds^{20,21} is often the *in situ* photolysis of $\text{M}(\text{CO})_6$ in the presence of L , the interaction of tungsten hexacarbonyl and hexaphenylcarbodiphosphorane in the presence of UV light was studied. The mass spectrum of the photochemical product showed a peak for the parent ion $(\text{CO})_5\text{WC}_2\text{P}(\text{C}_6\text{H}_5)_3^+$ (m/e 586), followed by peaks which showed successive loss of carbon monoxide to the ion $\text{WP}(\text{C}_6\text{H}_5)_3^+$ (m/e 474). An infrared spectrum of the original product in the carbonyl stretching region showed that $(\text{CO})_5\text{WP}(\text{C}_6\text{H}_5)_3$ was not present. Hence rearrangement and loss of C_2 must have occurred in the mass spectrometer. The presence of a peak C_2^+ (m/e 24) was detected.

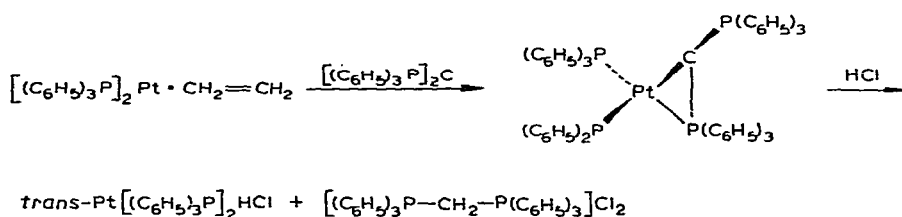
The infrared spectrum of the photochemical product shows three $\nu(\text{CO})$ bands which can be assigned to a pentacarbonyl complex with C_{4v} symmetry about the central atom. The highest frequency band at 2087 cm^{-1} is tentatively assigned to $\nu(-\text{C}\equiv\text{C}-)$ stretching frequency. The following general equation describes the photochemical transformation:



The structure of the product with the acetylenic ligand is similar to that observed by Goldberg, Duesler and Raymond^{22a} for the compound obtained from hexaphenylcarbodiphosphorane and manganese pentacarbonyl bromide^{22b}. Although sufficient data are not available yet to describe a mechanism for the photochemical transformation, the elements of a classical Wittig reaction are present. It is interesting to note that the application of a classical Wittig reaction with "bis-ylides" and metal carbonyls yields acetylenic ligands instead of the olefinic ligands commonly observed in organic carbonyl chemistry*.

Hexaphenylcarbodiphosphorane and ethylenebis(triphenylphosphine)platinum

Hexaphenylcarbodiphosphorane bears a structural resemblance to bis(triphenylphosphine)platinum. Since the coordinatively unsaturated platinum compound will complex ethylene, a similar coordination of the carbon-phosphorus bond in hexaphenylcarbodiphosphorane to bis(triphenylphosphine)platinum was studied. Such coordination would attempt to elucidate the allenic nature of the carbodiphosphorane and the phosphorus-carbon bonds. The experimentally observed reaction sequence is shown below:

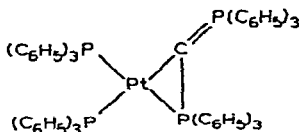


The most important conclusion from NMR spectral evidence indicates that coordination of the carbodiphosphorane to the platinum complex reduces the symmetry of the entire moiety with all phosphorus atoms in different magnetic environments. Since peak 1, Fig. 3, has ¹⁹⁵Pt satellites, it must represent a triphenylphosphine group directly bonded to platinum. Peak 3 must also represent a triphenylphosphine group bonded to platinum although no ¹⁹⁵Pt satellites were observed at 25°. This result is not unusual since NMR spectra of other low valent triphenylphosphine platinum complexes with rapidly exchanging ligands often do not show ¹⁹⁵Pt-³¹P coupling at ambient temperatures¹². The individual assignment of peaks 1 and 3 to a particular triphenylphosphine group bound to platinum is uncertain. Perhaps the most deshielded triphenylphosphine phosphorus atom, hence the one occurring at lower field, is *trans* to the pentacoordinate carbodiphosphorane triphenylphosphine group.

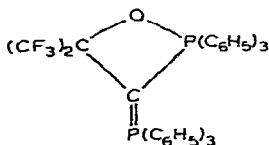
Cryoscopic molecular weight measurements show that the complex is approximately 50% dissociated in solution of 10⁻³ M in complex, although the present spectral evidence does not indicate whether triphenylphosphine or carbodiphosphorane is dissociating from the molecule.

The non-equivalency of carbodiphosphorane ³¹P atoms is most interesting and can be explained if a cyclic adduct is formed,

* Phosphorus ylides of the type Ph₃P=CRR' and metal carbonyls yield an entirely different set of products³¹.



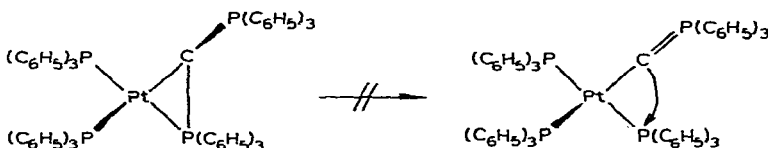
This is a three-membered ring heterocycle with a pentacoordinated phosphorus atom bound to platinum, three benzene rings and the carbon atom of the carbodiphosphorane. Although three-membered rings which incorporate the carbodiphosphorane moiety are not known, a four-membered oxaphosphetane complex of hexafluoroacetone²³ is known and the ³¹P atoms of the complex form an AB pattern of non-equivalent atoms,



The proximity of the carbodiphosphorane phosphorus atom to platinum promotes a magnetically different environment, and hence a different chemical shift for this atom.

The carbodiphosphorane phosphorus atom clearly has not formed a strong covalent bond to platinum since ¹⁹⁵Pt satellites are not observed for peaks 2 or 4. Furthermore, the chemical shift of a phosphorus covalently bound to five substituents usually occurs above H₃PO₄, whereas phosphorus atoms of an ylide nature have chemical shifts below H₃PO₄.²⁴ Thus both of the carbodiphosphorane phosphorus atoms in the complex have ylide character, although interaction of the platinum atom with one of them must be enough to prevent formation of a mesomeric structure.

Chemical evidence also suggests that complete migration of the carbodiphosphorane phosphorus atom to platinum *does not* occur and this is consistent with the NMR evidence of four distinct triphenylphosphine groups for the complex in solution.



EXPERIMENTAL SECTION

Operations

All operations with hexaphenylcarbodiphosphorane and transition metal adducts were performed under dry oxygen-free nitrogen or argon. The equipment for transferring inert gases and compounds has been described previously²⁵. The infrared spectra were recorded on a Beckman IR-7 (prism grating) instrument which was calibrated in the 1700–2050 cm⁻¹ region with polystyrene film and atmospheric water vapor²⁶.

Mass spectra were recorded at 70 eV on an AEI MS-9 instrument.

Chemical analyses were performed by Schwarzkopf Microanalytical Laboratory, 56-19 37th Avenue, Woodside, New York, 11377.

Molecular weight measurements were made with a cryoscopy cell designed by Dilts and Shriver²⁷.

The ³¹P NMR spectra were recorded on a Varian Associates XL-100 instrument which utilized the pulse Fourier transform method of peak presentations. The samples were dissolved in toluene in a 10 mm tube and referenced to external H₃PO₄ in D₂O. All peaks were proton decoupled.

Materials

Hexaphenylcarbodiphosphorane was synthesized by the method of Ramirez *et al.*²⁸. Chromium, molybdenum, and tungsten hexacarbonyl compounds were obtained from Pressure Chemical Company, 3419-25 Smallman Street, Pittsburg, Pennsylvania, 15201 and sublimed before use. Ethylenebis(triphenylphosphine)platinum was prepared according to the method of Cook and Jauhal²⁹. Solvents were distilled directly into reaction flasks from lithium aluminum hydride.

A. Hexaphenylcarbodiphosphorane and tungsten pentacarbonyl in THF

Tungsten hexacarbonyl (0.25 g, 0.71 mmol) in 50 ml of THF was subjected to UV irradiation with a Hanovia utility model lamp for 3-4 h. After photolytic removal of 1 molar equivalent of carbon monoxide, the yellow-orange THF solution was added to a THF solution of the carbodiphosphorane (0.38 g, 0.71 mmol). The yellow-orange oil was dissolved in 10 ml of THF followed by the addition of 3 ml of pentane. The cloudy yellow solution was separated from a small amount of brown oil. Additional drops of pentane were added to insure removal of any remaining droplets of brown oil. The resultant cloudy yellow solution was cooled overnight at 0° whereupon small yellow-orange crystals were obtained, m.p. 132° (dec.). (Found: C, 59.46; H, 4.20; P, 6.60; mol.wt. in benzene, 990. C₄₂H₃₀O₅P₂W calcd.: C, 58.62; H, 3.51; P, 7.19. C₄₂H₃₀O₅P₂W·C₄H₈O calcd.: C, 59.24; H, 4.11; P, 6.64%; mol.wt., 932.)

B. Hexaphenylcarbodiphosphorane and tungsten hexacarbonyl in presence of UV light

Hexaphenylcarbodiphosphorane (0.38 g, 0.71 mmol) and tungsten hexacarbonyl (0.75 g, 2.13 mmol) in 40 ml of THF were irradiated with a Hanovia Quartz mercury-vapor utility lamp for 2.5 h. The resultant brown solution was filtered and THF removed under vacuum to yield a brown oil. Excess tungsten hexacarbonyl was removed from the product under high vacuum at 40°. The brown oil was dissolved in 15 ml of THF followed by the addition of 3 ml of pentane. A yellow solution was decanted from the dark brown oil which separated from solution. Additional drops of pentane were introduced to the yellow solution until no further separation of oil occurred. The resultant yellow solution was set to cool overnight at 0° whereupon yellow needles were obtained (5-10%), m.p. 140-142°. The crystals were stable in air for several hours, although THF solutions of the product show some decomposition in air. (Found: C, 49.25; H, 2.37; O, 13.04; P, 4.72; W, 29.99. C₂₅H₁₅O₅PW calcd.: C, 49.20; H, 2.48; O, 13.11; P, 5.08; W, 30.14%.)

C. Hexaphenylcarbodiphosphorane and ethylenebis(triphenylphosphine)platinum

To a 10 ml red-orange solution of ethylenebis(triphenylphosphine)platinum

(0.3 g, 0.402 mmol) was added 10 ml of a benzene solution of hexaphenylcarbodiphosphorane (0.22 g, 0.402 mmol). After evolution of a gas the gold-yellow solution was stirred for 24 h. The solution was filtered and benzene removed to yield a yellow-orange solid (81%), m.p. 72–76°. The infrared spectrum in Nujol showed prominent bands at 795 and 560 cm^{-1} . These are assigned to $\nu[(\text{C}_6\text{H}_5)_3\text{P}=\text{C}]^{30}$ and $\nu(\text{Pt}-\text{C})$ respectively. (Found: C, 69.31; H, 4.70. $\text{C}_{73}\text{H}_{60}\text{P}_4\text{Pt}$ calcd.: C, 69.78; H, 4.81%.)

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