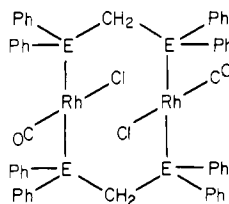
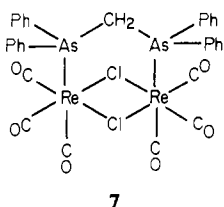


face-to-face bridged structure **6**.^{25,26} The coordination planes



6, E = P or As

of the two rhodium ions are parallel, but they are not perpendicular to the Rh-Rh vector. Rather, in $\text{Rh}_2(\text{dpm})_2(\text{CO})_2\text{Cl}_2$ the angle between the Rh-Rh vector and the rhodium coordination plane is 75.9° .²⁵ These coordination planes are tipped so that both chloride ions are folded in toward the adjacent rhodium atoms. Further tipping of these coordination planes should move the halide ions into bridging positions. Inspection of molecular models indicates that the formation of halo-bridged structures is entirely reasonable. $\text{Re}_2(\text{dam})_2(\text{CO})_6\text{Cl}_2$, whose structure is known from X-ray crystallographic study,²⁷ has the structure **7** which incorporates



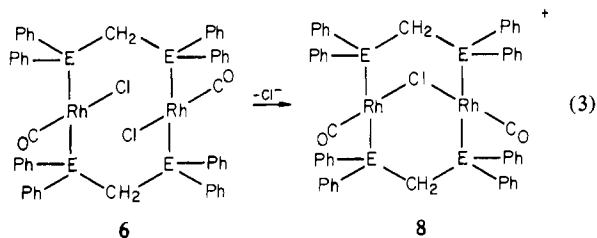
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some of the structural features of **4** and **5**. The reaction chemistry of **6** demonstrates the facility by which halo-bridged compounds may be formed from these face-to-face dimers. Treatment of **6** with a mild halide acceptor produces the A frame **8** via reaction 3.^{9,28}



While the information outlined above suggests a reasonable mechanism for dissociation of face-to-face d^8 dimers, another important question about these molecules remains unanswered. What factors govern the structure of dimeric vs. monomeric forms of the complexes? While the palladium dimers **3** dissociate readily, the rhodium dimers **6** show no evidence for dissociation. The stability of the dimers may be related to the strength of any metal-metal interaction that exists in the face-to-face dimers. That such an interaction occurs in the closely bound dimers of rhodium has been demonstrated.⁵ Moreover, this interaction may well be weakly bonding in nature. For palladium in **3**, the higher oxidation state (Pd(II) vs. Rh(I)) may contract the metal-metal orbitals so that the metal-metal interaction is weakened.

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Registry No. $\text{Pd}_2(\text{dpm})_3$, 37266-95-8; Cl_2 , 7782-50-5; Br_2 , 7726-95-6; I_2 , 7553-56-2; pentafluorophenyl disulfide, 1494-06-0; $\text{Pd}(\text{dpm})\text{Cl}_2$, 38425-01-3; $\text{Pd}(\text{dpm})\text{Br}_2$, 77462-41-0; $\text{Pd}(\text{dpm})\text{I}_2$, 77462-40-9; $\text{Pd}(\text{dpm})(\text{SC}_6\text{F}_5)_2$, 77462-39-6; $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$, 64345-29-5; $\text{Pd}_2(\text{dpm})_2\text{Br}_2$, 60482-68-0; $\text{Pd}_2(\text{dpm})_2\text{I}_2$, 67477-87-6; $\text{Pd}_2(\text{dpm})_2(\text{SC}_6\text{F}_5)_2$, 77462-38-5; $\text{Pd}_2(\text{dpm})_2\text{Cl}_4$, 77462-37-4; $\text{Pd}_2(\text{dpm})_2\text{Br}_4$, 77462-36-3; $\text{Pd}_2(\text{dpm})_2\text{I}_4$, 77462-35-2.

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Chemical and ^{31}P NMR Spectroscopic Investigations of $(\text{Ph}_3\text{P})_3(\text{CO})\text{Pt}_2(\mu\text{-S})$, a Molecule with a Robust Pt_2S Core. Applications of Selective Population Transfer to Isotopomer Identification

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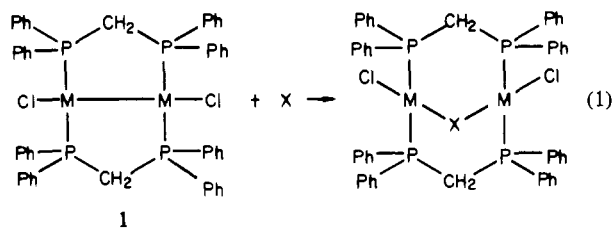
The $^{31}\text{P}\{\text{H}\}$ NMR spectra of $(\text{Ph}_3\text{P})_3(\text{OC})\text{Pt}_2(\mu\text{-S})$ and five derivatives have been analyzed. The utility of selective population transfer experiments in identifying resonances in the spectrum due to a single isotopomer and, consequently, in facilitating spectral analysis has been demonstrated. Substitution reactions of $(\text{Ph}_3\text{P})_3(\text{OC})\text{Pt}_2(\mu\text{-S})$ yield $(\text{Ph}_3\text{P})_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\text{Pt}_2(\mu\text{-S})$ and $(\text{Ph}_3\text{P})_2(\text{CH}_3\text{NC})_2\text{Pt}_2(\mu\text{-S})$. The Pt-Pt bonds of these compounds are inert to insertion reactions by carbon monoxide, methyl isocyanide, and acetylenes. Methyl iodide alkylates these complexes to produce $(\text{Ph}_3\text{P})_3(\text{OC})\text{Pt}_2(\mu\text{-SCH}_3)^+$ and $(\text{Ph}_3\text{P})_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\text{Pt}_2(\mu\text{-SCH}_3)^+$. $(\text{Ph}_3\text{P})_3(\text{OC})\text{Pt}_2(\mu\text{-S})$ reacts with carbon disulfide to form $(\text{Ph}_3\text{P})_2\text{Pt}_2\text{S}_2\text{CS}$.

Introduction

The metal-metal bond of palladium(I) and platinum(I) complexes bridged by bis(diphenylphosphino)methane or bis(diphenylarsino)methane undergoes insertion reactions (eq. 1) which are atypical of metal-metal single bonds. Insertions

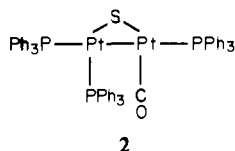
of carbon monoxide,¹⁻⁵ isocyanides,^{1,2} sulfur dioxide,^{6,7} sulfur,^{6,7} and diazonium cations⁸ proceed to place a single atom of the

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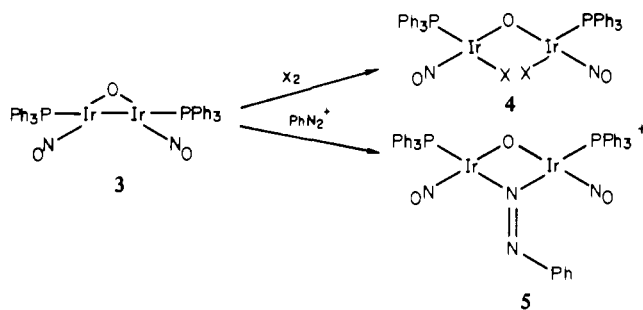
inserted ligand between the two metal atoms. Consequently, the metal-metal bond is broken and the metal atoms move about 0.5 Å further apart. In contrast, acetylenes insert into **1** to form a cis-dimetalated olefin with a C_2 bridge between the two metals.⁹

As part of a program designed to identify other molecules capable of undergoing these insertion reactions, the reaction chemistry of the sulfide bridged platinum(I) complex **2** has



been explored. This complex is readily available from the reaction of carbonyl sulfide and $\text{Pt}(\text{PPh}_3)_3$ ¹⁰ and its structure, with nearly planar coordination about each platinum atom, was established by X-ray structure determination.¹¹

Initially it was anticipated that the presence of a three-membered Pt_2S ring in **2** would enhance the reactivity of the Pt-Pt bond toward insertion reactions. Moreover **2** is iso-electronic with **3**.^{12,13} This latter complex has been shown



to react with halogens or mercuric halides to break the metal-metal bond and form **4**.^{12,14} It also reacts with diazonium cations to form **5**. The Ir-Ir distance in **3** is 2.555 Å while in **5** it is 3.063(6) Å.^{12,15} Thus the conversion of **3** to **5** is entirely analogous to the insertion reaction of **1**.

The results reported here, however, demonstrate that the Pt_2S ring of **2** is robust and that its reaction chemistry involves

substitution reactions rather than metal-metal bond cleavage.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2** and related compounds are complicated because of the presence of several isotopomers which occur due to the 34% natural abundance of ^{195}Pt ($I = 1/2$), the only naturally occurring platinum isotope with a nuclear spin. The observed spectrum of any one compound, therefore, consists of the sum of the spectra of all isotopomers of that molecule. In analyzing these spectra it is important to be able to identify the spectral transitions due to each of the various isotopomers present. If we were dealing with ^1H NMR spectra, this could be accomplished via homonuclear decoupling experiments. However, homonuclear decoupling is a less powerful technique in ^{31}P NMR because of the larger coupling constants involved. Furthermore, homonuclear decoupling is not normally available for nuclei other than protons.

The information available from selective population transfer (SPT)^{16,17} experiments is in many ways analogous to that obtained from homonuclear decoupling experiments, and its successful implementation is not dependent on first-order coupling. Selective population transfer (SPT) experiments in FT NMR are normally accomplished by selective inversion of a single transition followed by a nonselective observation pulse. Under appropriate conditions which include a small flip angle observation pulse, only transitions with a level in common with the perturbed transition are altered in intensity. Subtraction of this spectrum from an unperturbed spectrum results in a difference mode display bearing a close resemblance to an INDOR response in CW NMR. Utilization of a larger flip angle can result in intensity alterations of all transitions connected to the inverted transition. Here we use the latter conditions to identify all resonances associated with a particular isotopomer.

Experimental Section

Preparation of Compounds. $\text{Pt}_2\text{S}(\text{PPh}_3)_3(\text{CO})$. This complex was prepared through a modification of the procedure of Baird and Wilkinson.¹⁰ Carbonyl sulfide was bubbled through a suspension of $\text{Pt}(\text{PPh}_3)_3$ in pentane until the suspended solid was nearly white. This solid was collected, washed with pentane, and dissolved in a minimum volume of chloroform. The chloroform solution was filtered, and a large volume of pentane was added to precipitate the product as slightly oily, yellow crystals. These were collected by filtration, washed with a small volume of cold acetone (to remove a soluble yellow impurity) and pentane. Further purification was achieved by dissolution in dichloromethane, filtration, and crystallization of the product from the filtrate by the addition of pentane.

$\text{Pt}_2\text{S}(\text{PPh}_3)_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$. Bis(diphenylphosphino)methane (52 mg, 1.2×10^{-4} mol) and $\text{Pt}_2\text{S}(\text{PPh}_3)_3(\text{CO})$ (152 mg, 1.23×10^{-4} mol) were dissolved in 10 mL of dichloromethane, and 10 mL of anhydrous ethanol was added. The solvent was distilled until the volume was reduced to 5 mL. Upon cooling of the solution, yellow crystals of the product formed. These were collected by filtration and washed with ethanol. Further purification was accomplished by recrystallization from ethanol/dichloromethane (yield 90 mg, 57%). Anal. Calcd for $\text{C}_{61}\text{H}_{52}\text{P}_4\text{Pt}_2\text{S}$: C, 55.04; H, 3.94. Found: C, 55.11; H, 4.01. Molecular weight for $\text{C}_{61}\text{H}_{52}\text{P}_4\text{Pt}_2\text{S}$: calcd, 1331; found, 1330.

$\text{Pt}_2\text{S}(\text{PPh}_3)_2(\text{CNCH}_3)_2$. Methyl isocyanide (0.025 mL, 0.51 mmol) was added to a solution containing 175 mg (0.14 mmol) of $\text{Pt}_2\text{S}(\text{PPh}_3)_3(\text{CO})$ in 15 mL of dichloromethane. The resulting yellow solution was filtered, and pentane was added until the solution was cloudy. After cooling and storing the solution at -10°C for 1 day, the yellow crystalline product was collected, washed with pentane, and vacuum dried (yield 125 mg, 86%). Evaporation of the mother liquor produced a white solid identified as triphenylphosphine. Anal. Calcd for $\text{C}_{40}\text{H}_{36}\text{N}_2\text{P}_2\text{Pt}_2\text{S}$: C, 46.69; H, 3.53; N, 2.72; S, 3.12. Found: C, 46.44; H, 3.53; N, 2.72; S 3.12. Molecular weight for $\text{C}_{40}\text{H}_{36}\text{N}_2\text{P}_2\text{Pt}_2\text{S}$: calcd, 1029; found, 900.

$[\text{Pt}_2\text{SCH}_3(\text{PPh}_3)_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]\text{I}$. Methyl iodide (1 mL) was added to a solution of 150 mg (0.11 mmol) of $\text{Pt}_2\text{S}(\text{PPh}_3)_2$ -

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(Ph₂PCH₂PPh₂) in 10 mL of dichloromethane. After 24 h of standing, the solution was evaporated under a nitrogen stream to a volume of 5 mL and pentane was added to precipitate yellow orange oily crystals. These were collected, washed with pentane and methanol, and vacuum dried. The product was then dissolved in a minimum volume of dichloromethane, filtered, and reprecipitated by the addition of pentane to give yellow needles (yield 97 mg, 60%) (conductivity in acetonitrile solution $\Lambda_M = 106 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$). Anal. Calcd for C₆₂H₅₃IP₄Pt₂S: C, 50.44; H, 3.76. Found: C, 50.30; H, 4.00.

[Pt₂SCH₃(PPh₃)₃(CO)]PF₆. Methyl iodide (0.08 mL) was added to a solution of 103 mg of Pt₂S(PPh₃)₃CO in 10 mL of dichloromethane. After the solution stood for 24 h, pentane was added to precipitate a brown crystalline solid. After the solid was collected (68 mg), it was dissolved in methanol and a saturated aqueous solution of ammonium hexafluorophosphate was added to precipitate the yellow crystalline product. These were collected by filtration and vacuum dried. Purification was accomplished by dissolving the yellow solid in dichloromethane, filtering the solution, and adding ethyl ether to give yellow needles (conductivity in nitromethane solution $\Lambda = 77 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$). Anal. Calcd. for C₅₆H₄₈F₆OP₄Pt₂S: C, 48.14; H, 3.46; P, 8.87. Found: C, 49.07; H, 3.55; P, 8.22.

Reaction of Pt₂S(PPh₃)₃(CO) with Carbon Disulfide. Pt₂S(PPh₃)₃(CO) (200 mg) was dissolved in 5 mL of carbon disulfide, and the solution was rapidly filtered. Fine yellow-brown needles formed in the solution. So that precipitation of this product could be ensured, 5 mL of pentane was added to the solution, and it was then chilled to -10 °C. The crystals (138 mg, 69% based on triphenylphosphine) were removed by filtration and recrystallized from dichloromethane/ethyl ether. The product was identified as (Ph₃P)₂Pt₂CS¹⁸ ($\nu_{\text{C}=\text{S}}$, 1055 cm⁻¹). Anal. Calcd. for C₃₇H₃₀P₂PtS₃: C, 53.68; H, 3.65; P, 7.48. Found: C, 53.90; H, 4.12; P, 7.12. A second yellow product was obtained from addition of pentane to the mother liquor obtained from the original reaction after the removal of (Ph₃P)₂Pt₂CS. The infrared spectrum of this material exhibited bands due to triphenylphosphine, carbonyl ligands (ν_{CO} , 2025, 1980 cm⁻¹) and C=S ($\nu_{\text{C}=\text{S}}$, 1143 cm⁻¹). Attempts to purify it lead to its decomposition; consequently, it has not been identified.

Reaction of Pt₂S(PPh₃)₃CO with Iodine. Iodine (26.6 mg, 0.105 mmol) dissolved in 10 mL of dichloromethane was added to a solution of Pt₂S(PPh₃)₃(CO) (123 mg, 0.100 mmol) in 10 mL of dichloromethane. The solution was filtered, and pentane was added to the filtrate to yield yellow crystals of (Ph₃P)₂PtI₂ (50 mg, 73% based on Ph₃P available). The product was identified by comparison of the infrared spectrum, electronic spectrum, and thin-layer chromatographic behavior with authentic samples.

Physical Measurements. Infrared spectra were recorded from Nujol mulls on a Perkin-Elmer 180 infrared spectrometer. Electrical conductivities were determined by use of an Industrial Instrument conductivity bridge with 10⁻³ M acetonitrile or nitromethane solution. ¹H NMR and proton decoupled ³¹P NMR spectra were recorded on a Nicolet magnetic NT-200 Fourier Transform spectrometer at 200 and 81 MHz, respectively. The NT-200 spectrometer operated with quadrature detection and had 32 K of data storage memory as well as disk storage capability. The proton spectra were obtained in 5-mm tubes, while the ³¹P spectra were obtained in either 12- or 20-mm tubes. All ³¹P spectra were taken with broad-band proton decoupling, and an external 85% phosphoric acid reference was used. The high-frequency-positive convention, recommended by IUPAC, is used in reporting chemical shifts.

The ³¹P SPT experiments were accomplished by placing a long, weak 180° pulse on the line to be inverted, followed by a nonselective observation pulse. The observation pulse was made 30° or more in order to elicit differences in intensities of all transitions coupled to the inverted transition. Selectivity of the inverting pulse was ensured by making it at least twice as long as the inverse frequency separation of the next nearest line. No special equipment was necessary to implement this experiment, as the Nicolet Magnetic's NT-200 spectrometer was capable of being switched to a low-power mode under control of the spectrometer computer, with the strengths of the low-power pulse being adjustable through front panel attenuators. No frequency change was made in switching from high power to low power, so the spectrometer carrier frequency was always at the position of the line to be inverted. A period of 10 ms was allotted to accomplish

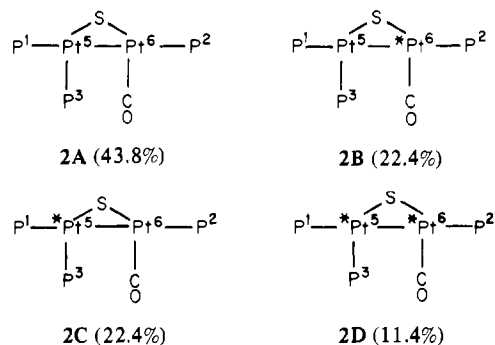
the switching from one power mode to the other.

So that there could be a guard against deterioration of the difference mode spectra due to changes in field homogeneity, etc., during accumulation of the data, spectra to be displayed in the difference mode were always taken in interlaced fashion. That is, up to several hundred scans of the normal spectrum were taken and stored, followed by the same number of scans of the SPT spectrum. Nicolet Magnetic's software allowed this procedure to be replicated automatically until adequate signal-to-noise had been achieved.

Simulations of the ³¹P{¹H} NMR spectra of the individual isotopomers were performed with use of the iterative simulation routine of the Nicolet software on a model 1180 Nicolet data system. This simulation routine is a modified version of Laocoon III. The fit of the simulation was based on matching the individual peak positions and the intensities of the observed and calculated spectra. Agreement between the calculated and measured peak position was within 1 Hz.

Results

The ³¹P{¹H} NMR Spectrum of (Ph₃P)₃(OC)Pt₂S (2). The ³¹P{¹H} NMR spectrum of **2** is complex as inspection of Figure 1, trace A, shows. In addition to containing three coupled but distinct phosphorus nuclei, the spectrum is complicated by the presence of four isotopomers which result from the presence of naturally abundant ¹⁹⁵Pt. These four isotopomers are labeled **2A–2D** and are shown along with their percentage



natural abundance. The ³¹P{¹H} NMR spectrum of **2** then is the sum of four spectra, one arising from each of the isotopomers shown. To analyze the spectrum it is necessary to sort out and assign the spectral features of the individual isotopomers. This has been done by using a combination of SPT experiments and computer-generated spectra simulations.

The analysis began with the identification of the spectral features due to **2A**. The pattern due to **2A** should be particularly intense because **2A** is the most abundant isotopomer (43.8%), and it has the simplest splitting pattern (ABX). The 12 intense features at the center of the spectrum may be assigned to a (nearly) ABX pattern when reasonable assumptions about the magnitude and signs of the various P–P coupling constants are made. Those 12 features are displayed in Figure 2, trace A, which is a simulation of the ABX spectrum of **2A**. In order to be certain that this ABX pattern was correctly identified and that the phosphorus coupling constants were correctly evaluated, we undertook a SPT experiment before continuing the analysis. The results of that experiment are shown in Figure 1, trace B. This spectrum is a difference mode spectrum taken by subtracting the spectrum obtained after selective inversion of the line at 19.6 ppm from the normal spectrum. The difference mode spectrum shows only those transitions whose intensities have been altered as a result of the SPT. Since an intense line was chosen for inversion, the lines in the subtracted spectrum are all expected to belong to isotopomer **2A**. A qualitative explanation for the intensity alterations may be obtained with the aid of Figure 3 which shows the ABX coupling scheme. If X₁ is the transition irradiated, then the populations at L₁ and L₂ are inverted and all transitions having either L₁ or L₂ in common will have altered intensity. However, these experiments were conducted

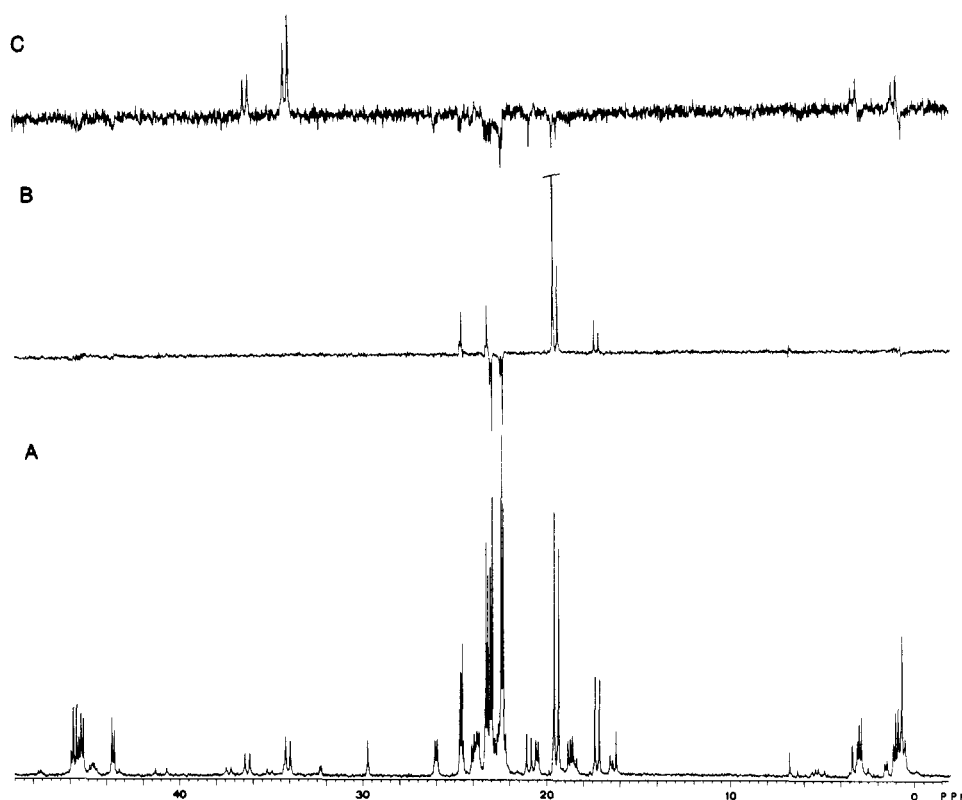


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $(\text{Ph}_3\text{P})_3(\text{OC})\text{Pt}_2(\mu\text{-S})$ in a 20-mm tube with a pulse angle of 30° : A, 12000 accumulations of the spectrum; B, the difference spectrum after selective inversion of the line at 19.6 ppm identifying the 12 lines of the ABX spectrum; C, the difference spectrum after selective inversion of the line at 34.0 ppm.

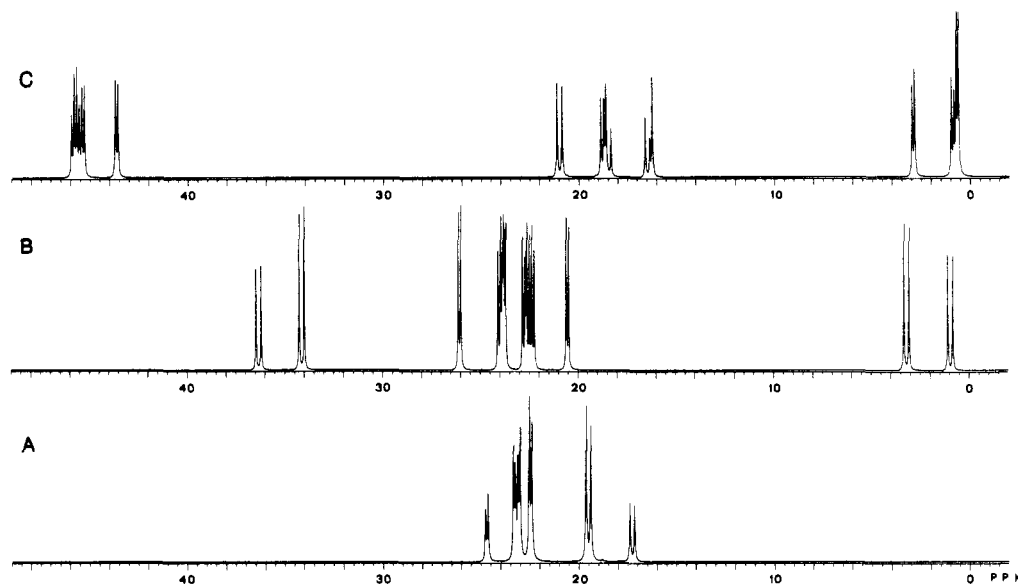


Figure 2. Simulations of the spectra of the individual isotopomers of $(\text{Ph}_3\text{P})_3(\text{OC})\text{Pt}_2(\mu\text{-S})$. (A) For **2A**, the parameters used are as follows: $\delta(\text{P}_1)$ 23.32, $\delta(\text{P}_2)$ 18.65, $\delta(\text{P}_3)$ 23.16, $J(\text{P}_1, \text{P}_2) = \pm 179.8$ Hz, $J(\text{P}_2, \text{P}_3) = \pm 21.5$, $J(\text{P}_1, \text{P}_3) = \mp 10.5$. (B) For **2B** (with the parameters for **2A**): $J(\text{Pt}_6, \text{P}_2) = \pm 2663.1$, $J(\text{Pt}_6, \text{P}_1) = \pm 279.9$, $J(\text{Pt}_6, \text{P}_3) = \mp 116.9$. (C) For **2C** (with the parameters for **2A**): $J(\text{Pt}_5, \text{P}_1) = \pm 3462.2$ Hz, $J(\text{Pt}_5, \text{P}_2) = \pm 204.1$, $J(\text{Pt}_5, \text{P}_3) = \pm 3613.0$.

with a short delay time and an observe pulse of 30° or more so that intensity alterations of the entire ABX system were solicited. The existence of the 12 lines in the spectrum confirms this and clearly identifies the ABX pattern belonging to isotopomer **2A**.

From the observed parameters, particularly the large value of one P-P coupling constant, it is possible at this stage to assign the two strongly coupled phosphorus atoms to the ligands trans to the Pt-Pt bond and the other phosphorus uniquely to P_3 . With the identification of the lines due to **2A** ensured, the analysis can proceed to identifying the two singly

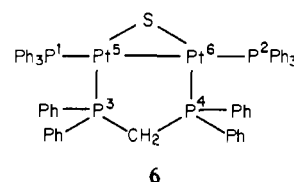
labeled isotopomers **2B** and **2C**. The essence of the difference between **2B** and **2C** may be seen in the assignment of the large one bond Pt-P coupling constants. There are three of these, one from **2B** and two from **2C**. Our analysis focused on the features between 34 and 46 ppm in the spectrum. While groups of lines are seen which may be assigned to splitting by the three Pt-P coupling constants, there is no obvious way to ascertain which sets of lines belong to **2B** and which belong to **2C** without knowing which set of lines in **2A** belongs to P_1 or P_2 . To make this assignment unambiguous, we undertook a second SPT experiment. In this case the line at 34 ppm was

chosen for inversion. The difference spectrum obtained is shown in Figure 1, trace C. Lines at ca 36, 34, 3, and 1 ppm are readily identified and can be assigned to a single isotopomer. Additional features occur in the region 20–26 ppm. These features are weaker and do not reproduce well in the figure. They are less clear than the other features because they occur in a region of the spectrum where there is imperfect cancellation due to the intense features of **2A**. Moreover, the line irradiated and the lines affected have low intensity so that they are more difficult to detect in a difference spectrum. It is significant to note, however, that no features are found in the difference spectrum in the region 43–46 ppm. The features observed in trace C of Figure 1 can be assigned to **2B** since only one set of lines due to one-bond Pt–P coupling are found. The chemical shift of P_2 is identified by the satellites generated by the large one-bond Pt–P coupling constant, therefore allowing unambiguous assignments of P_1 and P_2 . A simulation of the spectrum of **2B** is shown in Figure 2, trace B. The remaining intense features in the spectrum of Figure 1, trace A, were assigned to **2C**, and the simulated spectrum of this species is reproduced in Figure 2, trace C.

It is important to take note of the signs of the coupling constants. In an ABX spectrum only the relative signs of J_{AX} and J_{BX} and $|J_{AB}|$ can be determined. That is, in **2A** reversing the signs of $J(P_1, P_2)$ and $J(P_2, P_3)$ will not affect the appearance of the spectrum. However, since the present spectrum departs from the strictly ABX case we can get information about the relative sign of J_{AB} , because different sign assignments lead to the same transition energies but a different distribution of intensities. According to the simulations, $J(P_1, P_2)$ and $J(P_2, P_3)$ have the same sign, while $J(P_1, P_3)$ has the opposite sign. The computer simulations of **2B** indicate that $J(P_1, Pt_6)$ and $J(P_2, Pt_6)$ have the same sign, while $J(P_3, Pt_6)$ has the opposite sign; and the signs of these three coupling constants are independent of the already determined signs of the set of P–P couplings. The computer simulations of **2C** indicate that $J(P_1, Pt_5)$, $J(P_2, Pt_5)$, and $J(P_3, Pt_5)$ all have the same sign; and again these signs are independent of the set of P–P couplings. The coupling constants will be reported as correlated sets denoted in braces. Within any braced set, the relative signs of the coupling constants are fixed and known; the absolute signs have not been determined experimentally. There is no relationship between the signs of two different correlated sets. The relationship between the sets of Pt–P couplings are also unknown. These subsets are enclosed in broken brackets. If the spectrum of the doubly Pt labeled isotopomer were observed and assigned, the relationship of the signs within these sets should be determinable. For example, the parameters obtained from the analysis of $Pt_2S(CO)(PPh_3)_2$ are $\delta(P_1)$, 23.32 ppm; $\delta(P_3)$, 23.16; $\delta(P_2)$, 18.65; $\{J(P_1, P_2) = \pm 179.8$ Hz; $J(P_1, P_3) = \mp 10.5$; $J(P_2, P_3) = \pm 21.5\}$; $\{J(P_1, Pt_5) = \pm 3462$; $J(P_2, Pt_5) = \pm 204.1$; $J(P_3, Pt_5) = \pm 3613.0\}$; $\{J(P_1, Pt_6) = \pm 279.9$; $J(P_2, Pt_6) = \pm 2663.1$; $J(P_3, Pt_6) = \mp 116.9\}$. These parameters are consistent with the coupling constants observed in other diplatinum phosphine complexes.^{4,7,19}

Most of the lines from isotopomer **2D** are too weak to be identified well enough to attempt a simulation. The Pt_5 – Pt_6 coupling, the only coupling needed to simulate **2D**, is unknown due to enormous range of possible values and the complexity of the spectra.

Reactions of $(Ph_3P)_3(CO)Pt_2S$. Addition of $Ph_2PCH_2PPh_2$ to **2** in a mixture of dichloromethane and ethanol produces the substitution product **6**. The infrared spectrum of **6** shows that the carbonyl group has been lost since there is no absorption in the region where terminal or bridging carbonyl groups absorb. The $^{31}P\{^1H\}$ spectrum indicates that **6** has

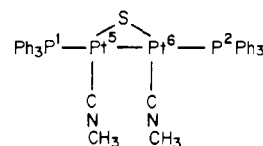


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higher symmetry than **2**. The spectrum is dominated by intense features at 29.4 (due to PPh_3) and -7.9 ppm (due to $Ph_2PCH_2PPh_2$). These are due to the two distinct phosphorus nuclei in the isotopomer of **6** which is not labeled with ^{195}Pt . This portion of the spectrum belongs to the $AA'XX'$ spin system, but the features are too compressed to allow the P–P couplings to be ascertained. The spectrum of the singly labeled isotopomer (which occurs in only one form due to the chemical equivalence of the two platinum ions) consists of 64 equally intense lines. Analysis of this spectrum produces the following assignment of coupling constants: $\{J(P_1, Pt_5) \pm 3191.6$; $J(P_1, Pt_6) = \pm 231.2\}$; $\{J(P_3, Pt_5) = \pm 3537.5$; $J(P_3, Pt_6) = \mp 108.6\}$; $\{J(P_1, P_2) = 174.9\}$; $\{J(P_1, P_3 \text{ or } P_4) = \mp 14.7$; $J(P_1, P_3 \text{ or } P_4) = \pm 7.6\}$. The isotopomer with two ^{195}Pt ions produces two pairs of weak peaks one centered around each of the phosphorus chemical shifts with separations given by $|J(P_1, Pt_5) + J(P_1, Pt_6)| = 3422.3$ Hz and $|J(P_3, Pt_5) + J(P_3, Pt_6)| = 3428.75$. The line separations require that $J(P_1, P_5)$ and $J(P_1, Pt_6)$ have the same sign, while $J(P_3, Pt_5)$ and $J(P_3, Pt_6)$ have opposite signs. These relative sign assignments agree with those made in simulating the spectra of the singly labeled isotopomers. The line positions calculated on the basis of these separations (4091.8, 1074.0, 668.8, and -2354.0 Hz) are in good agreement with the observed line positions (4090.6, 1073.0, 667.5, and -2355.7 Hz). The other peaks in the spectrum of this isotopomer were too weak to be detected, and as a result $J(Pt_5, Pt_6)$ has not been assigned.

The 1H NMR spectrum of **6** shows a complex phenyl multiplet between 6.9 and 7.5 ppm and a methylene multiplet centered at 5.33 ppm. Due to coupling to ^{195}Pt , the methylene resonance is split into a 1:8:18:8:1 quintet⁷ with $J(Pt, H) = 34.1$ Hz, a value similar to that observed in other platinum complexes with this bridging diphosphine.^{7,19} Each of these lines is further split into a 1:2:3:4:3:2:1 septet due to coupling to the two pairs of phosphorus atoms. The P–H coupling constants are 10.2 and 5.1 Hz. These values are also consistent with the H–P coupling constants found for other related binuclear complexes³ although it is not possible to unambiguously assign the coupling constants to the specific P–H interactions involved.

Addition of methyl isocyanide to **2** results in the loss of carbon monoxide and triphenylphosphine to yield **7**. The



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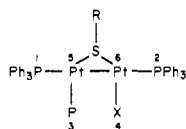
infrared spectrum of **7** exhibits a terminal isocyanide stretch at 2160 cm^{-1} (Nujol mull) and no carbonyl absorptions. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 26.8 ppm due to the unlabeled isotopomer and an eight line pattern for the singly labeled form $\{J(P_1, P_2) = 178.1$ Hz; $\{J(P_1, Pt_5) = \pm 3054.4$; $J(P_1, Pt_6) = \pm 215.2\}$. The only discernible lines due to the doubly labeled isotopomer are a pair of lines centered about the phosphorus chemical shift with a separation given by $|J(P_1, Pt_5) + J(P_1, Pt_6)|$ (calcd 3269.6, found 3269.6 Hz); the separation between these lines requires that $J(P_1, Pt_5)$ and $J(P_1, Pt_6)$ have the same sign.

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Table I. Coupling Constants (Hz) for Binuclear Platinum Complexes^{a,b}

compd	<i>J</i> (1,2)	<i>J</i> (1,3)	<i>J</i> (1,4)	<i>J</i> (1,5)	<i>J</i> (1,6)	<i>J</i> (2,3)	<i>J</i> (2,5)	<i>J</i> (2,6)	<i>J</i> (3,4)	<i>J</i> (3,5)	<i>J</i> (3,6)
(Ph ₃ P) ₃ (CO)Pt ₂ S	±179.8 ⁱ	∓10.5 ⁱ		±3462.2 ⁱⁱ	±279.9 ⁱⁱⁱ	±21.5 ⁱ	±204.1 ⁱⁱ	±2663.1 ⁱⁱⁱ		±3613.0 ⁱⁱ	∓116.9 ⁱⁱⁱ
(Ph ₃ P) ₃ (CO)Pt ₂ SCH ₃ ⁺	±164.2 ⁱ	∓13.3 ⁱ		±3270 ⁱⁱ	±136 ⁱⁱⁱ	±19.3 ⁱ	±176 ⁱⁱ	±2598 ⁱⁱⁱ		±3833 ⁱⁱ	∓95 ⁱⁱⁱ
(Ph ₃ P) ₂ (dpm)Pt ₂ S	174.9	∓14.7 ⁱ	±7.6 ⁱ	±3191.6 ⁱⁱ	±231.2 ⁱⁱ	<i>J</i> (1,4) ^c	<i>J</i> (1,6) ^c	<i>J</i> (1,5) ^c	37.9	±3537.5 ⁱⁱⁱ	∓108.6 ⁱⁱⁱ
(Ph ₃ P) ₂ (dpm)Pt ₂ SCH ₃ ⁺	160	±16 ⁱ	∓10 ⁱ	±3040 ⁱⁱ	±175 ⁱⁱ	<i>J</i> (1,4) ^c	<i>J</i> (1,6) ^c	<i>J</i> (1,5) ^c	25	±3896 ⁱⁱⁱ	∓89 ⁱⁱⁱ
(Ph ₃ P) ₂ (CH ₃ NC) ₂ Pt ₂ S	178.1			±3054.4 ⁱ	±215.2 ⁱ		<i>J</i> (1,6) ^c	<i>J</i> (1,5) ^c			

^a The numbering system for this table is



^b Coupling constants with a common superscript have correlated signs. Correlations are only valid within an individual compound. ^c Symmetrically equivalent coupling constants are indicated.

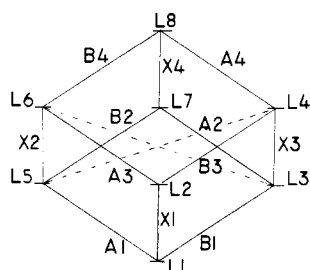


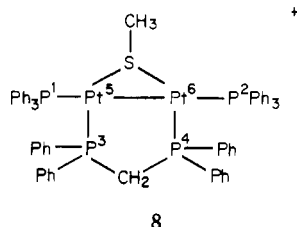
Figure 3. The energy level and transition diagram of an ABX spin system. The broken lines are X transitions (or combination lines) which become forbidden in the APX limit.

The ¹H NMR spectrum of **7** shows a complex phenyl absorbance and a symmetrical methyl pattern at 2.79 ppm. This resonance consists of a strong central triplet flanked symmetrically by three pairs of less intense satellites. All features have been successfully simulated by using the following parameters in conjunction with parameters previously determined: *J*(H,Pt₅) = 8 Hz; *J*(H,Pt₆) = 3 Hz; *J*(P,H) = 1.4 Hz. The values for *J*(H,Pt₅) and *J*(H,Pt₆) are consistent with the parameters previously found for the equatorial isocyanide ligands in Pt₂(CNCH₃)₆^{2+,18}

The assignment of geometry to **7** is based on the need for the triphenylphosphine ligands to occupy symmetrically equivalent sites, the larger value of *J*(P₁,P₂) which is consistent with the trans-PPtP geometry, and steric interactions which would resist an interchanging of the phosphine and isocyanide ligands.

Attempts to insert carbon monoxide or methyl isocyanide into the Pt–Pt bond of these compounds have not succeeded. Thus **2**, **6**, and **7** in dichloromethane solution are unreactive toward carbon monoxide at 1-atm pressure. No chemical transformation occurs when methyl isocyanide is added to solutions of **6** or **7**.

Methyl iodide readily alkylates both **2** and **3**. The site of alkylation of **3** is readily identified as the sulfur atom so that the product contains the cation **8**. The ³¹P{¹H} NMR spec-

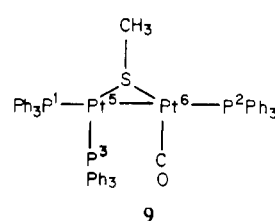


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trum of the salt [(Ph₃P)₂(Ph₂PCH₂PPh₂)Pt₂SCH₃][I] indicates

that the symmetry of **3** has been preserved after alkylation and there are only two phosphorus environments in **8**. The spectrum of **8** closely resembles that of **3** and has been successfully analyzed in terms of the following parameters: δ(PPh₃) 21.39; δ(Ph₂PCH₂PPh₂) -4.06; {*J*(P₁,Pt₅) = ±3040; *J*(P₁,Pt₆) = ±175}, {*J*(P₃,Pt₅) = ±3896; *J*(P₃,Pt₆) = ∓89}; {*J*(P₁,P₂) = 160}; {*J*(P₁,P₃ or P₄) = ±16; *J*(P₁,P₃ or P₄) = ∓10}; {*J*(P₃,P₄) = 25}. The isotomer with two ¹⁹⁵Pt ions produces two pairs of weak peaks at 3343.4, 133.16 and 1574.2, -2233.8 Hz whose positions are predicted to be 3345.2, 131.2, 1575.3, and -2232.7 Hz on the basis of the previously assigned coupling constants and chemical shifts. Again the low abundance of doubly ¹⁹⁵Pt labeled isotomer has precluded the determination of *J*(Pt,Pt). In the ¹H NMR spectra, the methyl group of the thiol ligand appears as a quintet of triplets due to coupling of the two trans phosphines and ¹⁹⁵Pt: δ 1.51, *J*(P,H) = 5.4 Hz; *J*(Pt,H) = 41.6 Hz.

Alkylation of **2** with methyl iodide produces the cation **9**



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which has been purified of its hexafluorophosphate salt. The infrared spectrum of this salt contains absorption due to ν(CO) at 2043 cm⁻¹ and ν(P–F) at 838 in addition to bands similar in position to the spectral features of **2**. The ³¹P{¹H} NMR spectrum of **9** shows considerable similarity to that of **2**, an observation which is consistent with alkylation at sulfur. A selective population transfer experiment was undertaken to unambiguously assign the chemical shifts of P₁ and P₂. The spectrum has been analyzed in terms of the following parameters: δ(P₁) 18.7; δ(P₂) 15.4; δ(P₃) 22.1; {*J*(P₁,P₂) = ±164.2 Hz; *J*(P₁,P₃) = ∓13.3; *J*(P₂,P₃) = ±19.3}, {*J*(P₁,Pt₅) = ±3270; *J*(P₂,Pt₅) = ±176; *J*(P₃,Pt₅) ±3833}, {*J*(P₁,Pt₆) = ±136; *J*(P₂,Pt₆) = ±2598; *J*(P₃,Pt₆) = ∓95}. The counterion PF₆⁻ exhibits a septet in the ³¹P{¹H} at -143.5 ppm (*J*(PF) = 712.8 Hz). The ¹H NMR spectrum of **6** in CDCl₃ shows a quintet of doublets for the methyl group due to coupling to ¹⁹⁵Pt and to one trans phosphine: δ 1.10, *J*(H,P) = 5.4 Hz, *J*(Pt,H) = 41.4 Hz. The parameters are similar to those found for **8**.

Oxidation of **2** with iodine produces (Ph₃P)₂PtI₂ (a mixture of cis and trans isomers) as the only identifiable product.

The reaction of **2** with carbon disulfide produces (Ph₃P)₂PtS₂CS in 69% yield. Small quantities of a second product which rapidly decomposed were also observed but it

was not possible to characterize this species.

No reaction between **2** and diphenylacetylene or dimethyl acetylenedicarboxylate was observed.

Discussion

The results described here indicate that the Pt₂S core in these binuclear Pt(I) complexes is remarkably stable. The metal-metal bond is unreactive toward insertion of small molecules like carbon monoxide and isocyanides. Substitution reactions proceed readily at positions 3 and 4. This is perhaps not surprising since in all cases investigated substitution at these positions alleviates steric interaction between these two proximate positions. Substitution at the 1 and 2 positions has not been achieved. In this context, it should be noted that substitution of M₂(CNCH₃)₆²⁺ (M = Pd, Pt) by triphenylphosphine occurs exclusively at the positions trans to the metal-metal bond.²⁰

The coupling constants for these platinum complexes are organized in Table I for ready comparison. The comparable coupling constants are remarkably similar in the different compounds. Notice also that methylation at sulfur causes a uniform effect, i.e., all coupling constants diminish in absolute magnitude except for *J*(3,5) and *J*(1,3) which increase. Since ¹*J*(P,Pt) can be expected to be positive,²¹ the signs of ²*J*(P,Pt)

can be confidently assigned. For a nearly linear Pt-Pt-P unit, ²*J*(P,Pt) (that is *J*(1,6) and *J*(2,5)) has the same sign as ¹*J*(P,Pt) and can be assumed to be positive. However, with the Pt-Pt-P angle near 90°, ²*J*(P,Pt) is smaller in absolute magnitude and its sign is negative; that is, *J*(3,6) has the opposite sign from *J*(3,5), the direct Pt-P coupling, whose sign may be confidently taken as positive. Similarly, in (Ph₂MeP)₂Pt₂(dpm)₂²⁺, the linear ²*J*(P,Pt) is large and positive (+750 Hz) while the bent ²*J*(P,Pt) is smaller in magnitude and negative (-120 Hz). This relationship may have utility in other structural work. The other coupling constants have similar magnitudes to those determined for related compounds.^{4,7,19}

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-7924575) for support, Matthey Bishop for a loan of precious metal salts, and Dr. B. E. Mann for helpful discussions. Purchase of the NMR spectrometer by the UCD NMR Facility was made possible by an NSF instrumentation grant (CHE-7904832) to the Department of Chemistry.

Registry No. **2**, 27664-43-3; **6**, 77462-34-1; **7**, 77462-33-0; **8**, iodide salt, 77462-32-9; **9**, hexafluorophosphate salt, 77462-31-8; (Ph₃P)₂PtS₂CS, 65354-15-6; *cis*-(PPh₃)₂PtI₂, 35085-00-8; Pt(PPh₃)₃, 13517-35-6; CS₂, 75-15-0; I₂, 7553-56-2; *trans*-(Ph₃P)₂PtI₂, 35085-01-9.

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Arene Transition-Metal Chemistry. 6. Hydride Reduction of η⁶-Arene Iridium(I) Complexes¹

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Arene complexes of the type [Ir(η⁶-C₆R₆)(η⁴-c-1,5-C₈H₁₂)⁺](BF₄⁻) (R = H or CH₃) react rapidly with LiB(C₂H₅)₃H to produce the cyclohexadienyl complexes [Ir(η⁵-C₆R₆H)(η⁴-c-1,5-C₈H₁₂)] (R = H or CH₃). Reduction of [Ir(η⁶-C₆D₆)(η⁴-c-1,5-C₈H₁₂)⁺](BF₄⁻) verified that the added hydrogen appears in the exo position of the cyclohexadienyl ring. The site of hydride attack is discussed in terms of related reactions reported in the literature.

Introduction

It has long been recognized that arenes coordinated to transition metals are activated with respect to nucleophilic attack.³ The importance of this reaction in organic synthesis has recently been reviewed.^{4,5} In connection with our interest in the chemistry of coordinated arenes^{1,2} and the general problem of nucleophilic attack on coordinated hydrocarbons,^{6,7} we undertook a study of the reaction of LiB(C₂H₅)₃H with

[Ir(η⁶-C₆R₆)(η⁴-c-1,5-C₈H₁₂)⁺](BF₄⁻) complexes (R = H, D, or CH₃).

Experimental Section

General Information. Synthetic procedures and solvent purification methods have been described in a previous paper.¹ [Ir(η⁶-C₆R₆)(η⁴-COD)⁺](BF₄⁻) complexes (COD = 1,5-cyclooctadiene), R = H or CH₃, were prepared according to the literature procedures.^{1,2} LiB(C₂H₅)₃H (1.0 M) in tetrahydrofuran was purchased from Aldrich Chemical Co., Milwaukee, WI.

Infrared spectra were recorded as Nujol or halocarbon oil mulls between NaCl or KBr windows on a Perkin-Elmer 597 spectrometer; peaks are reported in cm⁻¹. The following abbreviations are used in reporting infrared data: w = weak, m = moderate, v = very.

Proton NMR spectra were recorded at 90 MHz on a Varian EM-390 spectrometer or at 180 MHz on a modified Bruker 42-kG multinuclear, pulse-FT NMR spectrometer equipped with Nicolet Technology Corp. software. Chemical shifts of all ¹H NMR spectra are reported with use of the δ scale; positive shifts are downfield from internal Me₄Si standard. The numbers and symbols in parentheses following the chemical shift value indicate the peak multiplicity (m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet, br =

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