complexes having bridged halogen atoms. In these binuclear complexes, the charge-transfer interaction between Cu(I) and bpy is remarkably weakened upon the addition of CO, and consequently CO competes with bpy concerning the interaction with Cu(I) atom. Then, the bondings of Cu–L and Cu–CO are delicately balanced by the halide ions, as is illustrated by the variation of the CO affinity of halogeno derivatives in Table III. In this sense the bridged halogen atoms take an important role in the reaction with CO.

Finally, the equilibrium constants of [(bpy)CuCl₂Cu-(bpy)CO] remarkably depend on solvent as shown in Table III. In a series of ketones, noncoordinating solvents, the following order is obtained: $K(\text{MP}) > K(\text{3-butanone}) > K(\text{acetone})$. In other words, the larger the bulk dielectric constant of solvent, the smaller the equilibrium constant. It is well-known[27] that the metal–CO bond has usually a low dipole moment and is electronically neutral. On this basis, the nonpolar media can be available for a tight Cu–CO bonding. Therefore, the solvent effect, regarded as a media effect, is characterized by bulk properties of the solvent such as the dielectric constant.

Conclusion. In summarizing the above results and discussion, the following conclusion is drawn. Binuclear [CuXL]₂ complexes reversibly react with CO. The resultant CO adducts are monocarbonylated five-coordinate complexes. Their stability is influenced by the several factors. (1) Effect of halide ions. This effect is primarily ascribed to their electronegativity. (2) The flexibility of the precursor complex to accept a square-pyramidal configuration. This flexibility is attributed to the specific binuclear structure having bridged halide ions. (3) Solvent effect on Cu–CO bonding. Nonpolar solvents promote the formation of Cu–CO bonding.

Registry No. 2, 77482-32-7; **3,** 77482-33-8; **4,** 39210-78-1; **5,** 74829-17-7; **6,** 77482-34-9; **7,** 77482-35-0; [CuBr(bpy)]₂, 77482-36-1; [CuI(bpy)]₂, 39210-77-0; [CuCl(phen)]₂, 77482-37-2; [Cu(phen)₂]Cl, 77482-38-3; [Cu(phen)₂]ClO₄, 23624-03-5; [Cu(CH₃CN)₄]ClO₄, 14057-91-1.

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Halogen Additions to Bis(diphenylphosphino)methane Complexes of Palladium. Interrelationships of Monomeric and Dimeric Complexes of Pd(II), Pd(I), and Pd(0)

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Addition of halogens (Cl₂, Br₂, I₂) and pentafluorophenyl disulfide to Pd₂(dpm)₃ (dpm = bis(diphenylphosphino)methane) proceeds stepwise, under stoichiometric control, to yield Pd₂(dpm)₂X₂ and Pd(dpm)X₂ as isolable products. Proton and phosphorus NMR data are reported for these complexes. During the oxidation of Pd₂(dpm)₂X₂ to Pd(dpm)X₂, Pd₂(dpm)₂X₄ is an intermediate which has been observed and identified by ¹H and ³¹P{¹H} NMR spectroscopy. Speculation on the mechanism of the conversion of Pd₂(dpm)₂X₂ to Pd(dpm)X₂ (bridging to chelating dpm) is offered.

Complexes with bridging bis(diphenylphosphino)methane (dpm) ligands have been reported for three different oxidation states of palladium: Pd(0) in Pd₂(dpm)₃,[1] Pd(I) in Pd₂-(dpm)₂X₂ (X = halide or pseudohalide),[2] and Pd(II) in Pd-(dpm)X₂.[3,4] Reactions interconverting these oxidation states must involve either ligand loss or the conversion of the dpm ligand from a bridging to a chelating form. While the versatility of bridging dpm ligands is known to facilitate a number of novel chemical reactions (metal–metal bond forming reactions,[5–7] metal–metal bond breaking reactions,[2,8–10] and reactions forming side-on bound bridging carbonyl[11] and isocyanide[12] ligands), little attention has been paid to reactions

in which the nature or number of dpm ligands changes. In general, conditions have been found where reactions involving dinuclear, doubly bridged complexes give dimeric products in high yield and with little evidence for monomeric or more highly polymerized side products. However, we have been aware for some time that certain reactions of dinuclear dpm complexes proceed to give mononuclear products. This is particularly true when elevated temperatures (>50 °C) are used. We have reported that the oxidation of dimeric Rh₂-(dpm)₂(CN-*n*-Bu)₄²⁺ by some disulfides produces monomeric Rh(III) complexes rather than dimeric Rh(II) species like those which are formed by the corresponding oxidation by halogens.[13] The specific reaction paths involved in depolymerization or polymerization for dpm complexes have not as yet been explored.

The relationship between Pd(I) and Pd(II) dpm complexes is a case where depolymerization is important. Pd(I)–dpm complexes of the type Pd₂(dpm)₂X₂ (X = anionic ligand, usually a halide or pseudohalide) possess the structure **1** in which two nearly planar metal centers are joined through a direct Pd–Pd bond. This structural type has been established through crystallographic studies of Pd₂(dpm)₂Br₂[14] and Pd₂-(dpm)₂Cl(SnCl₃)[15] and the isoelectronic Pt(I) complex Pt₂-

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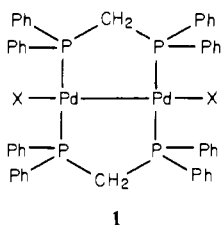
1

(dpm)$_2$Cl$_2$.[16] In contrast, crystallographic studies of the Pd(II) complexes Pd(dpm)Cl$_2$[3] and Pd(dpm)(SCN)$_2$[4] have shown that these possess the chelated structure **2**. From the
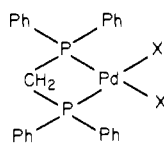
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structural observations, the question arises whether oxidative addition of halogens to the Pd(I) dimers **1** produces the Pd(II) monomers **2**, and if so, when in the process does the phosphine ligand rearrange from the bridged to the chelated form? Here we report low-temperature NMR spectroscopic studies in which some intermediates can be observed.

Experimental Section

Preparation of Compounds. Pd$_2$(dpm)$_3$,[1] Pd$_2$(dpm)$_2$X$_2$,[2] and Pd-(dpm)X$_2$[3,4] were prepared by established routes.

Pd$_2$(Ph$_2$PCH$_2$PPh$_2$)$_2$(SC$_6$F$_5$)$_2$. Pentafluorophenyl disulfide (0.0090 g, 0.22 mmol) was added to a solution of 0.30 g (0.22 mmol) of Pd$_2$(dpm)$_3$ in 15 mL of oxygen-free dichloromethane. Cyclohexane (15 mL) was added to the deep red solution, and it was evaporated under a nitrogen stream to a volume of 10 mL. During the evaporation, the product formed deep red crystals; these were collected and washed with cyclohexane. Purification was achieved by recrystallization from dichloromethane/cyclohexane. ^{1}H NMR spectroscopy indicates that the product crystallizes as a cyclohexane solvate; yield 80%. Anal. Calcd for C$_{62}$H$_{44}$F$_{10}$P$_4$Pd$_2$S$_2$: C, 53.97; H, 3.21. Found: C, 54.02; H, 3.51.

Pd(Ph$_2$PCH$_2$PPh$_2$)(SC$_6$F$_5$)$_2$. Pentafluorophenyl disulfide (29 mg, 0.073 mmol) was added to a solution of 83 mg (0.060 mmol) of Pd$_2$(dpm)$_2$(SC$_6$H$_5$)$_2$ in 10 mL of dichloromethane. The orange solution was filtered, and ether was added to the filtrate to precipitate the product as fine yellow needles. These were collected by filtration, washed with ether, and recrystallized from dichloromethane/ether; yield 84 mg, 79%. Anal. Calcd for C$_{37}$H$_{22}$F$_{10}$P$_2$PdS$_2$: C, 49.99; H, 2.49. Found: C, 49.64; H, 2.38.

Reaction of Pd$_2$(dpm)$_3$ with Pd(dpm)I$_2$. Samples of Pd$_2$(dpm)$_3$ (0.1212 g, 0.089 mmol) and Pd(dpm)I$_2$ (0.132 g, 0.178 mmol) were dissolved in 10 mL of dichloromethane. After 2 h of standing, the solution was filtered and the product was precipitated through the addition of ether; yield 0.19 g, 87%. The product was identified as Pd$_2$(dpm)$_2$I$_2$ by comparison of thin-layer chromatograms and electronic and ^{1}H NMR spectra with an authentic sample.

Physical Measurements. ^{1}H (5-mm tubes, 200 MHz) and ^{31}P{^{1}H} (12-mm tubes, 81 MHz) were recorded on a Nicolet NT-200 Fourier Transform spectrometer. An external 85% phosphoric acid reference was used for ^{31}P NMR spectra and the high-frequency-positive convention, recommended by IUPAC, is used in reporting chemical shifts.

Results and Discussion

Reaction Chemistry. Addition of 1 equiv of iodine or pentafluorophenyl disulfide to Pd$_2$(dpm)$_3$ in dichloromethane solution at room temperature results in the smooth conversions to Pd$_2$(dpm)$_2$I$_2$ and Pd$_2$(dpm)$_2$(SC$_6$F$_5$)$_2$, respectively. Both have been isolated in good yield (80%). No evidence has been

Table I. NMR Parameters for Palladium Complexes

complex	^{1}H[a]		^{31}P[b]
	shift, ppm	J_{P-H}, Hz	shift, ppm
Pd(dpm)Cl$_2$	4.28	10.8 (t)[c]	−53.7
Pd(dpm)Br$_2$	4.33	10.6 (t)	−55.65
Pd(dpm)I$_2$	4.55	10.4 (t)	−62.7
Pd(dpm)(SC$_6$F$_5$)$_2$	4.13	10.05 (t)	−39.30
Pd$_2$(dpm)$_2$Cl$_2$	4.17	4.0 (q)	−2.5
Pd$_2$(dpm)$_2$Br$_2$	4.22	4.0 (q)	−4.71
Pd$_2$(dpm)$_2$I$_2$	4.27	4.0 (q)	−10.3
Pd$_2$(dpm)$_2$(SC$_6$F$_5$)$_2$	4.12	4.1 (q)	−2.6
Pd$_2$(dpm)$_3$	3.00 (br)	d	14.6
Pd$_2$(dpm)$_2$Cl$_4$[e]	4.55[b]	4.6 (q)	8.5
Pd$_2$(dpm)$_2$Br$_4$[e]	4.6	d	4.90
Pd$_2$(dpm)$_2$I$_4$[e]	5.18	4.0 (q)	−0.73

[a] In CD$_2$Cl$_2$ solution. [b] In CDCl$_3$ solution. [c] t = 1:2:1 triplet, q = 1:4:6:4:1 quintet. [d] J_{P-H} is unresolved. [e] Transient intermediates observed at −40 °C.

found for the formation of species of the type Pd$_2$(dpm)$_3$X$_2$. These reactions offer a new route to the formation of Pd(I) dimers, and they resemble the transannular addition of halogens to Rh(I) dimers [Rh$_2$(dpm)$_2$(CNR)$_4$]$^{2+}$ to produce metal–metal bonded Rh(II) complexes, [Rh$_2$(dpm)$_2$-(CNR)$_4$X$_2$]$^{2+}$. Further addition of iodine to Pd$_2$(dpm)$_2$I$_2$ and pentafluorophenyl disulfide to Pd$_2$(dpm)$_2$(SC$_6$F$_5$)$_2$ produces solid, crystalline Pd(dpm)I$_2$ and Pd(dpm)(SC$_6$F$_5$)$_2$, respectively. This behavior differs from the oxidative stability of the Rh(II) dimers [Rh$_2$(dpm)$_2$(CNR)$_4$X$_2$]$^{2+}$ which do not react with excess halogen to form monomeric Rh(III) complexes.[5] The difference in behavior may be linked to structural and electronic differences if the production of a Rh(II) dimer is governed by kinetic rather than thermodynamic properties. Complexes of the type Pd$_2$(dpm)$_2$X$_2$ are 16-electron species which have vacant coordination sites accessible for halogen addition whereas complexes of the type [Rh$_2$(dpm)$_2$-(CNR)$_4$X$_2$]$^{2+}$ are coordinately saturated 18-electron compounds.

Redox condensation between Pd(0) and Pd(II) complexes has previously been used to generate Pd(I) dimers. A similar reaction occurs in dichloromethane solution between Pd$_2$-(dpm)$_3$ and Pd(dpm)I$_2$ where the product Pd$_2$(dpm)$_2$I$_2$ forms in 87% isolated yields.

NMR Characterization of Isolated Pd(II) and Pd(I) Complexes. The ^{31}P{^{1}H} and ^{1}H NMR parameters for the dimers, Pd$_2$(dpm)$_2$X$_2$ (X = I, Br, Cl), and Pd(II) monomers, Pd-(dpm)X$_2$, are reported in Table I. Both types of complexes contain a single chemically unique phosphorus site; consequently each molecule displays a characteristic singlet in its ^{31}P{^{1}H} spectrum. For the Pd(I) dimers, these resonances occur in the region −1.5 to −10.5 ppm while for the Pd(II) monomers, the resonances occur in the region −53.5 to −62.7 ppm. In both cases changing the halide from Cl to Br to I results in a shift to lower frequency. The chemical shift of the ^{31}P resonance in these Pd(II) monomers is unusual because it occurs at lower frequency than the free phosphine whose phosphorus resonance occurs at −21.6 ppm. Coordination of phosphines generally results in a shift of the ^{31}P resonance to higher frequency and an empirical linear relation between ΔP (as defined by eq 1)

$$\Delta P = \delta p(\text{complex}) - \delta p(\text{ligand}) \qquad (1)$$

and δp for the free ligand has been noted.[17,18] However it has been pointed out that complexes such as Pt(dpm)Cl$_2$ and Pt(dpm)(CH$_3$)$_2$ deviate from this empirical correlation and, like the palladium–dpm complexes, show low-frequency
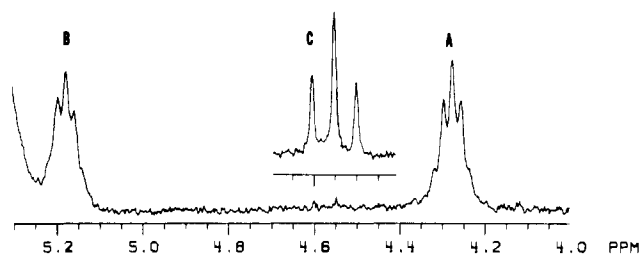
Figure 1. The 200-MHz spectrum of a CD_2Cl_2 solution containing $Pd_2(dpm)_2I_2$ and a 0.5 molar equiv of I_2 at -40 °C. The quintet A is due to $Pd_2(dpm)_2I_2$, while quintet B is due to $Pd_2(dpm)_2I_4$. The inset C shows the triplet due to $Pd(dpm)I_2$. Only the portion of the spectrum due to methylene protons is shown.

shifts.[19] The unusual shift for these Pd(II) and Pt(II) monomers cannot simply relate to the presence of a four-membered chelate ring since the chelated complexes $M(CO)_4$dpm (M = Cr and Mo) show that usual high-frequency shift.[20] Nor is the shift of the Pd(II) monomers explained by unusual strain in the C–P–C angles. Decreasing the C–P–C angles in trivalent phosphorus compounds does induce low-frequency shifts.[21] However, inspection of the crystallographic data[3] for $Pd(dpm)Cl_2$, $Pd(Ph_2PCH_2CH_2PPh_2)Cl_2$, $Pd(dpe)Cl_2$, and $Pd(Ph_2PCH_2CH_2CH_2PPh_2)$, $Pd(dpp)Cl_2$, shows no unusual decrease in the C–P–C angles for $Pd(dpm)Cl_2$. The ^{31}P chemical shifts for $Pd(dpe)Cl_2$ and $Pd(dpp)Cl_2$ show the normal high-frequency shifts with respect to their free ligands. Further study of the empirical correlation between the ^{31}P chemical shifts of coordinated and free phosphines is clearly warranted.

The ^1H NMR resonances for the methylene protons of the diphosphine ligand are structure sensitive. For both the Pd(I) and the Pd(II) complexes, these resonances occur in the region 4.0–4.6 ppm. In both cases, the resonance pattern indicates that the protons of each methylene group appear to be equivalent (over the temperature range -40 to $+30$ °C) despite the fact that, in a static five-membered Pd_2P_2C or four-membered PdP_2C ring, these two protons are inequivalent. Thus rapid flipping of these rings must be occurring.

The spin–spin splitting due to ^{31}P differs in the two types of complexes. For the chelated Pd(II) complexes, a triplet due to coupling of the protons to two equivalent phosphorus atoms is observed for the methylene protons. The coupling constant is ca. 10 Hz. For the bridged Pd(I) complexes, the methylene resonance appears as a symmetrical 1:4:6:4:1 quintet with a smaller P–H coupling (ca. 4 Hz). The quintet arises because of the well-known virtual coupling phenomenon observed for complexes involving trans phosphine units. For the present case, the trans P–P coupling is much larger than the P–H coupling. As a result, the methylene protons appear to be coupled to four equivalent phosphorus nuclei. The magnitude of the coupling constant is similar to that observed for the methyl protons in trans-methyldiphenylphosphine units.[8]

NMR Studies of the Addition of Halogens to $Pd_2(dpm)_2X_2$.
The addition of halogens proceeds through the transient existence of a binuclear species. This reaction may be summarized by eq 2. Addition of a solution of iodine to a solution of $Pd_2(dpm)_2I_2$ at -40 °C produces an intermediate which has been detected by ^{31}P and ^1H NMR spectroscopy. The ^1H NMR spectra for $Pd_2(dpm)_2I_2$, the intermediate 3, and Pd-$(dpm)I_2$ are shown in Figure 1. The methylene resonance of the intermediate appears as a 1:4:6:4:1 quintet at 5.18 ppm
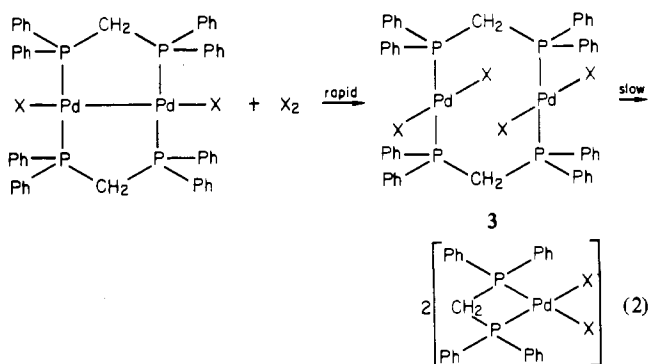

with $J_{P-H} = 4.0$ Hz. These parameters require that the intermediate have a symmetrically bridged, dimeric structure with trans dpm ligands. Structure 3 is in complete accord with these requirements. On standing at -15 °C or on warming to room temperature, the quintet at 5.18 ppm decreases in intensity as the methylene triplet due to $Pd(dpm)I_2$ grows. The ^{31}P NMR spectral changes parallel the proton spectra. Addition of a chloroform solution of iodine to a chloroform solution of $Pd_2(dpm)_2I_2$ causes a new resonance to grow at -0.73 ppm while the resonance due to $Pd_2(dpm)_2I_2$ decays. On standing at 15 °C the intensity of this resonances decays in first-order fashion with a half-life of 360 s and the characteristic resonance of $Pd(dpm)I_2$ grows. The observation of a single phosphorus resonance for the intermediate is in accord with structure 3. The chemical shift for this resonance is compatible with a bridged rather than a chelated geometry for the dpm ligand. The intermediate has been observed in both chloroform and dichloromethane solution although its decay to $Pd(dpm)I_2$ is more rapid in dichloromethane.

The course of oxidation is similar with other halogens. Addition of bromine to $Pd_2(dpm)_2Br_2$ produces $Pd_2(dpm)_2Br_4$ as a transient intermediate and the addition of chlorine to $Pd_2(dpm)_2Cl_2$ forms $Pd_2(dpm)_2Cl_4$ which subsequently separates to form $Pd(dpm)Cl_2$. The NMR characteristics of these intermediates are presented in Table I.

The mechanism of the second step of reaction 1, the mode of dissociation of the binuclear intermediate, deserves attention. This reaction occurs readily in the absence of added ligands. The kinetic behavior is consistent with a unimolecular reaction. The transformation can be viewed as a series of substitution reactions. Since substitution reactions of planar, d^8 metal complexes are generally associative rather than dissociative,[22] it is unlikely that the intermediate simply fragments by direct Pd–P bond rupture. Rather, we suspect that halide bridges form prior to Pd–P bond breaking.[23] The formation of halide bridges will convert the 16-electron, four-coordinate palladium centers into 18-electron, five-coordinate ones from which phosphine dissociation can proceed readily. Specifically, structural rearrangements to 4 or 5^{24} are realistic possibilities. The likelihood of such rearrangements is supported by the available structural information on other dpm-bridged complexes. Structural studies on the stable dimers $Rh_2(dpm)_2$-$(CO)_2Cl_2$ and $Rh_2(dam)_2(CO)_2Cl_2$ reveal that they have the

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(23) Unfortunately there is no good kinetic model available for comparison. Typical substitution reactions involve attack on a metal complex by an external nucleophile which enters from bulk solution. In the case of fragmentation of $Pd_2(dpm)_2X_4$, however, the nucleophile that forms our proposed five-coordinate intermediates is already part of the complex. Consequently complications arising from proximity and strain effects cloud any comparison with simple substitution.

(24) The spectroscopic data for $Pd_2(dpm)_2X_4$ are also completely compatible with either structure 4 or 5 representing the ground-state geometry of these intermediates. We prefer structure 3 for these intermediates because of the rarity of five-coordinate palladium(II).

Ph—P—Ph ... Pd ... structures **4** and **5**
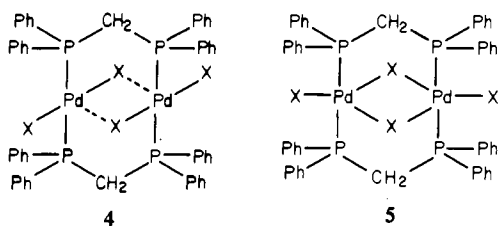
face-to-face bridged structure **6**.[25,26] The coordination planes
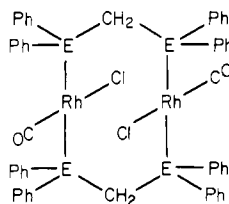
6, E = P or As

of the two rhodium ions are parallel, but they are not perpendicular to the Rh–Rh vector. Rather, in Rh$_2$(dpm)$_2$-(CO)$_2$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. Re$_2$-(dam)$_2$(CO)$_6$Cl$_2$, whose structure is known from X-ray crystallographic study,[27] has the structure **7** which incorporates
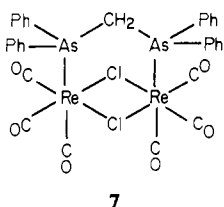
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some of the structural features of **4** and **5**. The reaction chemistry of **6** demonstrates the facility by which halo-bridged compounds may be formed from these face-to-face dimers. Treatment of **6** with a mild halide acceptor produces the A frame **8** via reaction 3.[9,28]

$$\text{(3)}$$

6   **8**
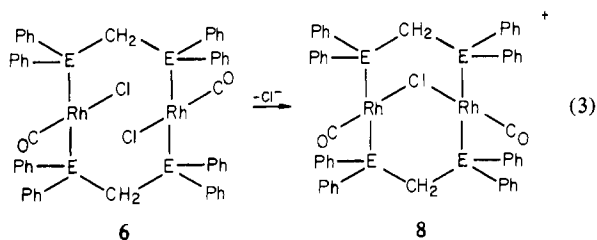
While the information outlined above suggests a reasonable mechanism for dissociation of face-to-face d^8 dimers, another important question about these molecules remains unanswered. What factors govern the structure of dimeric vs. monomeric forms of the complexes? While the palladium dimers **3** dissociate 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.

Registry No. Pd$_2$(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; Pd-(dpm)Cl$_2$, 38425-01-3; Pd(dpm)Br$_2$, 77462-41-0; Pd(dpm)I$_2$, 77462-40-9; Pd(dpm)(SC$_6$F$_5$)$_2$, 77462-39-6; Pd$_2$(dpm)$_2$Cl$_2$, 64345-29-5; Pd$_2$(dpm)$_2$Br$_2$, 60482-68-0; Pd$_2$(dpm)$_2$I$_2$, 67477-87-6; Pd$_2$-(dpm)$_2$(SC$_6$F$_5$)$_2$, 77462-38-5; Pd$_2$(dpm)$_2$Cl$_4$, 77462-37-4; Pd$_2$-(dpm)$_2$Br$_4$, 77462-36-3; Pd$_2$(dpm)$_2$I$_4$, 77462-35-2.

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

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The ^{31}P{^{1}H} NMR spectra of (Ph$_3$P)$_3$(OC)Pt$_2$(μ-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 (Ph$_3$P)$_3$(OC)Pt$_2$(μ-S) yield (Ph$_3$P)$_2$(Ph$_2$PCH$_2$PPh$_2$)Pt$_2$(μ-S) and (Ph$_3$P)$_2$(CH$_3$NC)$_2$Pt$_2$(μ-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 (Ph$_3$P)$_3$(OC)Pt$_2$(μ-SCH$_3$)$^+$ and (Ph$_3$P)$_2$(Ph$_2$PCH$_2$PPh$_2$)Pt$_2$(μ-SCH$_3$)$^+$. (Ph$_3$P)$_3$(OC)Pt$_2$(μ-S) reacts with carbon disulfide to form (Ph$_3$P)$_2$PtS$_2$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 cations[8] proceed to place a single atom of the

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