Kinetic and Mechanistic Aspects of Sulfur Abstraction from $Pd_2X_2(\mu\text{-}S)(\mu\text{-}dpm)_2$ Using dpm or dpmMe [X = Halide, dpm = Bis(diphenylphosphino)methane, dpmMe = 1,1′-Bis(diphenylphosphino)ethane] and Catalytic Conversion of H_2S to H_2

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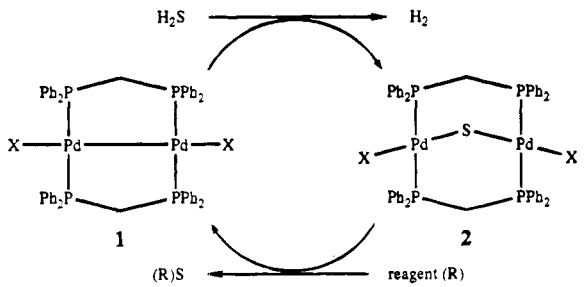
Solution kinetic and mechanistic studies were performed on the abstraction of sulfur from $Pd_2X_2(\mu\text{-}S)(\mu\text{-}dpm)_2$ [X = Cl (**2a**), Br (**2b**), I (**2c**)] using bis(diphenylphosphino)methane (dpm) to give, respectively, $Pd_2X_2(dpm)_2$ [X = Cl (**1a**), Br (**1b**), I (**1c**)] and dpm(S). The reaction is first-order in both **2** and dpm with the reactivity trend in $CHCl_3$ being X = Cl > Br > I. The activation parameters for the chloride system are $\Delta H^{\ddagger} = 41 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -127 \pm 10$ J K^{-1} mol^{-1}, and for the bromide, $\Delta H^{\ddagger} = 38 \pm 1$ kJ mol^{-1} and $\Delta S^{\ddagger} = -144 \pm 4$ J K^{-1} mol^{-1}, showing the entropy term is dominant in governing reactivity. Low-temperature NMR studies did not reveal the presence of observable intermediates. **2b** and **1b** undergo rapid diphosphine ligand exchange with dpm-d_2; with **2b**, prior to any S-abstraction, $Pd_2Br_2(\mu\text{-}S)(dpm)(dpm\text{-}d_2)$ (**7b**) and $Pd_2Br_2(\mu\text{-}S)(dpm\text{-}d_2)_2$ (**8b**) are present, while $Pd_2Br_2(dpm)(dpm\text{-}d_2)$ (**3b**) and $Pd_2Br_2(dpm\text{-}d_2)_2$ (**4b**) are formed, as well as **1b** and dpm(S)-d_2, in the abstraction reaction of **2b** with dpm-d_2. The distribution of products is close to statistical on the basis of the stoichiometries of the reactants. Reaction of **2b** with 1,1′-bis(diphenylphosphino)ethane (dpmMe) proceeds in an analogous way generating **1b**, $Pd_2Br_2(dpm)(dpmMe)$ (**5b**), $Pd_2Br_2(dpmMe)_2$ (**6b**), dpm(S), and dpmMe(S). In contrast, **1b** undergoes slow diphosphine ligand exchange with dpmMe to form **5b** and **6b**; **2b** undergoes no ligand exchange with dpmMe prior to the S-abstraction reaction. The findings are rationalized in terms of postulated intermediates and transition states that include formulations with three equivalent diphosphines. No sulfur abstraction occurs on treating **2b** with PPh_3, PPh_2Me, or $Ph_2P(CH_2)_3PPh_2$.

Introduction

The discovery in this laboratory of the stoichiometric abstraction of sulfur from H_2S using dinuclear Pd^I_2−dpm complexes in solution[1-3] (process **1** → **2**) has stimulated our interest in transition metal−H_2S chemistry. The major goal is to develop catalytic systems for the generation of H_2 from H_2S, for example, by converting complex **2** back to complex **1**.



A range of complexes of type **1** has been studied, where X = halogen, OAc, NO_3, NCO, SCN, and SH, and one or both dpm ligands have been replaced by $Ph_2PCH(Me)PPh_2$ (abbreviated dpmMe) or the 2-pyridylphosphines PPh_npy_{3-n} (n = 0−2).[2-6] Kinetic and mechanistic studies have provided a good understanding of the forward reaction (**1** → **2**), and at low temperatures hydrido mercapto intermediates have been detected, their structure being dependent on the nature of X.[2,3,6] Complexes of type **1**, containing a metal−metal bond, and the bridged-sulfide, A-frame, type **2**, have been characterized structurally.[7] The removal of the sulfur from **2** as elemental sulfur is attractive, but the net catalyzed reaction $H_2S \rightarrow H_2 + {}^1/_8S_8(s)$ is thermodynamically unfavorable (*e.g.* at 298 K, ΔH° = 20 kJ, ΔS° = −43 kJ deg^{-1}),[8] and is not practical at least under purely thermal conditions. Plasma-chemical conversions of H_2S to H_2 and elemental sulfur have been achieved.[9]

We have pursued thermal catalytic conversions of H_2S and in this context have found that the bridged S can be removed from **2** completely or partially in solution reactions by using a range of R reagents (*e.g.* an O-atom donor,[3] phosphines, CO, CN^-, biphenyl, or butadiene,[6] and Br_2 or I_2[10]). Of the phosphines tested, dpm gave quantitative reconversion of **2** to **1**, while itself being converted to the monosulfide dpm(S) (eq 1); thus, this discovery leads to the catalyzed, thermal reaction

$$\mathbf{2} + \text{dpm} \rightarrow \mathbf{1} + \text{dpm(S)} \qquad (1)$$

$$\text{dpm} + H_2S \xrightarrow{\mathbf{1}\text{ or }\mathbf{2}} \text{dpm(S)} + H_2 \qquad (2)$$

shown in eq 2,[11] which appears to be the first reported,

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(1) Lee, C.-L.; Besenyei, G.; James, B. R.; Nelson, D. A.; Lilga, M. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1175.
(2) Barnabas, A. F.; Sallin, D.; James, B. R. *Can. J. Chem.* **1989**, *64*, 2009.
(3) Besenyei, G.; Lee, C.-L.; Gulinski, J.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Inorg. Chem.* **1987**, *26*, 3622.
(4) Lee, C.-L.; Yang, Y. P.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Organometallics* **1986**, *5*, 2220.
(5) Xie, Y.; Lee, C.-L.; Yang, Y.; Rettig, S. J.; James, B. R. *Can. J. Chem.* **1992**, *70*, 751.
(6) Weng, W. Z.; Sallin, D.; James, B. R. To be published.
(7) (a) Holloway, R. G.; Penfold, B. R.; Colton, R.; McCormick, M. J. *J. Chem. Soc., Chem. Commun.* **1976**, 485. (b) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996.
(8) Harvey, K. B.; Porter, G. B. *Introduction to Physical Inorganic Chemistry*; Addison-Wesley: Reading, MA, 1962; p 296.
(9) (a) Harkness, J. B. L.; Gorski, A. J.; Daniels, E. J. U.S. Patent 5 211 923, 1991; *Chem. Abstr.* **1993**, *119*, 75745f. (b) Harkness, J. B. L.; Gorski, A. J.; Daniels, E. J. *Proc. Intersoc. Energy Convers. Eng. Conf.* **1990**, *6*, 197.

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homogeneously catalyzed conversion of H_2S to H_2. This present paper reports kinetic and mechanistic details of the reaction of **2** with dpm for the X = Br (**2b**) system, along with semiquantitative and qualitative observations for the X = Cl (**2a**) and I (**2c**) systems.

Experimental Section

The materials used, synthetic procedures for the ligands and complexes, and instrumentation used for ^{31}P and ^1H NMR spectra and UV/vis spectra have been largely described previously.[2-4] The dpm (Aldrich), 1,2-bis(diphenylphosphino)ethane (dpe) (Strem), 1,3-bis(diphenylphosphino)propane (dpp) (Strem), PPh_3 and PPh_2Me (Strem), and sulfur (Aldrich) were pure and were used as received. dpm(S),[12] dpmMe,[4] and the complexes $PdCl_2(PhCN)_2$,[13] $Pd_2(dba)_3{\cdot}CHCl_3$,[14] **1a**–**c**,[15] and **2a**–**c**[3] were synthesized using published methods. All experiments were performed under N_2 unless otherwise specified.

dpm-d_2. Lithium diphenylphosphide, $LiPPh_2$ (22.6 g, 0.118 mol, in 250 mL of THF),[16] was slowly added dropwise to a solution of CD_2Cl_2 (5 g, 0.059 mol, in 50 mL of THF) over a period of ~2 h. The solvent of the resulting yellow mixture was rotovaped off before 200 mL of CH_2Cl_2 was added to redissolve the crude product. The CH_2Cl_2 solution was washed with 4 × 100 mL of H_2O and then dried over $CaSO_4$. Removal of the solvent gave a light yellow solid which was dissolved in 50 mL of a CH_2Cl_2–hexane (1:2) mixture and chromatographed through a column (8 × 40 cm) of silica gel with the same solvent as eluent. The first ~250 mL of eluate was discarded, and then the eluate was collected as 4 × 20 mL fractions and analyzed using TLC. The required product was the last substance to emerge; ~500 mL of eluate was then collected. The solvents were removed to give a crystalline white solid; yield ~5 g (22%). The compound was characterized using ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (Table 1). Anal. Calcd for $C_{25}H_{20}D_2P_2$: C, 77.72; H, 5.74. Found: C, 77.70; H, 5.77.

dpm(S)-d_2. dpm-d_2 (100 mg, 0.259 mmol) and S_8 (8.30 mg, 0.032 mmol) were dissolved in hot hexanes (~10 mL), and the solution was refluxed overnight. The solution was then cooled down to room temperature (RT; ~20 °C) and white crystals subsequently formed (within several hours). The solid was collected and identified as dpm(S)-d_2 using NMR spectroscopy (Table 1); yield ~50 mg (46%). Anal. Calcd for $C_{25}H_{20}D_2P_2S$: C, 71.76; H, 5.30. Found: C, 71.71; H, 5.38.

dpmMe(S). dpmMe (100 mg, 0.251 mmol) and S_8 (8.00 mg, 0.031 mmol) were dissolved in hot ethanol (~5 mL), and the solution was refluxed briefly (~10 min). The solution was then cooled to RT, and white crystals subsequently formed (within 1 h). The solvent was removed leaving a white solid above an oily white film. The solid was gently scraped off, dried *in vacuo*, and identified as dpmMe(S) using NMR spectroscopy (Table 1); yield ~30 mg (28%). Anal. Calcd for $C_{26}H_{24}P_2S$: C, 72.54; H, 5.62. Found: C, 71.89; H, 5.54.

Pd_2Br_2(dpm-d_2)$_2{\cdot}2H_2O$ (4b). $PdCl_2(PhCN)_2$ (0.41 g, 1.01 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.55 g, 0.53 mmol), and dpm-d_2 (0.82 g, 2.1 mmol) were refluxed in $CDCl_3$ (50 mL) for 30 min. After being cooled, the resulting red solution was filtered to remove any insoluble materials and the filtrate reduced in volume to ~10 mL. The yellow-orange product, which precipitated after the addition of Et_2O (25 mL), was then filtered out, washed with acetone (2 × 10 mL) to remove any Pd(II) monomer, and dried *in vacuo*. The yield of the product, Pd_2Cl_2(dpm-d_2)$_2$ is ~1.0 g (90%). Some of this complex (0.25 g, 0.24 mmol) was redissolved in ~10 mL of $CDCl_3$ and a solution of NaBr (0.25 g, 2.4 mmol) in aqueous methanol added (~5 mL CH_3OD:~0.5 mL D_2O). The resulting solution was filtered and concentrated under vacuum until red crystals formed. Et_2O (40 mL) was added to complete the precipitation. The solid was filtered out and quickly washed with aqueous methanol (2 × 10 mL) and Et_2O (2 × 10 mL) and then dried *in vacuo*; yield 0.26 g (96%). **4b** was characterized using NMR spectroscopy (Table 1). Anal. Calcd for $C_{50}H_{40}Br_2D_4P_4Pd_2{\cdot}2H_2O$: C, 50.84; H, 4.06. Found: C, 50.75; H, 3.83. (The presence of H_2O was evidenced by ^1H NMR.)

$Pd_2Br_2(\mu\text{-}S)$(dpm-d_2)$_2$ (8b). Pd_2Cl_2(dpm-d_2)$_2$ (0.50 g, 0.48 mmol) (see above) was dissolved in $CDCl_3$ (50 mL), and H_2S gas was bubbled through the solution for 20 min at RT; the color changed from orange-red to brown with accompanying precipitation of a brown solid that was completed by gradual addition of Et_2O (50 mL). The product, $Pd_2Cl_2(\mu\text{-}S)$(dpm-d_2)$_2$, was filtered out, washed successively with acetone (2 × 10 mL) and Et_2O (10 mL), and then dried *in vacuo*; yield 0.50 g (97%). The solid was redissolved in $CDCl_3$ (50 mL), and a solution of NaBr (0.5 g, ~5 mmol) in aqueous methanol (10 mL CH_3OD:1 mL D_2O) was added. The resulting mixture was filtered and concentrated under vacuum until brown crystals formed. Et_2O (30 mL) was added to complete the precipitation. The solid was filtered out, washed with aqueous methanol (2 × 10 mL) and Et_2O (2 × 10 mL), and then dried *in vacuo*; yield 0.52 g (95%). **8b** was characterized by

Table 1. NMR Data for the Dinuclear Palladium Complexes, Diphosphines, and Diphosphine Monosulfides

compd[a]	δ (^1H)[b]	δ (^{31}P)[c]
$Pd_2Cl_2(dpm)_2$ (**1a**)	4.17[d] (4.0)	−5.5
$Pd_2Br_2(dpm)_2$ (**1b**)	4.19[d] (4.0)	−6.15
	4.24[e]	−5.5[e]
$Pd_2I_2(dpm)_2$ (**1c**)	4.23[d] (4.0)	−11.3
$Pd_2Cl_2(\mu\text{-}S)(dpm)_2$ (**2a**)	2.79[f] (12.6, 3.5)	5.52
	4.73 (12.6, 6.1)	
$Pd_2Br_2(\mu\text{-}S)(dpm)_2$ (**2b**)	2.88[f] (12.8, 3.2) (2.90[e])	5.96
		6.14[e]
	4.83 (12.8, 7.6)	
$Pd_2I_2(\mu\text{-}S)(dpm)_2$ (**2c**)	3.06[f] (14.0, 3.0)	6.08
	4.95 (14.0, 6.0)	
$Pd_2Br_2(dpm)$(dpm-d_2) (**3b**)	4.19[g]	−6.30[h]
	4.24[e]	−5.7[e]
Pd_2Br_2(dpm-d_2)$_2$ (**4b**)	*i*	−6.35
$Pd_2Br_2(dpm)$(dpmMe) (**5b**)	4.98,[j,e] 4.55,[k] 3.72[k]	*l*
	1.00[k] (Me)	
Pd_2Br_2(dpmMe)$_2$ (**6b**)	4.98[m,e]	16.1[e]
	1.00[n,e] (Me)	
$Pd_2Br_2(\mu\text{-}S)$(dpm)(dpm-d_2) (**7b**)	2.88,[g,e] 4.83[g]	5.95[h,e]
$Pd_2Br_2(\mu\text{-}S)$(dpm-d_2)$_2$ (**8b**)	*i*	6.00[e]
$Pd_2I_4(dpm)_2$	5.14[d,e] (3.6)	−1.52[e]
dpm	2.81[o,e] (1.6)	−22.5[e]
dpm-d_2	*i*	−23.0[e]
dpm(S)	3.36[p] (12.6, 1.1)	−28.1, 40.1 (75.9)[q]
	3.35[e]	
dpm(S)-d_2	*i*	−28.3, 39.9 (76.4)[q]
dpmMe	3.20[r] (7.2)	−6.94
	0.99[k] (Me) (7.5, 10.2)	
dpmMe(S)	3.64[s,e]	−13.4, 51.9 (94.3)[q]
	1.16[k,e] (Me) (7.4, 10.2)	

[a] The μ-symbol for the bridging diphosphine ligand(s) is omitted for convenience throughout this table and the text. [b] In CD_2Cl_2, unless stated otherwise, at 20 °C with respect to TMS; J_{HH} and/or J_{PH} values in hertz are given in parentheses; signals for CH_2 protons unless indicated otherwise. [c] Singlets in CD_2Cl_2 at 20 °C with respect to 85% H_3PO_4, downfield being positive. [d] Quintet. [e] In $CDCl_3$. [f] Doublets of quintets for each of 2 sets of CH_2 protons. [g] Assumed triplet. [h] "Tight" AB quartet. [i] No CH_2 protons observed. [j] Triplet of quartets. [k] Doublet of triplets. [l] AA'BB' pattern (see Figure 7). [m] Quartet of quintets. [n] Doublet of quintets. [o] Triplet. [p] Doublet of doublets. [q] AB pattern, J_{PP} values in hertz given in parentheses. [r] Quartet. [s] Multiplet.

(10) Wong, T. Y. H.; James, B. R. Work in progress.
(11) Barnabas, A. F. M. Sc. Dissertation, University of British Columbia, Vancouver, 1989.
(12) (a) Grim, S. O.; Mitchell, J. D. *Syn. React. Inorg. Metal-Org. Chem.* **1974**, *4*, 221. (b) Grim, S. O.; Walton, E. D. *Inorg. Chem.* **1980**, *19*, 1982.
(13) (a) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1941**, *63*, 2088. (b) Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 216.
(14) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.
(15) (a) Balch, A. L.; Benner, L. S. *Inorg. Synth.* **1982**, *21*, 47. (b) Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099.
(16) Luther, G. W., III; Beyerle, G. *Inorg. Synth.* **1977**, *17*, 186.

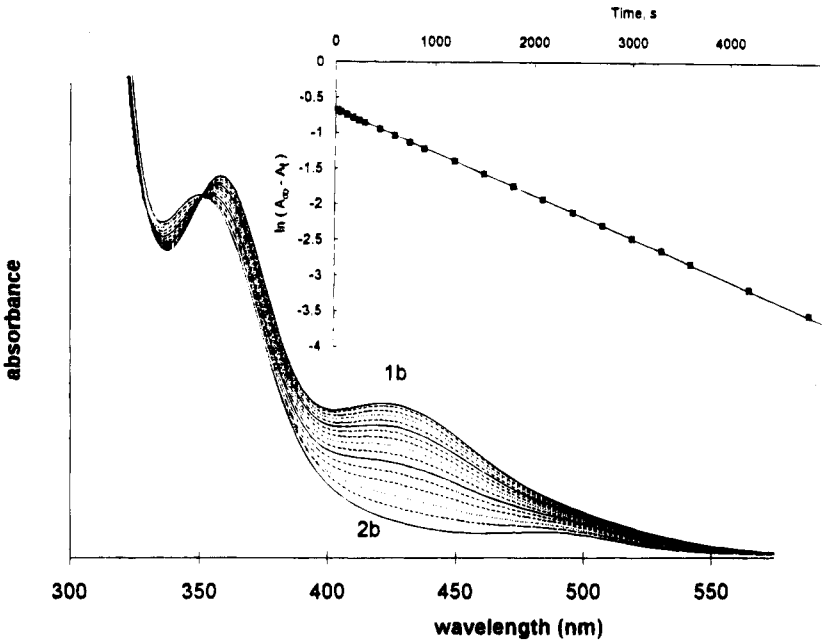


Figure 1. Visible absorption spectral changes (350−550 nm region) as a function of time for a $CHCl_3$ solution of $Pd_2Br_2(\mu\text{-}S)(\mu\text{-dpm})_2$ (**2b**) (6.52×10^{-5} M) on addition of dpm (1.96×10^{-2} M) at 25 °C. Inset: a rate-plot analyzed for a pseudo-first-order dependence on **2b**; A_t and A_∞ represent the absorption at 428 nm at times t and ∞, respectively.

NMR spectroscopy (Table 1). Anal. Calcd for $C_{50}H_{40}Br_2D_4P_4Pd_2S$: C, 50.95; H, 3.77. Found: C, 50.27; H, 3.80.

Kinetic Measurements. The kinetics of the reconversion reaction (**2** → **1**) in $CHCl_3$ (for X = Cl, Br, I) were monitored spectrophotometrically in a thermostated Perkin-Elmer 552A instrument using quartz cells of path lengths of 1.0 cm fitted with a rubber septum. A 2.00 mL solution of dpm of appropriate concentration was placed in the cell and thermostated at the required temperature (20−35 °C); the complex **2** was then injected as a solution (0.125 mL). The cell was shaken to ensure complete mixing prior to monitoring optical density changes at some appropriate, fixed wavelength. The concentration of **2** ranged $(0.81-13.0) \times 10^{-5}$ M, and that of dpm $(6.5-26.1) \times 10^{-3}$ M; thus pseudo-first-order conditions were maintained and standard log(absorbance difference) vs time plots gave excellent linearity for at least 2.5−3 half-lives, from which the pseudo-first-order rate constants, k_{obs}, were readily evaluated.

Mechanistic Studies. (a) NMR Scale. Variable-temperature and equilibrium studies were performed on the NMR scale by reacting complexes with appropriate amounts of diphosphine or phosphine. Thus, for example, **1b** (10 mg, 0.009 mmol) or **2b** (10 mg, 0.0085 mmol) was reacted at RT in $CDCl_3$ or CD_2Cl_2 (0.5 mL) with dpm-d_2 or dpmMe in either a 1:1 or a 1:5 mol ratio (in 0.1 mL solution). The samples were analyzed using ^1H and $^{31}P\{^1H\}$ NMR spectroscopy immediately and after periods of time up to 72 h. Under low-temperature conditions, accurately weighed out samples of **2a**, **2b**, or **2c** were dissolved in the appropriate solvent (~ 0.5 mL) in a septum-sealed NMR tube which was placed in a dry ice/acetone slush bath (−78 °C). A 0.1 mL solution of dpm (5 mol equiv excess) was then injected, and the shaken sample was analyzed immediately and after periods of time up to 72 h. The temperature was then raised in 20 °C increments to a final 20 °C, and the spectra were recorded at each new temperature.

(b) Synthetic Scale. The bromide **2b** (100 mg, 0.085 mmol) was reacted with either dpm-d_2 (32.9 mg, 0.085 mmol) or dpmMe (34.0 mg, 0.085 mmol) in 20 mL of CH_2Cl_2 or $CHCl_3$, the reaction being monitored by thin-layer chromatography and/or UV−vis spectroscopy. Employing Schlenk techniques, the experiments were conducted on a scale such that products could be isolated in sufficient amounts for analyses of both the Pd complexes and the dpm compounds. Upon completion (approximately 2 h), the solution was reduced in volume to 5 mL before 20 mL of Et_2O was added to precipitate the palladium product(s). The filtrate was passed through a column of silica to remove all traces of metal compounds with the eluate collected. The solvent was rotovaped off to give a colorless oil, which was dissolved in minimal hot ethanol; cooling in a dry ice/acetone bath induced precipitation of a white solid, the diphosphine monosulfide. The ethanol solvent was slowly removed under vacuum and at low temperatures to avoid re-formation of the oil. All products were dried *in vacuo* prior to analyses using ^1H and $^{31}P\{^1H\}$ NMR spectroscopy in $CDCl_3$.

Results

Reaction 1 and its stoichiometry were readily demonstrated by NMR (Table 1). Complexes **2a**−**2c** reveal a singlet at δ 5.5−6.1 in the $^{31}P\{^1H\}$ NMR spectrum at ambient conditions in CH_2Cl_2 for the four equivalent P atoms,[3] while the corresponding singlets for **1a**−**1c** are in the δ −5.5 to −11.3 region.[1,2] The $^{31}P\{^1H\}$ NMR spectrum of the monosulfide dpm(S) consists of an AB doublet (δ −28.1, 40.1, J 75.9 Hz), the lower field signal being that of the P(V) center.[12] In the ^1H NMR spectra of **2a**−**2c**, the CH_2 resonances appear as AB doublets with additional coupling to the four P atoms, while in **1a**−**1c**, the equivalent CH_2 protons show a characteristic quintet pattern. Table 1 summarizes the NMR data measured in the present work for all the Pd complexes and diphosphine compounds.

The rates of the reconversion reaction **2** → **1** (eq 1) were noticed qualitatively during preliminary kinetic and mechanistic studies and were found to be dependent on the nature of the auxiliary ligand X and on the concentration of dpm used. The reactivity trend in $CHCl_3$ observed was X = Cl > Br > I, and of these, the bromide system was chosen for a detailed, classical spectrophotometric study. Only limited kinetic data for the chloride system and qualitative observations for the iodide system were obtained because of complexities based on the photosensitivity of **1a** and **1c**, respectively.[2,3,17]

The kinetics of the reconversion reaction were studied using solution electronic spectroscopy. Species **2** are brown and have absorption maxima in the 325−350 and in the 470−485 nm regions, while the products (**1**) are reddish-orange (Cl and Br), or purple (I), and have two or three absorption maxima in the 340−590 nm region.[2,3] Figure 1 shows spectral changes on

(17) Lyke, S. E.; Lilga, M. A.; Ozanich, R. M.; Nelson, D. A.; James, B. R.; Lee, C.-L. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *25*, 517.

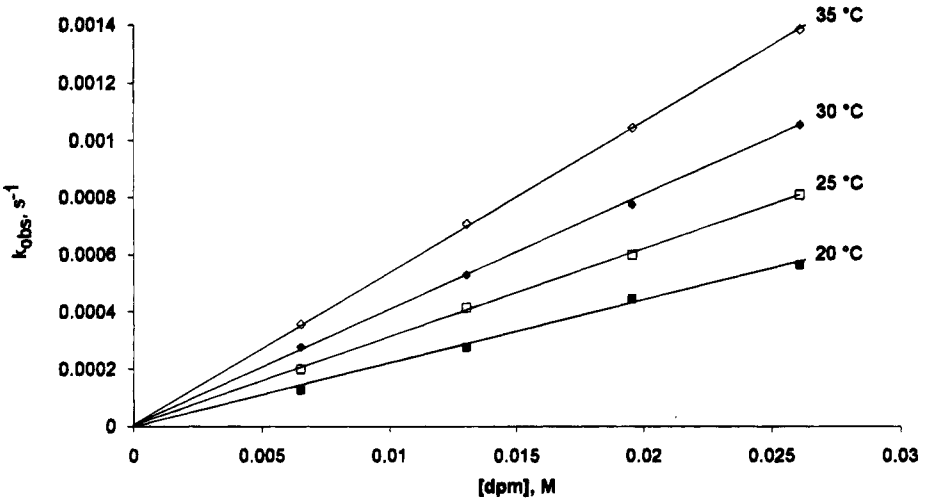


Figure 2. Dependence of the pseudo-first-order rate constants, k_{obs}, on [dpm] at [**2b**] = 6.52 x 10^{-5} M, in $CHCl_3$.

Table 2. Temperature Dependence for the Bimolecular Rate Constant of the Reaction of **2a** (k_{Cl}) and **2b** (k_{Br}) with dpm in $CHCl_3$

temp, K	k_{Cl}, M^{-1} s^{-1}	k_{Br}, M^{-1} s^{-1}
293	0.0667[a]	0.0229
298	0.0898	0.0308
303	0.125[a]	0.0396
308	0.157[a]	0.0524

[a] Obtained at a single [dpm] = 1.96 × 10^{-2} M.

treating a $CHCl_3$ solution of the bromide **2b** with dpm at 25 °C; rates for the bromide system are followed by observing the increasing absorption at 428 nm as a function of time, and the observed isosbestic point shows a well-behaved system. The pseudo-first-order rate constants, k_{obs}, obtained from the excellently linear semi-log plots (Figure 1, inset), are strictly first order in [dpm] (Figure 2) and are independent of the [**2b**] in the range (0.81−13.0) × 10^{-5} M. Thus, the rate law takes the simple form

$$\text{rate} = -\frac{d}{dt}[\mathbf{2b}] = k_{obs}[\mathbf{2b}] = k_{Br}[\text{dpm}][\mathbf{2b}] \qquad (3)$$

where k_{Br} is the bimolecular rate constant for the reaction. The temperature dependence data for k_{Br} (Table 2) are obtained similarly from the first-order plots at other temperatures (Figure 2); an Eyring plot of the data from 20 to 35 °C gives an excellent straight line and the activation parameters $\Delta H^{\ddagger}$ = 38 ± 1 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −144 ± 4 J K^{-1} mol^{-1}.

The corresponding studies on the faster chloride system were performed, the increasing absorbance being monitored at 416 nm where spectral changes are greatest. Because of the photosensitivity of **1a**, specifically at the later stages of the reaction where isosbesticity is lost, more limited kinetic data were obtained. The reconversion reaction **2a** → **1a** was monitored when the solution was kept in the dark, with the optical density being recorded by a sampling rather than a continuous monitoring method. Analysis of the earlier visible spectral changes (2 half-lives), using an A_∞ value from the known absorption spectrum of **1a**, also gives results that are strictly first order in [dpm] (Figure 3). The pseudo-first-order rate constant is also found to be independent of the [**2a**] in the range (3.26−13.0) × 10^{-5} M. Thus, the rate law for the chloride system also takes the same form as eq 3, but with a bimolecular rate constant k_{Cl}. The temperature dependence data for k_{Cl} were obtained at a single [dpm] of 1.96 × 10^{-2} M and with [**2a**] = 6.52 × 10^{-5} M (Table 2); an Eyring plot is reasonably linear and gives the activation parameters $\Delta H^{\ddagger}$ = 41 ± 3 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −127 ± 10 J K^{-1} mol^{-1}.

Only qualitative observations could be made for the iodide system due to its inherent photosensitive nature; the light source (either laboratory light or that of the spectrophotometer) readily induces formation of the monomer $PdI_2(dpm)^2$ from **1c**, the product of the reconversion reaction. Under the same conditions used to study the other two systems, the iodide reaction is extremely slow, even at the higher temperatures, but the thermal reaction between **2c** and dpm gives the "expected" products, **1c** and dpm(S). Again, analysis of the early visible spectral changes, using an A_∞ value from the known absorption spectrum of **1c**, gives $k_{obs} \sim 7 \times 10^{-5}$ s^{-1} at 25 °C for a reaction with [dpm] = 6.53 × 10^{-3} M corresponding to a bimolecular k_I rate constant of 1 × 10^{-2} M^{-1} s^{-1}. The limited data show that the rate constant is about three times lower than k_{Br} and about nine times lower than k_{Cl}.

Low-temperature NMR studies were performed on all three systems, but no intermediates were observed en route to formation of **1** from **2**, even at temperatures as low as −80 °C (in CD_2Cl_2). For systems in $CDCl_3$, the probe temperature was raised in 20 °C increments, and new signals were first observed around −40 °C in each case and which corresponded to those of the products, **1** and dpm(S). NMR samples in CD_2Cl_2 were made up and sometimes left at −78 °C for 72 h before analyses were done in an attempt to allow sufficient time for formation of intermediates; again intermediates were not seen, although some **1** and dpm(S) were observed for both the chloride and bromide systems. For the iodide system, however, no products were formed, this being consistent with the kinetic studies which show the iodide reaction to be much slower. These NMR studies show that the reconversion reaction is kinetically possible at −80 °C (at least for the chloride and bromide systems), when dpm is present in a 5-fold excess at ~85 mM. Extrapolation of the k values of Table 2 to −78 °C gives k_{Cl} and k_{Br} values of 9.4 × 10^{-6} and 5.4 × 10^{-6} M^{-1} s^{-1}, respectively; use of these values at the noted conditions suggests conversions to **1a** and **1b** of ~20 and ~11%, respectively, while the observed values are about 25 and 15%. The kinetics of the reaction **2b** → **1b** were also studied in the presence of a bromide salt in order to find a possible kinetic role for an ionic species; addition of a 10- or 100-fold excess of tetrapropylammonium bromide to **2b** during a reaction with dpm at 25 °C produced no change in the observed rate constant. Also, in reactions between **2b** and dpm-d_2, and between $Pd_2Br_2(\mu\text{-}S)(\text{dpm-}d_2)_2$ (**8b**) and dpm

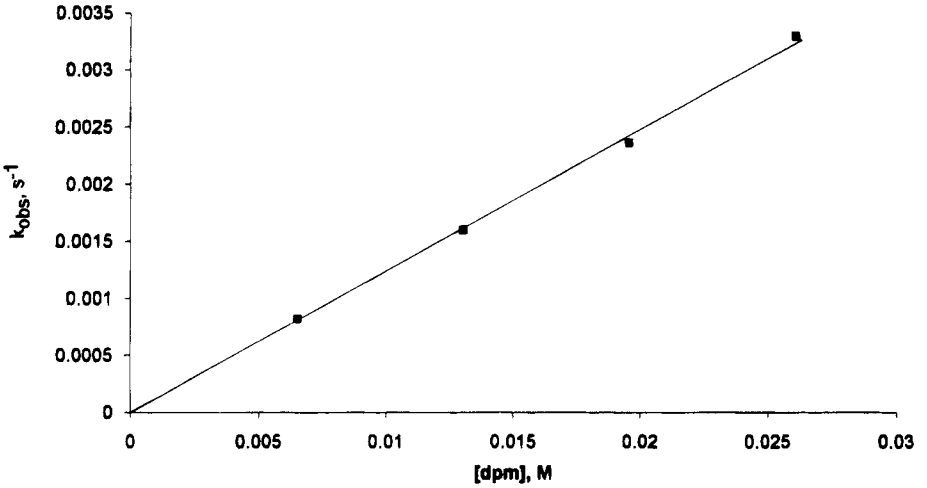


Figure 3. Dependence of the pseudo-first-order rate constants, k_{obs}, on [dpm] at [**2a**] = 6.52×10^{-5} M, in $CHCl_3$ at 30 °C.

or dpm-d_2, no kinetic isotope effect was seen in the observed rate constant at 30 °C.

During the reaction of **2b** with either deuterated dpm (dpm-d_2) or methylated dpm (dpmMe), the color changed from the brown of **2b** to reddish, as with dpm itself, and sulfur was again completely abstracted to give diphosphine monosulfides (see below). Complementary *in situ* NMR experiments (even when the phosphines were added in excess) showed that the products formed were the same as those obtained in the larger-scale synthetic experiments.

Although no kinetic measurements were done on the reaction of **2b** with dpmMe, *in situ* NMR experiments indicate that the reaction is some 30 times slower than that of **2b** with dpm (or dpm-d_2).

In the reaction of **2b** with dpm-d_2 at a 1:1 mole ratio, the ^1H spectrum of the Pd product(s) reveals the expected, less informative multiplet between δ 7.0 and 8.0 due to the phenyl rings of the phosphine ligands; also seen is the characteristic quintet at δ 4.19 due to the dpm CH_2 protons of the product **1b**. However, the ratio of the integrated areas of the multiplet to the quintet is ~15:1, not the 10:1 expected for the 40 phenyl protons and 4 CH_2 protons of **1b**, and moreover the $^{31}P\{^1H\}$ NMR spectrum shows not only the singlet of **1b** at δ −6.15 but also a "tight" AB quartet at δ −6.30. As discussed below, this quartet is due to the mono-dpm-d_2 substituted complex, Pd_2Br_2(dpm)(dpm-d_2) (**3b**), and this product is formed with **1b** in the ratio of probably about 1:1. The CH_2 resonance of **3b** is assumed to be a triplet that is buried under the δ 4.19 quintet; and indeed the "quintet" resonances are not of the classical 1:4:6:4:1 intensities because of the presence of the underlying triplet. The ^1H NMR spectrum of the phosphine monosulfide products reveals a doublet of doublets of reduced integration (1:15, relative to that of the phenyl protons) at δ 3.36, and in the $^{31}P\{^1H\}$ NMR spectrum, there is a second set of doublets slightly upfield to those at δ 40.1 and −28.1 that are due to dpm(S). The second set of signals, as also discussed below, is attributed to the deuterated monosulfide product, dpm(S)-d_2, and which is formed with dpm(S) in the ratio of 1:2. Of interest, in an *in situ* NMR experiment in $CDCl_3$ where **2b** is reacted with a 5-fold excess of dpm-d_2, the same final products are observed; however, dpm(S)-d_2 is formed in a slightly greater than 1:1 mole ratio to dpm(S), judging from a qualitative analysis of the $^{31}P\{^1H\}$ NMR spectrum (Figure 4). Although the signals due to the diphosphine monosulfide products are resolved, the signals of the Pd products appear as one broad singlet, as do those of dpm and dpm-d_2; the singlet at $\delta \sim -6$ is thought to result from a mixture of **1b**, **3b**, and the "disubstituted" Pd_2(dpm-d_2)$_2Br_2$ (**4b**) resulting from a ligand exchange of **1b** and/or **2b** with dpm-d_2, as discussed later. The ^1H NMR spectrum shows the expected Pd products at δ 4.24, the dpm(S) product at δ 3.35, and the dpm signal at δ 2.81. Analysis of the CH_2 region signals shows that the ratios of the integrated peak areas of the Pd products (**1b** + **3b** + **4b**) to dpm(S), dpm to dpm(S), and dpm to the Pd products are (to within 0.3) 2.3, 2.9, and 1.3 to 1, respectively. These results again reflect the combination of reaction 1 and the accompanying effects of diphosphine exchange of **1b** and **2b** with dpm-d_2 (see below).

Reaction of **2b** with dpmMe (1:1) after a few hours gave two immediately identifiable isolable Pd products, **1b** and Pd_2Br_2(dpm)(dpmMe) (**5b**),[4] with the latter dominant; furthermore, some Pd_2Br_2(dpmMe)$_2$ (**6b**)[4] is also probably present (Figure 5). Pd_2Br_2(dpm)(dpmMe) (**5b**) is characterized by four multiplets in the ^1H NMR:[4] a triplet of quartets centered at δ 4.98 (CH), a doublet of triplets at δ 1.00 (Me), and a doublet of triplets for each of the two CH_2 protons at δ 3.72 and at 4.55. Pd_2Br_2(dpmMe)$_2$ (**6b**) is characterized in the ^1H NMR spectrum[4] by a quartet of quintets at δ 4.98 (CH) and a doublet of quintets at δ 1.00 (Me); these multiplets overlap those due to **5b**, and the presence of a small amount (~10%) of **6b** is suspected because of the slightly greater than expected intensities of the δ 4.98 and 1.00 signals. The $^{31}P\{^1H\}$ NMR spectrum shows the singlet at δ −6.15 for **1b** and a complex AA′BB′ pattern for **5b** in the δ +18 to −10 region, analogous to that recorded for Pd_2Cl_2(dpm)(dpmMe);[4] the broad singlet expected for **6b** at δ 16.1[4] could be buried within the AA′BB′ pattern. The $^{31}P\{^1H\}$ NMR spectrum of the isolated diphosphine products shows just two sets of AB doublets: one set due to dpm(S) and the other, downfield at δ 51.9 and −13.4, due to dpmMe(S); the ratio of dpm(S) to dpmMe(S) is ~3:1, this result being consistent with the presence of more **5b** than **1b** in the isolated Pd products.

In terms of quantifying the extent of S-extraction via originally coordinated and added diphosphine, it was necessary to study diphosphine exchange with **1b** and **2b**. Thus **1b** was reacted with 1 mol equiv of dpm-d_2 in $CDCl_3$; a ^1H NMR triplet at δ 2.81 due to the CH_2 protons of dpm is seen "immediately", the integrated area being about half that of the quintet at δ 4.24 due to the CH_2 protons of the various Pd species present (**1b**, **3b**, and possibly **4b**). The $^{31}P\{^1H\}$ NMR spectrum shows the singlet of **1b** at δ −5.5 (which could also correspond to some **4b**), the tight AB quartet of **3b** (δ −5.7), and a singlet at δ −22.5 due to dpm. The spectra were invariant with time. Similarly, the ^1H NMR spectrum of **2b** in the presence of 1 mol equiv of dpm-d_2 shows (prior to any S-extraction) immediate generation of a triplet at δ 2.81 due to dpm, which overlaps

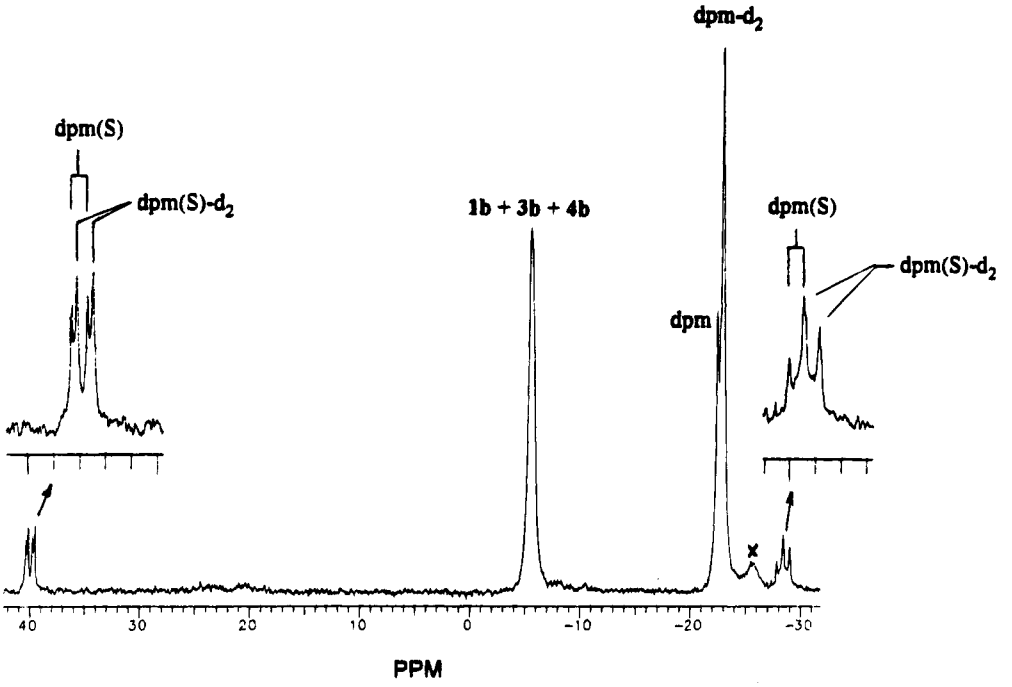


Figure 4. $^{31}P\{^1H\}$ NMR spectrum (121 MHz) of the completed *in situ* reaction between **2b** and dpm-d_2 (1:5 mole ratio) in $CDCl_3$ at RT (72 h) (X = unknown).

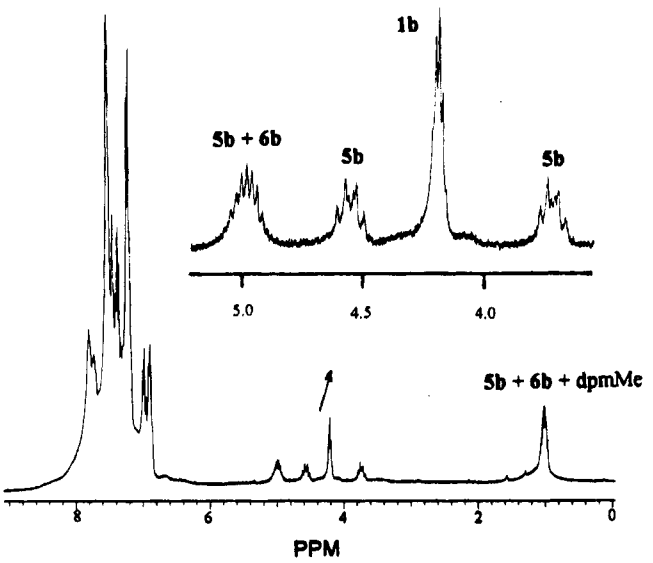


Figure 5. ^1H NMR spectrum (300 MHz) of the isolated Pd products from the reaction **2b** and dpmMe (1:1 mole ratio) in CD_2Cl_2 at RT.

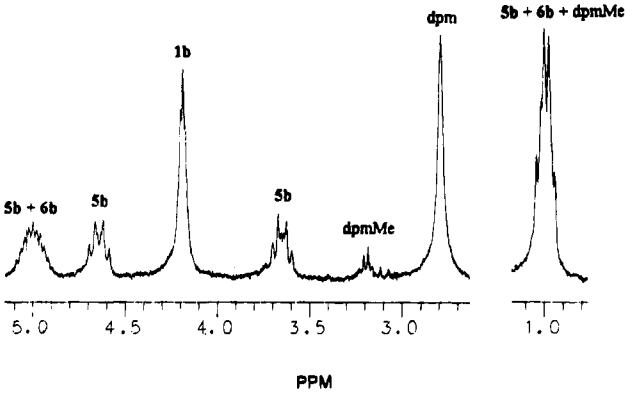


Figure 6. ^1H NMR spectrum (300 MHz) recorded at RT in $CDCl_3$ of **1b** on addition of 1 mol equiv of dpmMe (72 h).

the δ 2.90 signal of **2b**. As well, new peaks appear in the $^{31}P\{^1H\}$ NMR spectrum: an AB quartet δ 5.95, attributed to $Pd_2Br_2(\mu\text{-}S)(dpm)(dpm\text{-}d_2)$ (**7b**), overlaps the singlet of **2b** at δ 6.14 and the singlet of $Pd_2Br_2(\mu\text{-}S)(dpm\text{-}d_2)_2$ (**8b**) at δ 6.00, and a singlet at δ −22.5 due to dpm is seen beside the singlet of dpm-d_2 at δ −23.0.

Diphosphine exchange of **1b** with dpmMe was not studied in detail but was shown to occur, at a much slower rate in contrast to the rapidly established equilibrium of **1b** or **2b** with dpm-d_2. In a single *in situ* NMR experiment where **1b** was reacted with 1 mol equiv of dpmMe, the final ^1H and $^{31}P\{^1H\}$ NMR spectra (which are then invariant with time after ~3 days) indicate that significant amounts of $Pd_2Br_2(dpm)(dpmMe)$ (**5b**), $Pd_2Br_2(dpmMe)_2$ (**6b**), and dpm are formed (with some **1b** and dpmMe remaining) (Figures 6 and 7). The suggestion that **6b** is present is again based on "increased intensities" of the δ_H 4.98 and 1.00 signals (Figure 6) and a possible buried δ_P 16.1 singlet (Figure 7) (see above). Analysis of the various non-phenyl protons signals in the ^1H NMR spectrum gives the following absolute integrated values for **1b**, dpmMe, **5b**, dpm, and **6b** as 0.98, 0.91, 2.55, 2.27, and 0.58, respectively (with respect to the 60 phenyl protons of **1b** + dpmMe). Also in contrast to the rapidly established equilibrium of **2b** with dpm-d_2, **2b** does not undergo detectable diphosphine exchange with dpmMe (prior to any S-abstraction) as evidenced by NMR spectra.

Discussion

Kinetic results show that, at least for the chloride and bromide systems, the rate of the reconversion reaction (**2** → **1**) has a first-order dependence on both **2** and dpm. No intermediates were seen in low-temperature NMR studies, and this result, along with the observed isosbesticity in UV/vis spectroscopic studies, shows that reaction 1 can be represented as shown, making no distinction in the identity of the dpm ligands:

$$\underset{\mathbf{2}}{Pd_2X_2(\mu\text{-}S)(dpm)_2} + dpm \xrightarrow{k} \underset{\mathbf{1}}{Pd_2X_2(dpm)_2} + dpm(S) \qquad (1)$$

Labeling Experiments and Statistical Analysis. Experiments with dpm-d_2 have demonstrated that diphosphine exchange takes place with both **2** and **1**, with rapid equilibria being

established. The distribution of products, as a consequence, is considered to be statistical according to the stoichiometries of the reactants. For example, prior to S-abstraction, **2b** rapidly forms $Pd_2Br_2(\mu\text{-S})(dpm)(dpm\text{-}d_2)$ (**7b**) and $Pd_2Br_2(\mu\text{-S})(dpm\text{-}d_2)_2$ (**8b**). For an initial 1:1 ratio of **2b** and dpm-d_2, the following distribution of species will be present at equilibrium:

$$^2/_3Pd_2Br_2(\mu\text{-S})(dpm)(dpm\text{-}d_2) + {}^1/_3dpm\text{-}d_2 + {}^1/_3Pd_2Br_2(\mu\text{-S})(dpm)_2 + {}^2/_3dpm$$

Similarly, at an initial 1:1 ratio of **7b** and dpm-d_2, the distribution of species will be

$$^2/_3Pd_2Br_2(\mu\text{-S})(dpm)(dpm\text{-}d_2) + {}^1/_3dpm + {}^1/_3Pd_2Br_2(\mu\text{-S})(dpm\text{-}d_2)_2 + {}^2/_3dpm\text{-}d_2$$

The S-abstraction then occurs via the slow reactions 1 and 4−6.

$$Pd_2Br_2(\mu\text{-S})(dpm)_2\ (\mathbf{2b}) + dpm\text{-}d_2 \text{ or } Pd_2Br_2(\mu\text{-S})(dpm)(dpm\text{-}d_2)\ (\mathbf{7b}) + dpm \rightarrow {}^2/_3Pd_2Br_2(dpm)(dpm\text{-}d_2)\ (\mathbf{3b}) + {}^1/_3dpm(S)\text{-}d_2 + {}^1/_3Pd_2Br_2(dpm)_2\ (\mathbf{1b}) + {}^2/_3dpm(S) \quad (4)$$

$$Pd_2Br_2(\mu\text{-S})(dpm)(dpm\text{-}d_2)\ (\mathbf{7b}) + dpm\text{-}d_2 \text{ or } Pd_2Br_2(\mu\text{-S})(dpm\text{-}d_2)_2\ (\mathbf{8b}) + dpm \rightarrow {}^2/_3Pd_2Br_2(dpm)(dpm\text{-}d_2)\ (\mathbf{3b}) + {}^1/_3dpm(S) + {}^1/_3Pd_2Br_2(dpm\text{-}d_2)_2\ (\mathbf{4b}) + {}^2/_3dpm(S)\text{-}d_2 \quad (5)$$

$$Pd_2Br_2(\mu\text{-S})(dpm\text{-}d_2)_2\ (\mathbf{8b}) + dpm\text{-}d_2 \rightarrow Pd_2Br_2(dpm\text{-}d_2)_2\ (\mathbf{4b}) + dpm(S)\text{-}d_2 \quad (6)$$

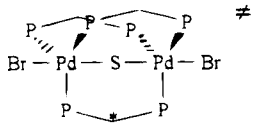
Rapid equilibria are then established within **1b** type species to generate $Pd_2Br_2(dpm)(dpm\text{-}d_2)$ (**3b**) and $Pd_2Br_2(dpm\text{-}d_2)_2$ (**4b**); at equilibrium an initial 1:1 ratio of **1b** and dpm-d_2 yields

$$^2/_3Pd_2Br_2(dpm)(dpm\text{-}d_2) + {}^1/_3dpm\text{-}d_2 + {}^1/_3Pd_2Br_2(dpm)_2 + {}^2/_3dpm$$

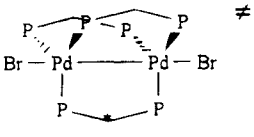
and similarly **3b** yields

$$^2/_3Pd_2Br_2(dpm)(dpm\text{-}d_2) + {}^1/_3dpm + {}^1/_3Pd_2Br_2(dpm\text{-}d_2)_2 + {}^2/_3dpm\text{-}d_2$$

To contend with the various equilibria occurring essentially with equal probability, a computer program[10] has been written to simulate the reconversion reaction with dpm-d_2; the program displays the statistical outcomes resulting from using different reactant ratios of **2b** and dpm-d_2. The program is based on the premise that the diphosphine exchange and S-abstraction reactions proceed via transition states where three diphosphines ligands are equivalent; *e.g.*, model **I** for the exchange and the S-abstraction reaction and **II** for the exchange within **1b** type species, where the phenyl groups are omitted for clarity and the asterisk implies $-CD_2-$.



I



II

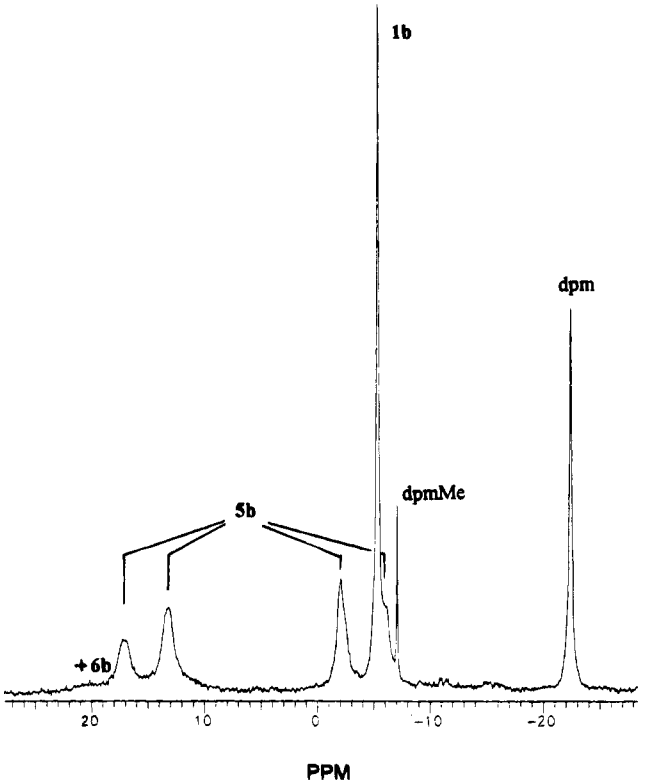


Figure 7. $^{31}P\{^1H\}$ NMR spectrum (121 MHz) recorded at RT in $CDCl_3$ of **1b** on addition of 1 mol equiv of dpmMe (72 h).

The reactant diphosphine could initially coordinate via an empty d_{z^2} orbital of the square planar Pd centers within **2b**, and product formation via **I** is then envisaged as S-abstraction by any one of the bridging phosphines with equal probability. This picture, in fact, leads to statistical product distributions that correspond closely to those observed. For example, 1:1 reaction between **2b** and dpm-d_2 gives the predicted overall stoichiometry of eq 7, and the experimental results are consistent with this

$$\underset{\mathbf{2b}}{Pd_2Br_2(\mu\text{-S})(dpm)_2} + dpm\text{-}d_2 \rightarrow \underset{\mathbf{1b}}{{}^4/_9Pd_2Br_2(dpm)_2} + \underset{\mathbf{3b}}{{}^4/_9Pd_2Br_2(dpm)(dpm\text{-}d_2)} + \underset{\mathbf{4b}}{{}^1/_9Pd_2Br_2(dpm\text{-}d_2)_2} + {}^2/_3dpm(S) + {}^1/_3dpm(S)\text{-}d_2 \quad (7)$$

prediction. The 2:1 ratio of dpm(S) to dpm(S)-d_2 is readily seen, but the ratios of the Pd species (**1b**:**3b**:**4b**) are less well-defined. The predicted integration ratio (15:1) for the phenyl to CH_2 proton NMR signals for the mixture of Pd products is found experimentally. Both **1b** and **3b** are definitely seen in the ^1H and $^{31}P\{^1H\}$ NMR spectra and are present in comparable amounts, while **4b** is assumed to be present in a smaller amount giving rise to a singlet within the δ_P resonances around −6. Similarly, the mixture of the phosphine monosulfide products gives a 15:1 ratio for the integration of the phenyl to CH_2 proton NMR signals. Further support for the statistical product distribution via "symmetrical" transition states comes from the *in situ* reaction of **2b** with a 5-fold excess of dpm-d_2 (Figure 4). Rapid exchange within **2b**, followed by slower S-abstraction, and then rapid exchange within **1b** gives the following statistical outcome:

$$\mathbf{2b} + 5dmp\text{-}d_2 \rightarrow 0.068\mathbf{1b} + 0.382\mathbf{3b} + 0.547\mathbf{4b} + 0.433dpm(S) + 0.564dpm(S)\text{-}d_2 + 1.048dpm + 2.955dpm\text{-}d_2 \quad (8)$$

The theoretical ratios of the integrated peak areas (CH_2 protons) of the Pd products to dpm(S), dpm to dpm(S), and dpm to the Pd products are, respectively, 1.2, 2.4, and 2.0 to 1. There is reasonable experimental agreement for the last two ratios, but a discrepancy is seen for the first; however, more importantly, the correct trends are observed: the integrated peak area of the Pd products is greater than that of dpm(S) but less than that of dpm. The $^{31}P\{^1H\}$ NMR spectrum (Figure 4) clearly shows the approximate 1:1 ratio of dpm(S) to dpm(S)-d_2. The proposal of a transition state such as **II** for the exchange between **1b** and dpm-d_2 (1:1) is supported by the observed 2:1 ratio for the CH_2 protons of the Pd products to those of dpm, as predicted (eq 9).

$$\mathbf{1b} + \text{dpm-}d_2 \rightarrow {}^4/_9\mathbf{1b} + {}^4/_9\mathbf{3b} + {}^1/_9\mathbf{4b} + {}^2/_3\text{dpm} + {}^1/_3\text{dpm-}d_2 \quad (9)$$

NMR data show that dpmMe undergoes slow diphosphine exchange with **1b** at a 1:1 ratio; the equilibrium established in ~3 d favors the formation of Pd_2Br_2(dpm)(dpmMe) (**5b**):

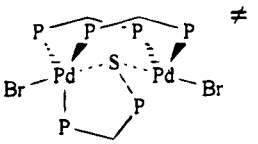
$$\mathbf{1b} + \text{dpmMe} \overset{K_1}{\rightleftharpoons} Pd_2Br_2(\text{dpm})(\text{dpmMe})\ (\mathbf{5b}) + \text{dpm} \quad (10)$$

$$Pd_2Br_2(\text{dpm})(\text{dpmMe}) + \text{dpmMe} \overset{K_2}{\rightleftharpoons} Pd_2Br_2(\text{dpmMe})_2\ (\mathbf{6b}) + \text{dpm} \quad (11)$$

The equilibrium constants at ~20 °C, calculated from the spectral integration values (Figure 6), are $K_1 \approx 6$ and $K_2 \approx 0.6$. NMR results show that **2b** does not undergo rapid diphosphine exchange with dpmMe, but some slower exchange could possibly occur on the time scale of the exchange of **1b** with dpmMe, which is also that of the S-abstraction by this phosphine. Nevertheless, the resulting product distributions for the reaction between **2b** and dpmMe are expected to differ from that for dpm because the phosphines are different. An approximate 3:1 ratio of dpm(S) to dpmMe(S) is seen in the $^{31}P\{^1H\}$ NMR spectrum, complementing the result that greater amounts of **5b** and **6b** than **1b** are observed. The preliminary experimental findings suggest that, as with dpm, the S-abstraction reaction with dpmMe probably proceeds via a transition state with close to equivalent diphosphine ligands.

Transition States and Intermediates. Transition states containing three equivalent diphosphines (see **I** and **II** above) account well for the observed product distributions, but clearly that the S-abstraction from **2b** is much slower than the exchange rules out **I** as a common transition state for these processes. More insight is gleaned on consideration of the reactivity of **2b** with other phosphines. Other tertiary phosphines, including PPh_3, PPh_2Me, and $Ph_2P(CH_2)_3PPh_2$ (dpp), surprisingly gave no S-abstraction, *i.e.* no phosphine sulfides or **1b** generated. With $Ph_2P(CH_2)_2PPh_2$ (dpe), however, small amounts of **1b** and dpm(S) were formed, but the major Pd species generated are as yet unidentified as the NMR spectra are complicated; no dpe(S) was seen. *In situ* treatment of **2b** with dpp (1:1) at RT resulted in a slow reaction (over ~3 d) and complex $^{31}P\{^1H\}$ and ^1H NMR spectra, attributable to an as yet uncharacterized species X (or mixture of species); remarkably, however, treatment of this solution with ~2 mol equiv of dpm resulted in slow but quantitative formation of dpm(S) and **1b** with regeneration of free dpp. The "X solution" could contain species with monodentate, "dangling" dpp, but no δ_P resonances in the region for free dpp ($\delta_P \sim -18$)[18] were seen; di- or polynuclear species formed by bridging dpp seem plausible. The uniqueness of dpm (and dpmMe) in quantitatively abstracting the sulfur could be satisfyingly pictured via **I** in which the S is in a trigonal prismatic arrangement of P atoms, these being forced closer to the sulfur than the P atoms within **2b**. Presumably if dpp bridges the two Pd atoms, it does so in a configuration not very different from the ground state of **2b** and which gives no S-abstraction. There could be sufficient flexibility in dpm and dpmMe to generate transition states such as **II**, the supposed pathway for diphosphine ligand exchange with **1b**. This flexibility could exist for dpe, but presumably this ligand prefers to form a 5-membered chelate ring at a single Pd site; this could induce conversion of a μ-dpm to an η^1-dpm with subsequent abstraction of S by the latter.

It should be noted that complexes of the type $Pd_2Cl_4(\mu\text{-}Bu^t_2P(CH_2)_nPBu^t_2)_2$ (n = 7, 10) are known;[19] these contain square-planar, d^8 Pd(II) moieties, and no metal−metal bond is involved. Species containing η^1-diphosphine ligands are well documented,[20-22] including η^1-dpm in complexes of the type $[Pt_2(L)(\mu\text{-dpm})_2(\eta^1\text{-dpm})]^+$, L = alkyl or H.[22] The possibility of dpm (and dpmMe) reacting with **2b** by binding in an η^1-fashion at one Pd center with the "free end" and then abstracting sulfur seems the most obvious pathway for formation of the diphosphine monosulfide which would involve incipient formation of a 5-membered ring; the findings of the product distribution using dpm-d_2 and dpmMe could be accommodated via rapid fluxionality between the η^1- and μ-diphosphines prior to S-abstraction. Such fluxionality offers the obvious pathway to diphosphine exchange with rapid on- and off-rates for the η^1-ligands (see below). That other phosphines do not abstract the sulfur implies the requirement of a 5-membered ring for this process, for which a realistic transition state is shown in **III**; if the diphosphines are indistinguishable, **III** is effectively 3-fold degenerate and the "averaged" transition state picture approximates to that shown in **I**.



III

The findings reveal that dpm reacts relatively rapidly with **2b** (to give exchange and S-abstraction) and with **1b** (exchange), and yet dpmMe and dpp (and dpm(S) (see below)) react more slowly. Presumably, all the chelating phosphines must first react as η^1-nucleophiles; the difference in rates is not readily rationalized in terms of electronic or steric effects (indeed, regarding the latter, dpm might be more "encumbered" than dpp). The steps shown in eqs 12 and 13 can account for the observations. **III** is a reasonable transition state en route from

$$Pd_2Br_2(\mu\text{-S})(\mu\text{-dpm})_2 + (\text{P-P}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pd_2Br_2(\mu\text{-S})(\eta^1\text{-(P-P)})(\mu\text{-dpm})_2\ (\mathbf{IV}) \text{ or } Pd_2Br_2(\mu\text{-S})(\eta^1\text{-(P-P)})(\mu\text{-dpm})(\eta^1\text{-dpm}) \quad (12)$$

$$\mathbf{IV} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Pd_2Br_2(\mu\text{-dpm})(\mu\text{-(P-P)})(\eta^1\text{-dpm(S)})\ (\mathbf{V}) \xrightarrow{\text{fast}} \text{products} \quad (13)$$

IV to **V**. It seems reasonable that, for all the P-P systems, the

(18) James, B. R.; Mahajan, D. *Can. J. Chem.* **1979**, *57*, 180.

k_1 values are comparable; the findings require that, for dpm or dpm-d_2, the k_1/k_{-1} equilibrium is established rapidly, but the k_2 step can compete sufficiently with the k_{-1} step to result in S-abstraction, *i.e.* the bite of the dpm ligand makes it highly favorable for forming the 5-membered Pd−S−P−CH_2-P ring. Diphosphine exchange with dpm (or dpm-d_2) within type **2b** species is pictured as proceeding via reaction 12, with an originally coordinated diphosphine having the same probability as leaving as the incoming diphosphine. The S-abstraction occurs via eq 13, all three dpm ligands (because of the rapidly established k_1/k_{-1} equilibrium) having an equal probability of abstracting the S. A steady state treatment for **IV** gives the rate expression for S-abstraction

$$\text{rate} = \frac{k_1 k_2}{k_{-1} + k_2}[\mathbf{2b}][\text{P-P}] \qquad (14)$$

consistent with our experimental findings, *e.g.* with $k_{Br} = k_1k_2(k_{-1} + k_2)^{-1}$. For the other phosphines, the k_2 step cannot compete effectively with the k_{-1} step, and the k_{-1} value for these phosphines must also be greater than the k_{-1} value for dpm/dpm-d_2 because the exchange (*e.g.* with dpmMe) is established much more slowly. The rate law for S-abstraction using other phosphines thus approximates to $(k_1/k_{-1})k_2$[**2b**]-[P-P].

The experimental findings show that the dpm/dpm-d_2 exchange for **2b** at RT is established in less than seconds for solutions typically $\sim 10^{-2}$ M in both complex and phosphine, while the S-abstraction occurs with a rate constant of ~ 0.03 M^{-1} s^{-1}. Qualitatively, typical, somewhat arbitrary values that would satisfy the above analysis are $k_1 \sim 10^3$ M^{-1} s^{-1}, $k_{-1} \sim 10^2$ s^{-1}, and $k_2 \sim 10^{-3}$ s^{-1}; the S-abstraction via **IV** is $\sim 10^{-5}$ times less probable than loss of the η^1-dpm.

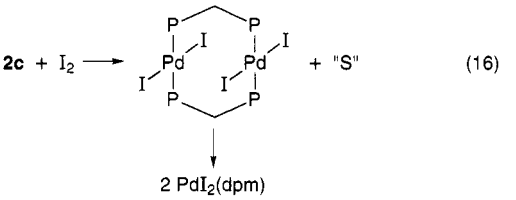
Within type **1b** species, the rapid exchange involving dpm-d_2 can be accounted for by an equilibrium (eq 15) involving

$$Pd_2Br_2(\mu\text{-dpm})_2 + \text{dpm-}d_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pd_2Br_2(\eta^1\text{-dpm-}d_2)(\mu\text{-dpm})_2\ (\mathbf{VI}) \text{ or } Pd_2Br_2(\eta^1\text{-dpm-}d_2)(\eta^1\text{-dpm})(\mu\text{-dpm}) \qquad (15)$$

intermediate **VI**. The transition state for this exchange could be akin to that shown in **II** but with one Pd−P bond at each metal being stretched toward an η^1-(P-P) configuration en route to **VI.** The slow exchange of dpmMe with **1b** (as with **2b**) implies that loss of an η^1-dpmMe from a species such as **VI** (as with **IV**) occurs much more readily than loss of η^1-dpm, possibly because of steric factors.

Of note also is that *in situ* treatment of **2b** with dpm(S) (1:1) yields over several days an uncharacterized species Y (or mixture of species) that on subsequent reaction with dpm (1:1) slowly generates **1b** and 2 mol equiv of dpm(S). Y could be a species such as $Pd_2Br_2(\mu\text{-S})(\mu\text{-dpm})_2(\eta^1\text{-dpm(S)})$ or $Pd_2Br_2(\mu\text{-S})(\eta^1\text{-dpm})(\mu\text{-dpm})(\eta^1\text{-dpm(S)})$, while subsequent reaction with dpm could slowly replace the coordinated dpm(S) and lead then to an intermediate such as **IV** with P-P = dpm.

Of interest, we find that **2c**, $Pd_2I_2(\mu\text{-S})(dpm)_2$, reacts with I_2 in $CDCl_3$ at RT according to eq 16;[10] the NMR data (Table 1)



(16)

of the Pd_2 intermediate correspond well to those of the tetraiodo species, characterized previously by Hunt and Balch[23] in a study of the reaction of I_2 with $Pd_2I_2(dpm)_2$ (**1c**). That transannular addition can occur across an A-frame complex, reaction 16, albeit with destruction of the A-frame, offers some support for reactivity via a transition state such as **I** or **III**, the diphosphine addition resembling in the broadest sense the addition of two iodide ligands. Thus, in eq 16 the bridged sulfide is formally oxidized by I_2 to elemental sulfur, with the electron transfer presumably proceeding from the (μ-S) through the metal atoms toward the attacking I_2 reagent and a transition state akin to **I** or **III** but with the P-P replaced by I-I. Indeed, the conversion of the **2** to **1** species could, in principle, involve incipient formation of a S atom (*cf.* eq 16) that is then scavenged as a phosphine monosulfide.

The reactivity trend for reaction 1, X = Cl > Br > I, can be rationalized in terms of transition state **I**. The activation parameters for the chloro and bromo systems reveal that the dominant factor governing reactivity is the entropy term (−127 and −144 for the chloro and bromo systems, respectively). A large, unfavorable ΔS value is reasonable for the addition of the dpm ligand to **2b** to generate **I** or **III**, and this is expected to be more difficult when the auxiliary ligand is the bulkier bromide (vs chloride), because of interactions with the phenyl groups. For the iodo system, ΔS is predicted to be still more negative. The essentially constant ΔH value for the chloro and bromo systems tends to imply that the energy required to form a transition state such as **I** or **III** is similar in the two systems; any contribution from the *trans*-effect of the halides (Br > Cl)[24] must be small.

Catalytic Conversion of H_2S. As noted in the Introduction, the demonstration of the conversion of **1** to **2**, and the reconversion using dpm, constitutes a catalytic cycle for reaction 2 which could be catalyzed by complex **1** or **2**. A few experiments have confirmed the existence of the catalysis.[10] For example, a 10^{-3} M solution of $Pd_2Br_2(dpm)_2$ (**1b**) in CH_2Cl_2 at RT under 1 atm H_2S converts 0.02 M dpm completely to dpm(S) in a few hours; under these conditions when the [H_2S] $\approx$ 0.6 M, the rate of S-abstraction is about half that of the H_2S reaction with **1b**.[2] The presence of the H_2S in excess (vs dpm) leads to the palladium being recovered in the bridged-sulfide form **2b**.

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(19) (a) Al-Salem, N. A.; Empall, H. D.; Markham, R.; Shaw, B. L; Weeks, B. J. *Chem. Soc., Dalton Trans.* **1979**, 1972. (b) Shaw, B. L. In *Catalytic Aspects of Metal Phosphine Complexes, Advances in Chemistry Series*; Alyea, C., Meek, D. W., Eds.; American Chemical Society: Washington, DC, 1982; Vol. 196, Chapter 6.
(20) Ball, R. G.; Domazetis, G.; Dolphin, D.; James, B. R.; Trotter, J. *Inorg. Chem.* **1981**, *20*, 1556.
(21) Keiter, R. L.; Rheingold, A. L.; Hamerski, J. J.; Castle, C. K. *Organometallics* **1983**, *2*, 1635.
(22) (a) Brown, M. P.; Yavari, A.; Hill, R. H.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2421. (b) Azam, K. A.; Brown, M. P.; Hill, R. H.; Puddephatt, R. J.; Yavari, A. *Organometallics* **1984**, *3*, 697.
(23) Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 2267.
(24) Appleton, T. G.; Clark, H. L.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.