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Synthesis and Characterization of Dinuclear Palladium Complexes with Bridging Selenide or Selenoxide Ligands, Including X-ray Characterization of *anti*-$Pd_2Cl_2(\mu\text{-}Se)(\mu\text{-}dpmMe)_2$ [dpmMe = 1,1-Bis(diphenylphosphino)ethane]

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The complexes $Pd_2Cl_2(P\text{-}P)_2$, where (P-P) = μ-bis(diphenylphosphino)methane, dpm, or μ-1,1-bis(diphenylphosphino)ethane, dpmMe, react with elemental selenium to give the A-frame adducts $Pd_2Cl_2(\mu\text{-}Se)(P\text{-}P)_2$, which can be oxidized by *t*-BuOOH to the μ-SeO derivatives. Reaction of H_2Se with $Pd_2Cl_2(dpm)_2$ generates $Pd_2Cl_{2-n}(SeH)_n(\mu\text{-}Se)(dpm)_2$ species ($n = 0-2$). *anti*-$Pd_2Cl_2(\mu\text{-}Se)(dpmMe)_2$ (**2d**) crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.986(2)$ Å, $b = 24.141(2)$ Å, $c = 18.921(2$ Å), $\beta = 106.64(1)°$, $V = 5243.2(11)$' Å^3, and $Z = 4$; the structure was refined against F^2 to wR2 = 0.1338 (R1 = 0.0476) for 9838 reflections with $I > 2\sigma(I)$. **2d** is the first structurally characterized A-frame complex with *anti* disposition of substituents at the methylene C atoms of the diphosphine ligands. A correlation between the ^{77}Se NMR shift measured for $Pd_2Cl_2(\mu\text{-}Se)(P\text{-}P)_2$ and the equilibrium constant for the reversible binding of CO by the $Pd_2Cl_2(P\text{-}P)_2$ species reflects factors affecting binding at the apical site.

Introduction

Bis(diphenylphosphino)methane(dpm) has been used extensively as a bidentate, bridging ligand within homo- and heterobimetallic complexes, and the chemistry of such dpm-containing species[1] has been reviewed.[2]

Because of our general interest in utilization of metal complexes in gas separation processes,[3] with the initial specific aim of immobilizing $Pd_2X_2(dpm)_2$-type moieties (X = halogen; **1a**) for selective binding of CO in gas streams,[3b] we subsequently used a methylated-dpm, 1,1-bis(diphenylphosphino)ethane(dpmMe) with the aim of modeling a supported $CH_2CH(PPh_3)_2$ group, and synthesized the mixed (dmp)(dpmMe) complex **1b** and the *syn*- and *anti*-isomers of the bis(dpmMe) complex (**1c** and **1d**, respectively).[4,5] [*syn* and *anti* refer to the disposition of the Me groups with respect to the Pd−C−Pd plane—see eq 2 below].

We have studied the interaction of **1a−d** with H_2S in solution, and found that **1a−c** react quantitatively according to eq 1, with

$$Pd_2Cl_2(P\text{-}P)_2 + H_2S \rightarrow Pd_2Cl_2(\mu\text{-}S)(P\text{-}P)_2 + H_2 \qquad (1)$$

abstraction of the S atom and generation of H_2, while the nonreactivity of **1d** towards H_2S was attributed to steric reasons;[4−7] **1d** is similarly unreactive toward CO and SO_2, while **1a−c** reversibly form the A-frame species $Pd_2Cl_2(\mu\text{-}Y)(P\text{-}P)_2$ where Y = CO or SO_2.[2,4,5] The $Pd_2Cl_2(\mu\text{-}S)(dpm)_2$ species (*cf.* eq 1) can also be synthesized by treatment of **1a** with elemental sulfur.[8] The discovery of reaction 1 prompted us to investigate the analogous type reaction with H_2Se. Although metal complexes with bare chalcogenide ions are common,[9] A-frames with Se in the apical position are rare.[10] We thus decided to extend our earlier studies on the μ-S species to the corresponding μ-Se compounds.

In this paper, we report details on the reaction of **1a** with H_2Se, and on the reactions of **1a−d** with elemental Se, and include the structural analysis of *anti*-$Pd_2Cl_2(\mu\text{-}Se)(dpmMe)_2$; μ-SeO complexes are also described. Preliminary results have been published previously.[11]

Experimental Section

General Data. The complexes $Pd_2Cl_2(P\text{-}P)_2$, (P-P) = dpm or dpmMe, were prepared by published procedures.[4,5,12] H_2Se was generated from Al_2Se_3 (Alfa Products) by addition of dilute H_2SO_4 (1 mL in 5 mL of H_2O) under a N_2 stream and was used immediately without purification. Amorphous, red selenium was prepared from SeO_2 (Alfa) and an aqueous N_2H_4 solution (Alfa).[13] ^tBuOOH (Aldrich) was available as a 70% aqueous solution. ^1H (5-mm tubes, 400 MHz) and $^{31}P\{^1H\}$ (10-mm tubes, 32.44 MHz) NMR spectra were recorded at room temperature on Bruker WH-400 and WP-80 FT instruments,

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(1) The bridging symbol μ is omitted for convenience for all the P-P ligands described in this paper.

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Table 1. NMR Spectroscopic Data for Type **2** and **3** Compounds[a]

	methylene or methine protons			methyl protons			$^{31}P\{^1H\}$
complex	δ_H	J_{HH}	J_{HP}	δ_H	J_{HH}	J_{HP}	δ_P
2a	4.91 (dqn)	13.05	5.76				4.0 (s)
	3.63 (dqn)	13.05	3.51				
2b	5.71 (tq)	7.37	13.92	1.01 (dt)	7.37	10.26	*b*
	4.72 (dt)	12.89	12.16				
	3.61 (dt)	12.89	8.93				
2c	5.60 (qqn)	7.18	7.31	0.95 (dqn)	7.18	6.10	18.6 (s)
2d	5.86 (tq)	7.29	13.75	1.33 (dt)	7.29	13.16	*c*
	4.09 (un)			0.98 (dt)	7.83	10.07	
2a′[d]	4.98 (dt)	13.07	6.15				*e*
	3.80 (dt)	13.07	3.44				
2a″[f]	5.03 (dqn)	13.31	5.76				13.2 (s)
	4.00 (dqn)	13.31	3.45				
3a	6.09 (dt)	13.13	13.29				*g*
	4.01 (dt)	14.25	8.50				
	2.64 (m)						
	2.53 (m)						
3b[h]	6.76 (tq)	7.03	16.03	1.04 (dt)	7.03	10.38	*i*
(major	3.80 (dt)	14.24	8.61				
isomer)	2.46 (dtt)[j]	14.24	12.23				
3c	6.72 (tq)	7.23	16.05	1.10 (dt)	7.23	9.79	*k*
	4.22 (tq)	7.12	10.94	1.02 (dt)	7.12	10.25	
3d[l]	6.97 (tq)	7.33	15.47	1.13 (dt)	7.33	12.70	*g*
	3.53 (tqt)[m]	7.00	15.00	1.00 (dt)	7.00	10.26	

[a] In CD_2Cl_2 or $CDCl_3$ at ~20 °C; proton integrations are correct throughout; s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = overlapping multiplets, un = unresolved multiplet; *J* in Hz. [b] AA′BB′ multiplet; $\delta_A \sim 26.5$, $\delta_B \sim 16.3$, $J_{AB} \approx J_{A'B'} \approx 555$. [c] AA′BB′ multiplet; $\delta_A \sim 17.8$, $\delta_B \sim 6.2$, $J_{AB} \approx J_{A'B'} \approx 565$. [d] $\delta_{SeH} = -3.52$ (t), $J_{HP} = 13.0$. [e] Major peaks of AA′BB′ multiplet centered at δ 11.2 and 5.7. [f] $\delta_{SeH} = -3.55$(qn), $J_{HP} = 6.39$. [g] Decomposition in solution during acquisition of spectrum. [h] Unresolved resonances at δ 6.14, 4.38, 2.56, and 1.13 are assigned to minor isomer of **3b**. [i] Complex; mixture of isomers yields two AA′BB′ patterns. For major isomer, $\delta_A = 26.44$, $\delta_B = -2.26$, $J_{AB} = J_{A'B'} = 398.1$, $J_{AA'} = 28.8$, $J_{BB'} = 86.2$, and $J_{AB'} = J_{A'B} = -1.4$. [j] Long-range coupling to the remote P atoms ($J_{HP} = 6.9$). [k] AA′BB′ multiplet; $\delta_A = 27.1$, $\delta_B = 13.5$, $J_{AB} = J_{A'B'} = 395.5$, $J_{AA'} = 92.8$, $J_{BB'} = 37.9$, and $J_{AB'} = J_{A'B} = -2.2$. [l] The major stereoisomer (see text). [m] Long-range coupling to the remote P atoms ($J_{HP} \approx 3.0$).

respectively. ^{31}P NMR shifts are given relative to external 85% H_3PO_4, downfield being positive. ^{77}Se NMR spectra were recorded relative to external pure Me_2Se on a Varian XL-200 spectrometer operating at 38.15 MHz. IR spectra were recorded as Nujol mulls on a Nicolet 50X FT spectrometer. The synthetic reactions were monitored using Merck Kieselgel 60 F_{254} TLC plates and CH_2Cl_2/EtOAc (6:1 v/v) as eluent. Syntheses were carried out by using Schlenk glassware in well-ventilated fume hoods. Elemental analyses were carried out by P. Borda at the UBC laboratories.

Formation of $Pd_2Cl_2(\mu\text{-}Se)(P\text{-}P)_2$ Complexes using Elemental Se. $Pd_2Cl_2(\mu\text{-}Se)(dpm)_2$, 2a. $Pd_2Cl_2(dpm)_2$ (**1a**) (200 mg, 0.19 mmol) was dissolved in 20 mL of CH_2Cl_2 and 45 mg (0.57 mmol) of red, amorphous Se was added. Reaction was complete after 90 min of stirring. The unreacted Se was removed by filtration and the filtrate was concentrated to ~4 mL; addition of MeOH yielded brown crystals, which were dried overnight under vacuum at room temperature; yield 100 mg (47%). Reprecipitation from CH_2Cl_2 with MeOH gave **2a** in high purity. Anal. Calcd for $C_{50}H_{44}Cl_2P_4SePd_2$: C, 53.08; H, 3.92; Se, 6.98. Found: C, 52.76; H, 3.97; Se, 7.79. The ^1H and ^{31}P NMR spectroscopic data for all the Se-containing complexes are collected in Table 1.

$Pd_2Cl_2(\mu\text{-}Se)(dpm)(dpmMe)$, 2b. Reaction of $Pd_2Cl_2(dpm)(dpmMe)$ (**1b**) with red Se under conditions identical to those given above gave **2b** in 51% yield. Anal. Calcd for $C_{51}H_{46}Cl_2P_4SePd_2$: C, 53.48; H, 4.05; Se, 6.89. Found: C, 53.55. H, 4.09; Se, 7.72.

***syn*-$Pd_2Cl_2(\mu\text{-}Se)(dpmMe)_2$, 2c.** An approximately 2:1 mixture of *syn-* and *anti*-$Pd_2Cl_2(dpmMe)_2$[5] (206 mg, 0.19 mmol) was dissolved in 20 mL of CH_2Cl_2 in a Schlenk tube. Se (45 mg, 0.57 mmol) was added and the mixture stirred for 2 h at room temperature. The unreacted Se was filtered off and the filtrate was concentrated to ~5 mL; addition of MeOH precipitated light brown crystals of **2c**. Yield: 51 mg (51%). Anal. Calcd for $C_{52}H_{48}Cl_2P_4SePd_2$: C, 53.87; H, 4.17; Se, 6.81. Found: C, 53.38; H, 4.28; Se, 7.52. Analysis of the mother liquor by NMR spectroscopy showed the presence of unconverted *anti*-$Pd_2Cl_2(dpmMe)_2$ together with *syn-* and *anti*-$Pd_2Cl_2(\mu\text{-}Se)(dpmMe)_2$.

Table 2. Crystallographic Data for *anti*-$Pd_2Cl_2(\mu\text{-}Se)(dpmMe)_2 \cdot CH_2Cl_2$

formula	$C_{53}H_{50}Cl_4P_4Pd_2Se$	Z	4
fw	1244.37	ρ_{calc}, g/cm^3	1.576
cryst syst	monoclinic	*T*, °C	20
space group	$P2_1/c$ (no. 14)	λ, Å	1.5418
a, Å	11.986(2)	μ, mm^{-1}	9.626
b, Å	24.141(2)	final *R* indices [$I > 2\sigma(I)$]	
c, Å	18.912(2)	R1[a]	0.0476
β, deg	106.64(1)	wR2[b]	0.1338
V, Å^3	5243.2(11)		

[a] $R1 = \Sigma||F_o|| - ||F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2]^{1/2}$.

***anti*-$Pd_2Cl_2(\mu\text{-}Se)(dpmMe)_2$, 2d.** To *anti*-$Pd_2Cl_2$ $(dpmMe)_2$ (450 mg, 0.42 mmol) dissolved in 50 mL of CH_2Cl_2 was added Se (200 mg, 2.53 mmol) and the mixture (protected from light using Al foil) was stirred for 72 h at room temperature. Excess of Se was removed by filtration. Evaporation of the filtrate to ~5 mL and addition of MeOH led to the isolation of a brown product. Yield: 219 mg (45%). Anal. Calcd for $C_{52}H_{48}Cl_2P_4SePd_2$: C, 53.87; H, 4.17. Found: C, 53.75; H, 4.32.

Reaction of $Pd_2Cl_2(dpm)_2$ (1a) with H_2Se. **1a** (200 mg, 0.91 mmol) was dissolved in 25 mL of CH_2Cl_2 in a Schlenk tube, and the system was evacuated by freeze-thaw cycles; H_2Se was then transferred into the solution at −10 °C, and the mixture was stirred for various times and allowed to reach room temperature. Varying H_2Se/Pd_2 ratios were used, the details being given in the Results and Discussion section. After removal of excess H_2Se by pumping, product complexes were precipitated by addition of MeOH.

Conversion of 2a–d to $Pd_2Cl_2(\mu\text{-}SeO)(P\text{-}P)$, 3a–d. $Pd_2Cl_2(\mu\text{-}SeO)(dpm)_2$, 3a. To **2a** (200 mg, 0.18 mmol) dissolved in 50 mL CH_2Cl_2 under N_2 was added aqueous ^tBuOOH (200 μL 70%, 1.5 mmol) dissolved in 3 mL of CH_2Cl_2, and the mixture was stirred for 1 h at room temperature when the color changed from brown to dark orange. TLC indicated that a more polar product than the starting selenide was formed and that the reaction was almost complete (only traces of the **2a** remained). The volume was reduced to ~5 mL and **3a** was precipitated by addition of Et_2O. Yield: 170 mg (84%). Reprecipitation from CH_2Cl_2 with Et_2O or MeOH gave orange crystals. Anal. Calcd for $C_{50}H_{44}Cl_2OP_4SePd_2$: C, 52.34; H, 3.87; O, 1.39; Se, 6.88. Found: C, 52.19; H, 4.00; O, 1.50; Se, 7.69.

Oxidation of the other μ-Se adducts **2b–d** was performed in the same manner, and yielded respectively $Pd_2Cl_2(\mu\text{-}SeO)(dpm)(dpmMe)$, **3b** (85%), and *syn-* and *anti*-$Pd_2Cl_2(\mu\text{-}SeO)(dpmMe)_2$, **3c** (94%) and **3d** (56%). **3b**. Anal. Calcd for $C_{51}H_{46}Cl_2OP_4SePd_2$: C, 52.74; H, 3.99; O, 1.38; Se, 6.80. Found: C, 52.43; H, 3.99; O, 1.50; Se, 7.58. **3c** and **3d**. Anal. Calcd for $C_{52}H_{48}Cl_2OP_4SePd_2$: C, 53.13; H, 4.12; O, 1.36; Se, 6.72. Found (**3c**): C, 53.02; H, 4.17; O, 1.50; Se, 7.50. Found (**3d**): C, 52.39; H, 4.19; Se, 7.54.

X-ray Crystallographic Analysis of *anti*-$Pd_2Cl_2(\mu\text{-}Se)(dpmMe)_2 \cdot CH_2Cl_2$ ($2d \cdot CH_2Cl_2$). Transparent crystals of **2d**·CH_2Cl_2 suitable for X-ray analysis were prepared by diffusion of Et_2O vapor into a CH_2Cl_2 solution of complex;[6b] a crystal was mounted on an Enraf-Nonius CAD4, computer controlled kappa axis diffractometer. The determination of the unit cell and data collection were performed with Cu Kα radiation; cell constants and orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range of $25 < \theta < 27°$. Some crystal data are given in Table 2. Selected atomic coordinates and equivalent isotropic displacement parameters are listed in Table 3.

Intensity data were collected at ambient temperature, using the $\omega-\theta$ scan technique. The scan rate varied from 1 to 20°/min (in ω). The scan range (in deg) was determined as a function of θ to correct for the separation of the Kα doublet: θ scan width = 0.50 + 0.41 tan θ. For intense reflections, an attenuator was automatically inserted in front of the detector; 10 788 unique reflections were collected. As a check

Table 3. Selected Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\text{Å}^2 \times 10^3$)[a]

atom	*x*	*y*	*z*	*U*(eq)
Pd1	1910(1)	893(1)	1972(1)	32(1)
Pd2	2500(1)	1676(1)	3287(1)	34(1)
Se	2070(1)	1886(1)	1991(1)	39(1)
Cl1	1725(1)	−70(1)	1962(1)	52(1)
Cl2	2941(2)	1440(1)	4536(1)	62(1)
P1	15(1)	969(1)	2062(1)	36(1)
P2	3704(1)	960(1)	1755(1)	34(1)
P3	4391(1)	1400(1)	3341(1)	38(1)
P4	607(1)	1961(1)	3144(1)	37(1)
C1	4768(4)	1388(2)	2449(3)	40(1)
C2	−525(5)	1642(2)	2341(3)	41(1)
C3	6051(5)	1265(3)	2516(4)	58(2)
C4	−997(7)	2042(3)	1686(4)	69(2)
C5	−986(5)	828(3)	1147(3)	47(1)
C11	−342(4)	479(2)	2699(3)	38(1)
C17	3549(5)	1298(2)	873(3)	42(1)
C23	4493(4)	325(2)	1671(3)	38(1)
C29	4814(5)	720(2)	3745(3)	44(1)
C35	5438(5)	1900(3)	3873(3)	52(1)
C41	124(5)	1840(2)	3966(3)	43(1)

[a] *U*(eq) is defined as one-third of the trace of orthogonalized $\mathbf{U}_{ij}$ tensor.

on crystal and electronic stability, three representative reflections were measured every 60 min. The intensities of these standards remained constant within experimental error throughout data collection. Lorentz and polarization corrections were applied. An empirical spherical absorption correction (DIFBAS)[14] was applied at the end of isotropic refinement.

The structure was solved by direct methods (MULTAN)[15] which gave the positions of the Se, Pd, Cl, and P atoms. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atomic positions were generated from assumed geometries and were treated as riding atoms. A common isotropic *U* (0.082(4) Å^2) was refined for all hydrogen atoms. The structure was refined against all non-zero *I* by full-matrix least-squares mtheods using the SHELXL-93 program.[16] Scattering factors were taken from ref 17.

Details of the data collection and reduction, the structure solution and refinement, and complete tables of crystallographic data, atomic coordinates and equivalent isotropic thermal parameters, anistropic thermal parameters, and bond lengths and angles are included as Supporting Information.

Results and Discussion

The Bridged-Se Complexes. Complexes **1a**–**d** all react with elemental Se to form isolable, air-stable, light brown compounds with A-frame structures (**2a**–**d**, respectively), eq 2. Complex **2c**, *syn*-$Pd_2Cl_2(\mu\text{-Se})(dpmMe)_2$, can be made from the less readily accessible *syn*-precursor **1c**,[5] but is more readily obtained from the easy-to-obtain **1c/d** mixture.[5] Elemental Se exists as several allotropes[18] which may exhibit different reactivities; we used amorphous, red selenium.

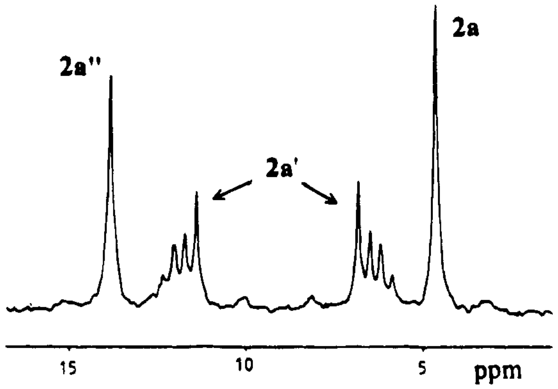
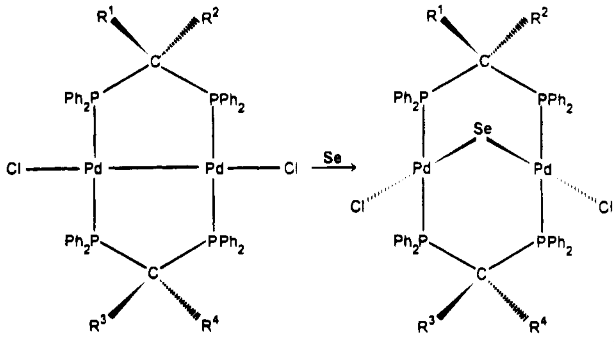


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of the product mixture from 2.5 h reaction of $Pd_2Cl_2(dpm)_2$ (**1a**) with a 15-fold excess of H_2Se at ambient conditions.



(2)

1a	$R^1 = R^2 = R^3 = R^4 = H$		**2a**
1b	$R^1 = R^2 = R^3 = H$,	$R^4 = CH_3$	**2b**
1c (*syn*)	$R^1 = R^3 = H$,	$R^2 = R^4 = CH_3$	**2c**
1d (*anti*)	$R^2 = R^3 = H$,	$R^1 = R^4 = CH_3$	**2d**

The μ-S analogues of **2a**, **2b**, and **2c** have been described in detail previously,[4,5,8] and the ^1H and $^{31}P\{^1H\}$ NMR spectra for such species (Table 1) are consistent with the structures illustrated in eq 2, and which have been verified by X-ray analysis in the case of $Pd_2Cl_2(\mu\text{-S})(dpm)_2$.[8] The ^1H NMR spectra for **2a** reveal the inequivalence of the CH_2 protons and the virtual coupling to the remote P nuclei; the $^{31}P\{^1H\}$ NMR spectrum gives a corresponding singlet. In principle, **2b** can exist as two possible isomers with the selenium bridge and methyl on the same (*syn*) or opposite (*anti*) sides of the Pd–C–Pd plane; the ^1H NMR spectrum, however, reveals just four resonances for the methyl, methine, and inequivalent CH_2 protons as in the precursor mixed-ligand complex **1b**,[4] and thus only one isomer is formed, presumably the *anti*-isomer for steric reasons (*cf.* Figure 2, discussed below). The inequivalence of the trans P atoms rules out any virtual coupling and the splitting patterns in the ^1H NMR are as expected. The $^{31}P\{^1H\}$ NMR spectrum of **2b** is in accord with an AA′BB′ system with large trans coupling.[4] Complex **2c**, like **2b**, may exist as two stereoisomers, but only one is seen, presumably where the two methyl groups are in pseudoequatorial positions (*cf.* Figure 2); the two CH (and Me) protons are equivalent, as are the P atoms, as demonstrated by the NMR data. In **2d**, whose solid state structure is presented in Figure 2, the two CH (and Me) groups are now inequivalent, and coupling occurs only to the adjacent P atoms; the δ 4.09 resonance of one of the methine protons (associated with the δ 0.98 Me group) was not well resolved. The $^{31}P\{^1H\}$ NMR spectrum of **2d** is that of an AA′BB′ system. Worth noting is that the J_{HP} values for **2b** and **2d** are roughly twice those for **2a** and **2c**, because with virtual coupling the observed coupling constant is the average of the couplings to the adjacent and remote P atoms, and the latter is zero.

Reactions analogous to those given in eq 1 but using H_2Se do occur, but there is also accompanying replacement of the

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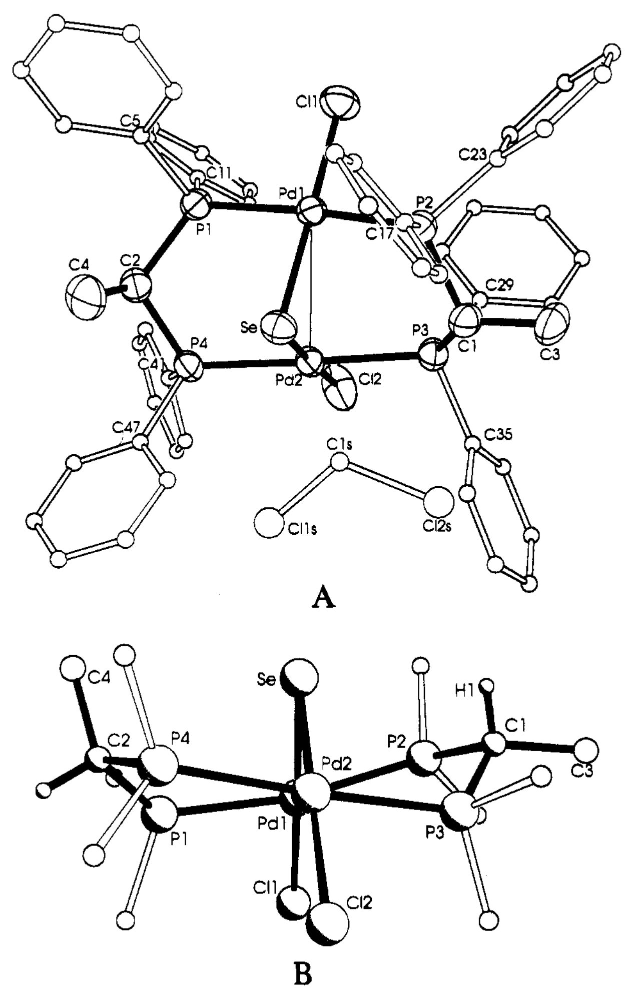

Figure 2. (a) Structure of *anti*-$Pd_2Cl_2(\mu\text{-}Se)(dpmMe)_2$ (**2d**). Only the *ipso* C atoms of the phenyl rings are labeled, and H atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. (b) Side view showing conformations of the rings and CH(Me) moieties.

Table 4. Selected Bond Lengths (Å) and Angles (deg)

	Bond Lengths		
Pd1−P2	2.307(1)	P1−C2	1.880(5)
Pd1−P1	2.334(1)	P2−C17	1.819(5)
Pd1−Cl1	2.335(1)	P2−C23	1.831(5)
Pd1−Se	2.404(1)	P2−C1	1.860(5)
Pd1−Pd2	3.042(1)	P3−C29	1.820(6)
Pd2−P4	2.311(1)	P3−C35	1.823(6)
Pd2−P3	2.337(1)	P3−C1	1.867(5)
Pd2−Cl2	2.339(1)	P4−C47	1.822(6)
Pd2−Se	2.410(1)	P4−C41	1.831(5)
P1−C11	1.824(5)	P4−C2	1.887(5)
P1−C5	1.834(6)	C1−C3	1.535(7)
C2−C4	1.544(8)		
	Bond Angles		
P2−Pd1−P1	169.72(5)	P4−Pd2−Pd1	95.65(3)
P2−Pd1−Cl1	99.15(5)	P3−Pd2−Pd1	81.57(3)
P1−Pd1−Cl1	89.23(5)	Cl2−Pd2−Pd1	127.31(5)
P2−Pd1−Se	81.86(3)	Se−Pd2−Pd1	50.71(2)
P1−Pd1−Se	89.79(4)	Pd1−Se−Pd2	78.39(2)
Cl1−Pd1−Se	178.98(4)	C2−P1−Pd1	120.6(2)
P2−Pd1−Pd2	95.25(3)	C1−P2−Pd1	113.5(2)
P1−Pd1−P2	83.97(3)	C1−P3−Pd2	116.6(2)
Cl1−Pd1−Pd2	128.68(4)	C2−P4−Pd2	115.4(2)
Se−Pd1−Pd2	50.90(2)	C3−C1−P2	114.7(4)
P4−Pd2−P3	175.88(5)	C3−C1−P3	115.2(4)
P4−Pd2−Cl2	96.95(5)	P2−C1−P3	110.6(3)
P3−Pd2−Cl2	87.16(5)	C4−C2−P1	113.1(4)
P4−Pd2−Se	84.38(4)	C4−C2−P4	113.8(4)
P3−Pd2−Se	91.50(4)	P1−C2−P4	110.6(3)
C12−Pd2−Se	177.81(4)		

chloride ligands by SeH^-, which is presumably related to the higher acidity of H_2Se compared to that of H_2S. The H_2Se reaction with $Pd_2Cl_2(dpm)_2$ (**1a**) near ambient conditions was studied in some detail. The ^1H and $^{31}P\{^1H\}$ NMR data (Table 1) for the Pd products isolated after a reaction time of 2.5 h with a 15-fold excess of H_2Se are consistent with the presence of **2a** and two other A-frame species $Pd_2Cl(SeH)(\mu\text{-}Se)(dpm)_2$ (**2a′**) and $Pd_2(SeH)_2(\mu\text{-}Se)(dpm)_2$ (**2a″**); complementing the assigned CH_2 resonances for **2a′** and **2a″** are high-field ^1H resonances for coordinated SeH^- at δ −3.52 t and δ −3.55 qn, respectively, the splittings resulting from coupling to two and four P atoms. The $^{31}P\{^1H\}$ spectrum of the mixture (Figure 1) reveals the singlets for **2a** and **2a″**, and the AA′BB′ pattern for **2a′**. Use of shorter reaction times (~10 min) with about a 4-fold excess of H_2Se led to a product mixture containing about a 4:1 ratio of **2a** and **2a′** with only traces of **2a″**. The varying intensity ratios of the peaks of **2a**, **2a′**, and **2a″** obtained under different experimental conditions establish that the spectra do result from a mixture of three species. Treatment of **2a** with about a 15-fold excess of H_2Se for 2.5 h produced much the same mixture as found using precursor **1a** under the same conditions. Complexes **2a′** and **2a″** presumably form by successive substitution of the chloride ligands of the initially formed **2a**; such ligand exchange is common within such dinuclear Pd_2 complexes.[4,6,12] Elemental analyses of some mixed products revealed higher Se and lower C and H values compared to those found for **2a**. The H_2 co-product of reaction 1 was detected,[6] and thus the abstraction of the chalcogen atom (X) from H_2X by metal complexes with liberation of H_2 is now well established.[6,7,11,19−22]

Preliminary data[23] show that *both* the *syn*- and *anti*-isomers of $Pd_2Cl_2(dpmMe)_2$ react with H_2Se; the μ-Se adducts are formed, again with the accompanying replacement of the chloride ligands by SeH^-.

Solid State Structure of *anti*-$Pd_2Cl_2(\mu\text{-}Se)(dpmMe)_2$ (2d). Although the NMR data provide conclusive evidence for the solution structure of **2d**, it was pleasing to obtain an X-ray structural analysis because, to our knowledge, this is the first structurally characterized A-frame adduct in which substitutents at the methylene C-atoms are in an *anti* disposition (see below in the **General Discussion**).

Two diagrams for the molecular structure of **2d** are shown in Figure 2. As in other A-frame molecules,[2,24] both twisted fused rings adopt boat conformations, the methylene C atoms being bent toward the Se bridge. In the structurally characterized *anti*-$Pd_2Cl_2(dpmMe)_2$ (**1d**),[4] both Me groups are in less crowded, equivalent pseudoequatorial positions, but in **2d** one of the Me groups has become twisted into a pseudoaxial position and the markedly different environments of the Me groups (and CH protons) are reflected in the well-separated ^1H NMR signals in solution.

Selected bond lengths and angles for **2d** are given in Table 4. The insertion of the Se atom cleaves the Pd−Pd bond of **1d**, and increases the separation of the Pd centers from 2.664 to 3.042 Å; this Pd−Pd distance is considerably shorter than that of 3.258 Å in $Pd_2Cl_2(\mu\text{-}S)(dpm)_2$[8] and the Pd−Se−Pd angle (78.4°) is correspondingly less than the Pd−S−Pd angle (90.3°).

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Table 5. Ring Conformation of the Eight-Membered Pd1−P2−C1−P3−Pd2−P4−C2−P1 Rings

torsion angle, deg	**2d**	**1d**
Pd1−P2−C1−P3	24.9	52.0
P2−C1−P3−Pd2	−54.2	−16.4
C1−P3−Pd2−P4	−2.6	−121.2
P3−Pd2−P4−C2	47.2	82.2
Pd2−P4−C2−P1	22.7	−12.8
P4−C2−P1−Pd1	−44.0	47.6
C2−P1−Pd1−P2	−50.5	−94.6
P1−Pd1−P2−C1	89.1	−16.7
rms torsion angle	48.4	67.2

These differences must reflect in part the larger size of Se (covalent radius 1.17 Å) *vs* S(1.04 Å); the Pd-Se bond lengths (average 2.407 Å) are longer than the Pd−S lengths (2.298 Å). However, although the overall structures of the Pd$_2$(P-P)$_2$ groups within **1d** and a corresponding dpm analogue are remarkably similar,[4] there are some steric constraints around the μ-Se atom of **2d** resulting from incorporation of the Me groups (see below) and it is possible that these play a role in differences in geometry of the A-frame moieties of **2d** and Pd$_2$Cl$_2$(μ-S)(dpm)$_2$.

The geometry at the Pd atoms of **2d** is distorted square planar with bond angles from 84.3−99.1°. The mean deviation of Se, Cl1, P1, and P2 from the least-squares plane around Pd1 is 0.063(3) Å with the metal being 0.058(1) Å out of the plane; corresponding values for the Se, Cl2, P3, P4/Pd2 moiety are 0.016(3) and 0.020(1) Å. The two planes form a dihedral angle of 76.0(3)°. The two Pd−Cl bond lengths are essentially the same and are about 0.08 Å shorter than those in **1d** where the chlorines are trans to the Pd-Pd bond.[4] At each Pd of **2d**, the two Pd−P bond lengths differ significantly (2.337 *vs* 2.311 Å, and 2.334 *vs* 2.307 Å); the values are larger than the uniform values of 2.291 Å in **1d**. Very similar differences are seen in the sets of Pd−P bond lengths within Pd$_2$Cl$_2$(μ-S)(dpm)$_2$.[8]

The Se-Pd-Cl units (179.0 and 177.8°) are more linear than those of the S−Pd−Cl units in Pd$_2$Cl$_2$(μ-S)(dpm)$_2$ (172 and 169.9°), while the P−Pd−P vectors are not perpendicular to the Se, Pd2, Cl2 plane and the structure is more distorted than that of the μ-S complex. Ring-puckering analysis[25] of the endocyclic torsion angles of **2d** and **1d**, the metal−metal bonded precursor (Table 5), shows that the 8-membered ring of **2d** is the less puckered [the ring-puckering amplitudes (Q) are 1.118(1) Å for **2d** and 1.540(1) Å for **1d**, with θ values of 73.9(2) and 90.7(1)°, respectively].

Of note, there are intramolecular interactions in **2d** between the μ-Se and (a) the *ortho*-hydrogen of an axial phenyl group (Se···H, 2.66 Å) and (b) the axial methyl group (Se···H, 2.82 Å). Such steric constraints are likely critical in governing possible formation of an A-frame adduct of an *anti*-precursor such as **1d**, and we have previously invoked[4,5] such effects to rationalize the nonreactivity of **1d** toward CO, SO$_2$ and H$_2$S (at 1 atm), in contrast, for example, to the ready formation of μ-CO, μ-SO$_2$, and μ-S species by Pd$_2$Cl$_2$(dpm)$_2$ (**1a**). Similarly, the formation of **2d** from **1d** takes about 3 days, while the corresponding reactions of elemental Se with **1a**−**c** are complete in 2−4 h.

Of note, CH$_2$Cl$_2$ solutions of **2d** at ambient conditions slowly isomerize to give the *syn*-isomer **2c**, while within the precursors under similar conditions **1c** slowly isomerizes to **1d**.[5] The findings overall establish that thermodynamically *anti*-Pd$_2$Cl$_2$(dpmMe)$_2$ is more stable than *syn*-Pd$_2$Cl$_2$(dpmMe)$_2$, while for the bridged, A-frame derivatives the reverse is true, the *syn*-isomer being more stable than the *anti*-isomer. The steric effects of the methyl groups determine these relationships, which have been used to design a high-yield synthesis of *syn*-Pd$_2$Cl$_2$(dpmMe)$_2$ via the *syn*-μ(CO) derivative.[5] These thermodynamic trends probably apply quite generally to a range of related systems (see below).

General Discussion on μ-Se and Other Related *syn*/*anti* Systems. The first reported μ-Se, A-frame complex, Rh$_2$(CO)$_2$(μ-Se)(dpm)$_2$, was made by substitution of the terminal chlorides of Rh$_2$Cl$_2$(CO)$_2$(dpm)$_2$ by the Se^{2-} anion.[10] Then, except for our work on the Pd$_2$(μ-Se) species, prepared using H$_2$Se or elemental Se reagents (and first noted in 1986[11]), the only other μ-Se work is that reported recently on the reaction of Ir$_2$(CO)$_3$(dpm)$_2$ with H$_2$Se, which yields a mixture of Ir$_2$(μ-Se) species.[19]

The more sluggish or nonreactivity of **1d** (*vs* **1a**−**c**) toward small molecules was noted above. The equilibrium constants at 20°C for CO bonding by **1a**−**d** in CH$_2$Cl$_2$ to form the Pd$_2$Cl$_2$(μ-CO)(P-P)$_2$ adducts decrease in the order: **1a** (2.4 × 10^5 M^{-1})[26] > **1b** (500 M^{-1})[4] > **1c** (100 M^{-1})[23] > **1d** (< 5 M^{-1}),[4] the trend presumably reflecting increasing steric hindrance at the bridging coordination site. Of interest, there is a correlation between these values and the ^{77}Se NMR shift of the μ-Se derivatives:[27] **2a** (δ −145.4), **2b** (δ −172.3), **2c** (δ −190.7), **2d** (δ −326.9). It has been established that δ_{Se} becomes more negative with increasing negative charge on the Se atom,[28] but it seems here that the shift data reflect as well geometrical changes upon substitution of a CH$_2$ proton by Me. The δ_{Se} value for **2d** is markedly negative compared to the other three values and likely reflects the closeness to the Se of the phenyl *o*-hydrogen atom and methyl group; this probably results in extension of the Pd-Se bond lengths, leading to a smaller Pd-Pd separation and a relatively small angle at the Se. This could generate a more ionic (negatively charged) selenium with a quite negative shift value.

To our knowledge, **2d** appears to be the first structurally characterized A-frame adduct in which substituents at the CH$_2$ of disphosphine bridges have *anti*-orientation. Indeed, apart from our earlier communication mentioning **2d** and the corresponding μ-SeO derivatives, **3d** (see below), we have been unable to find reports describing even solution characterization of such species. NMR data for the vinylidene-bridged complex Pd$_2$Cl$_2$(μ-C=CH$_2$)(dpmMe)$_2$ support a *syn*-arrangement of the Me groups, which are thought to occupy pseudoequatorial positions.[29] Similarly, NMR data for Rh$_2$(CO)$_2$(μ-Cl)(dpmMe)$_2^+$ imply a *syn*, A-frame species.[30] The structurally characterized Ir$_2$(CO)$_2$(μ-CO)[μ-Ph$_2$PCH(X)PPh$_2$]$_2$, where X = 2-pyridyl, is again a *syn*-isomer where the pyridyl nitrogens coordinate to the Ir centers on the same side of the complex;[31] the same geometry is possible for Rh$_2$(CO)$_2$(μ-S)[μ-Ph$_2$PCH(X)PPh$_2$]$_2$, although in solution the pyridyls are unbound.[31] One could perceive Ag$_3$[HC(PPh$_2$)$_3$]$_2^{3+}$ and a related gold complex[32] as A-frames containing an apical metal with a PPh$_2$ moiety from each bridging phosphine coordinated to form again a *syn*-arrangement of the phosphines i.e. an Ag$_2$(μ-Ag)[μ-Ph$_2$PCH(PPh$_2$)PPh$_2$] formulation.

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The occurrence of *syn* and *anti*-isomers within what might be called precursors to A-frame species is well documented. As well as the $Pd_2Cl_2(dpmMe)_2$ isomers **1c** and **1d** discussed here and elsewhere,[4-6] *syn* and *anti*-isomers of $Ag_2(dpmMe)_2^{2+}$ [30] and $Hg_2(dpmMe)_2^{4+}$ [33] have been detected by NMR studies but assignments to the respective isomers could not be made. The nature of $Au_2I_2(dpmMe)_2$ was not resolved.[34] The structurally characterized $Au_2Cl_2[\mu\text{-}Ph_2PCH(X)PPh_2]_2$, where X = CH_2OMe, is an *anti*-isomer,[35] and the same conformation has been ascribed to related gold complexes, for example, where X may be considered to be $Au(C_6F_5)$,[36] $Au(PPh_3)$[37] or $AuCH_2(PPh_3)$.[37]

The Bridged-SeO Complexes. We have reported previously on the bridged-sulfoxide (or dimetallic sulfoxide) species $Pd_2Cl_2(\mu\text{-SO})(dpm)_2$,[6] $Pd_2Cl_2(\mu\text{-SO})(dpm)(dmpMe)$,[6] and *syn*-$Pd_2Cl_2(\mu\text{-SO})$ $(dpmMe)_2$,[5] formed by O-atom donor oxidation (with H_2O_2 at room temperature or *m*-chloroperbenzoic acid at −20 °C) of the corresponding μ-S precursor; the first of these was structurally characterized and shown to contain pyramidally-bonded S,[6] while NMR data for the other two implied the corresponding geometry.

Corresponding oxidations of the μ-Se precursors **2a−d** to give the μ-SeO products (all containing pyramidal Se as shown by the NMR data) were most conveniently carried out using ^tBuOOH at ambient conditions. The incorporation of the O-atom, as in the μ-SO species, makes inequivalent all four of the CH_2 protons in $Pd_2Cl_2(\mu\text{-SeO})(dpm)_2$ (**3a**) and the sets of $CH(CH_3)$ protons in *anti*-$Pd_2Cl_2(\mu\text{-SeO})(dmpMe)_2$ (**3d**). For the latter, two stereoisomers are possible, depending on the orientation of the Se-bound O atom; the ^1H NMR data given (Table 1) are for the dominant isomer, and presumably refer to a species with the O atom bent toward the dpmMe with the pseudoequatorial Me (C3 in Figure 2); weak, unresolved absorptions are also seen at δ_H 6.66 and 4.19, and these might pertain to the methine protons of the other isomer. (The splitting pattern of the methine resonance of the main isomer reveals long-range coupling to the two remote P atoms). Acceptable $^{31}P\{^1H\}$ data were not obtained for **3a** or **3d** because of decomposition of the species noted during accumulation of the spectra; an observed isomerization of **3d** to the *syn*-isomer (**3c**, see below) also complicated measurements. Complex **3c**, *syn*-$Pd_2Cl_2(\mu\text{-SeO})(dpmMe)_2$, again has inequivalent CH (and Me) protons that each couple to adjacent P atoms; the relatively high J_{HP} values and the AA′BB′-type $^{31}P\{^1H\}$ spectrum reveal the inequivalence of the dpmMe ligands (the Me groups are presumably in pseudoequatorial positions).

The ^1H NMR spectrum of $Pd_2Cl_2(\mu\text{-SeO})(dpm)(dpmMe)$ (**3b**) displays two sets of resonances; data for the major component are given in the body of Table 1, while those of the minor component are given in footnote *h* (for the major isomer, the splitting pattern for the resonance of one of the inequivalent methylene protons reveals long range coupling to the remote P atoms). The two isomers (in a 7:1 ratio) almost certainly result from differences in the orientation of the oxygen atom attached to the Se and these are presumably formed from the single, assumed *anti*-isomer observed for **2b** (see above). A mixture of isomers (in a ratio of 7:3) was observed previously for the corresponding μ-SO adduct.[6b]

We remain unaware of any other dimetallic selenoxides, although transient formation of $Fe_2(CO)_6(\mu_3\text{-SeO})(\mu_3\text{-Se})Pt(PPh_3)_2$ has been demonstrated;[38] the **3a−d** species can be regarded as inorganic analogues of the organic selenoxides RSe(O)R,[39] which likewise have pyramidal geometry at the Se; IR bands found around 770 cm^{-1} for **3a−d** are assigned to ν(SeO), which compares to values of ~985 cm^{-1} for the corresponding μ-SO complexes.[6b]

The $Pd_2(\mu\text{-SeO})$ species **3a−d**, unlike the μ-SO analogues,[6] do not undergo further oxidation with O-atom donors to give $\mu\text{-SeO}_2$ derivatives. The μ-SO and μ-SeO moieties in the Pd_2 species both act as a three-center, two-electron donor; the chalcogen atom is pyramidal and has a remaining lone-pair of electrons.[6b] The μ-SeO must thus be less susceptible to electrophilic attack (by an O atom) than μ-SO. No $\mu\text{-SeO}_2$ species have been reported in the literature.

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Supporting Information Available: Tables of complete crystallographic data, atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles (8 pages). Ordering information is given on any current masthead page.

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