Table IV. Important Structural Features of $Re_2(\mu\text{-}X)_2Cl_4(LL)_2$ Compounds[a]

dist, Å or angle, deg	$Cl_2(dppe)_2$[6]	$Cl_2(dppm)_2$[3]	$Cl_2(dmpm)_2$[4]	$(SePh)_2(dppm)_2$[5]	$(SEt)_2(dto)_2$[b]
Re–Re	3.809 (1)	2.616 (1)	2.5807 (4)	2.656 (1)	2.5925 (9)
av Re–X	2.499 (3)	2.391 (2)	2.369 (1)	2.462 (1)	2.349 (15)
av Re–Cl	2.314 (7)	2.388 (5)	2.408 (2)	2.451 (9)	2.43 (2)
av Re–L	2.370 (1)	2.475 (5)	2.437 (1)	2.474 (8)	2.45 (6)
Re–X–Re	99.48 (13)	66.33 (5)	66.01 (5)	65.28 (4)	67.0 (3)
X–Re–X′	80.71 (14)	113.67 (5)	113.99 (7)	114.72 (4)	113.0 (1)

[a] Only the $(\mu\text{-}X)_2(LL)_2$ portions of the molecules are used to identify the compounds. [b] This work.

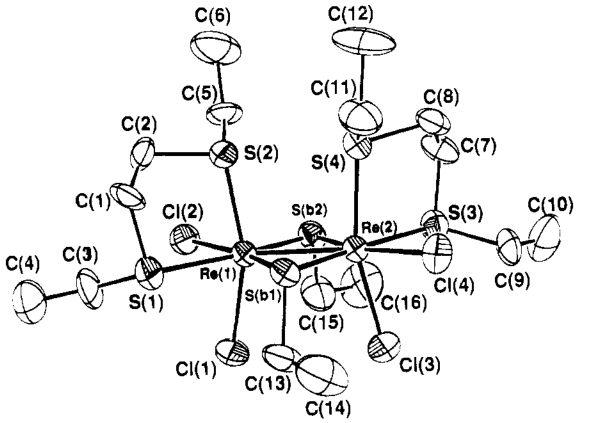

Figure 1. ORTEP view of the $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$ molecule. Thermal ellipsoids are at the 50% probability level.

two bridging ethyl thiolate ligands. Two of the chloride ligands are coordinated in axial positions, while the other two are bound in trans equatorial positions. Both dto ligands are coordinated in an axial/equatorial fashion and are positioned on the same side (the top in Figure 1) of the molecule. Similarly, the ethyl groups of the thiolate ligands are located on the same side of the molecule (pointing downward in Figure 1), i.e. in a syn conformation. There is a surprisingly large dissimilarity among the $Re–S_{terminal}$ distances; the axial sulfur atoms are an average of 0.13 Å closer to the rhenium atoms than the equatorial sulfur atoms.

The most significant feature of the structure is the short Re–Re bond length of 2.5925 (9) Å. A comparison of this value to those of other dirhenium(III) bioctahedral complexes is given in Table IV, along with several other structural parameters for these compounds. Despite the fact that there is no buttressing of the Re–Re unit in $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$, there is definitely an Re–Re bond, and it is shorter than those in most of the other structurally characterized $Re_2(\mu\text{-}X)_2Cl_4(LL)_2$ molecules.

Discussion

Synthesis. As mentioned in the Introduction, we originally intended to synthesize $Re_2(\mu\text{-}SR)_2Cl_4(LL)_2$ complexes with chelating LL ligands by oxidative addition of organic disulfides across the triple bond in $Re_2Cl_4(LL)_2$ compounds.[5] Dithioethers (SS) were chosen as the bidentate LL ligands because of their demonstrated ability to chelate, but not bridge in dimolybdenum and dirhenium compounds.[10,11] However, our efforts to prepare $Re_2Cl_4(SS)_2$ complexes from $[Re_2Cl_8]^{2-}$ have not been successful when SS is 2,5-dithiahexane or 3,6-dithiaoctane.[12]

We have also attempted to prepare $Re_2(\mu\text{-}SR)_2Cl_4(PP)_2$ complexes, in which PP is a chelating diphosphine, but so far no reaction has occurred between $Re_2Cl_4(PP)_2$ species and RSSR, where R is Me, Et, or Ph. Thus only by reacting quadruply bonded $[Re_2Cl_8]^{2-}$ with a mixture of a dithioether and a disulfide were we successful in synthesizing a compound of the desired type.

Structure. Clearly, the metal–metal distance in $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$ is consistent with an Re–Re bond order of 2. Thus this compound contains the first example of an unbuttressed Re–Re double bond in dirhenium(III) complexes of this type. The electronic configuration for this electron-rich bond is probably $\sigma^2\pi^2\delta^{*2}\delta^2$, although it is difficult to determine the correct order for the δ and δ^* orbitals.[5]

To our knowledge, the ligand arrangement in $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$ is unique among edge-sharing bioctahedra. Perhaps among unbuttressed compounds this new geometry is more favorable for metal–metal bond formation than that (see II above) adopted by $Re_2Cl_6(dppe)_2$.[3] It is noteworthy, however, that the analogous dimolybdenum compound $Mo_2(\mu\text{-}SEt)_2Cl_4(dto)_2$ contains an Mo–Mo bond with length 2.682 (1) Å, even though it has a structure of the $Re_2Cl_6(dppe)_2$ type so that all chloride ligands occupy axial positions and the dto ligands occupy equatorial positions.[2]

The nature of the bridging ligands is probably a more important factor influencing the metal–metal distance in such complexes. Excluding the diphosphine ligands, there are three different types of bridging ligands among the compounds listed in Table IV. Of these, the SePh ligand undoubtedly contains the largest bridging atom. Comparison of $Re_2Cl_6(dppm)_2$ with $Re_2(\mu\text{-}SePh)_2Cl_4(dppm)_2$ reveals that the Re–Re distance lengthens by 0.04 Å upon going from bridging Cl to bridging SePh. The smaller values of Re–X and X–Re–X′ for $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$ indicate that the bridging sulfur atoms take up a little less space than bridging chlorine atoms. On the basis of this factor alone, it is not particularly surprising that the title complex should have a short Re–Re distance. We are not, however, convinced that bridging ligands smaller than chloride are necessary for metal–metal bond formation in unbuttressed complexes of this type.

We intend to synthesize and characterize several more examples of both buttressed and unbuttressed $Re_2(\mu\text{-}X)_2Y_4(LL)_2$ complexes in order to better understand all factors responsible for metal–metal bond formation. Obviously, it is desirable to compare complexes with a minimum of differences. It is conceivable that a change in terminal LL ligands alone, such as from dppe to dto, might determine whether or not an Re–Re bond is formed.

Acknowledgment. We are grateful to The Robert A. Welch Foundation for financial support.

Supplementary Material Available: Details of the structure analysis, and tables of crystal data, bond distances, bond angles, and anisotropic thermal parameters (6 pages); a table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Intramolecular Bridging Ligand Exchange in [2,2-Bis((phenylthio)methyl)-1-(diphenylphosphino)propane]palladium(II) Chloride

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Received February 27, 1990

Due to the geometrical rigidity of tripodal ligands, complexation studies concerning the triphos **1a** and the related sulfur analogue

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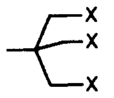
1b have received considerable attention recently.[1-3] However, few of the tripodal ligands with mixed phosphorus and sulfur donor atoms are known.[3] Such a tripodal ligand containing different donors enables the study of selective coordination toward transition metals. Here, we would like to report on the synthesis of the title complex and its fluxional coordination behavior.



1a, X = PPh_2
b, X = SPh

Experimental Section

General Information. Nuclear magnetic resonance spectra were recorded on either a Bruker AC-E 200 or a Bruker AM-300WB spectrometer. Phosphorus-31 NMR spectra were determined on a Bruker AC-E 200 spectrometer at 81.01 MHz.

All of the reactions, manipulations, and purification steps involving phosphines were performed under dry nitrogen atmosphere. Chemicals and solvents from commercial sources were used without further purification.

(2,2,5-Trimethyl-1,3-dioxan-5-yl)methyl Benzoate (5). To a stirred solution of **4** (25.28 g, 0.158 mol) in chloroform (80 mL) and pyridine (12 mL) was slowly added benzoyl chloride (21.2 g, 0.151 mol) at room temperature. The resulting mixture was boiled under reflux for 42 h, and then saturated sodium bicarbonate solution (50 mL) was added. The organic layer was washed with saturated NaCl solution and water and dried. This solution was concentrated, and the residue was passed through silica gel (20 g) with dichloromethane elution. The eluent was concentrated and distilled to give **5** as a clear, colorless liquid (33.98 g, 86%): bp 108–110 °C (0.1–0.2 mmHg); mp 57–58 °C; IR (neat) 1716 cm^{-1}; ^{1}H NMR δ 8.15–7.94 (m, 2 H), 7.65–7.35 (m, 3 H), 4.38 (s, 2 H), 3.76 (d, J = 12 Hz, 2 H), 3.67 (d, J = 12 Hz, 2 H), 1.43 (s, 3 H), 1.40 (s, 3 H), 0.94 (s, 3 H). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.90; H, 7.59.

2,2-Bis(hydroxymethyl)propan-1-yl Benzoate (6). A mixture of benzoate compound **5** (32.29 g, 0.122 mol), THF (50 mL), water (4 mL), and several drops of concentrated hydrochloric acid was heated to reflux for 0.5 h. Solvents were removed and the residue was distilled under vacuum to give diol **6** as a clear, colorless liquid (27.12 g, 99%): bp 148–150 °C (100–200 μmHg); mp 78–80 °C; IR (neat) 3484 (br), 1716 cm^{-1}; ^{1}H NMR δ 8.13–7.90 (m, 2 H), 7.65–7.25 (m, 3 H), 4.37 (s, 2 H), 3.63 (s, 4 H), 3.25–2.80 (br, 2 H), 0.94 (s, 3 H). Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.07; H, 7.53.

2,2-Bis(((methylsulfonyl)oxy)methyl)propan-1-yl Benzoate (7). To a stirred solution of diol **6** (16.88 g, 75.3 mmol) and triethylamine (25.2 mL) in dichloromethane (150 mL) was added methylsulfonyl chloride (12.8 mL, 18.94 g, 165.3 mmol) at 0 °C. The resulting mixture was allowed to stir at ice-bath temperature for 30 min. Water (50 mL) was added, and the organic layer was separated. The organic portion was washed with 10% aqueous HCl (50 mL), saturated $NaHCO_3$ solution, and saturated NaCl solution and dried. The solution was concentrated and recrystallized from dichloromethane and hexane to give **7** as a white crystalline solid: mp 112–113 °C; IR (CH_2Cl_2) 1720 (s), 1361, 1177 cm^{-1}; ^{1}H NMR δ 8.10–7.85 (m, 2 H), 7.62–7.25 (m, 3 H), 4.30 (s, 2 H), 4.22 (s, 4 H), 3.03 (s, 6 H), 1.16 (s, 3 H). Anal. Calcd for $C_{14}H_{20}O_8S_2$: C, 44.20; H, 5.30. Found: C, 44.40; H, 5.20.

2,2-Bis((phenylthio)methyl)propan-1-ol (9). To a mixture of THF (100 mL) and absolute ethanol (20 mL) was added freshly cut sodium metal (1.20 g, 52.2 mmol). After all of the sodium reacted, thiophenol (5.6 mL, 6.01 g, 54.5 mmol) was added and stirred for 30 min. Compound **7** (9.0 g, 23.66 mmol) was added, and the solution was refluxed for 30 h. The reaction mixture was quenched with aqueous KOH and extracted with ether (2 × 50 mL). The organic extracts were combined and concentrated. The residue was redissolved in THF/water/NaOH and heated to reflux for 10 h. The resulting mixture was extracted with ether (2 × 50 mL), and the extracts were dried and concentrated. The residue was chromatographed on silica gel (60 g) with elution of hexane, hexane/ethyl acetate (95:5 (v/v)), and hexane/ethyl acetate (70:30). The eluent of 30% ethyl acetate in hexane was collected and concentrated to give sulfide **9** as a viscous liquid (5.81 g, 81%): IR (CH_2Cl_2) 3475 cm^{-1}; ^{1}H NMR δ 7.44–7.07 (m, 10 H), 3.51 (s, 2 H), 3.05 (s, 4 H), 1.70 (s, 1 H), 1.03 (s, 3 H). Anal. Calcd for $C_{17}H_{20}OS_2$: C, 67.07; H, 6.62. Found: C, 66.89; H, 6.81.

2,2-Bis((phenylthio)methyl)propan-1-yl Methanesulfonate (10). To a solution of **9** (4.0 g, 13.1 mmol) and triethylamine (2.4 mL) in dichloromethane (60 mL) was added methylsulfonyl chloride (1.1 mL, 1.63 g, 14.2 mmol) slowly at 0 °C. The resulting mixture was allowed to warm to 25 °C and stirred for 2 h. The reaction mixture was washed with water (50 mL), 10% hydrochloric acid (50 mL), saturated sodium bicarbonate solution (50 mL), and saturated NaCl solution and dried. Removal of solvent and chromatography on silica gel (30 g) gave the desired product **10** as a viscous, colorless liquid (4.86 g, 97%): ^{1}H NMR δ 7.50–7.08 (m, 10 H), 4.13 (s, 2 H), 3.07 (s, 4 H), 2.75 (s, 3 H), 1.09 (s, 3 H). Anal. Calcd for $C_{18}H_{22}O_3S_3$: C, 56.52; H, 5.80. Found: C, 56.46; H, 5.96.

2,2-Bis((phenylthio)methyl)-1-(diphenylphosphino)propane (2). Into a round-bottomed flask was placed triphenylphosphine (2.61 g, 9.95 mmol) in THF (40 mL) under nitrogen atmosphere. Fresh-cut lithium (0.3 g, 42.8 mmol) was washed with hexane and allowed to fall directly into the above solution. The lithium suspension mixture was stirred and became deep red color in a few minutes. This solution was stirred overnight and then filtered to remove the excess lithium. The filtration was conducted by passing the phosphide anion solution through glass wool into a second degassed flask. The red solution was cooled to 0 °C and *tert*-butyl chloride (1.12 mL, 0.95 g, 10.2 mmol) was added dropwise to destroy phenyllithium. Compound **10** (2.50 g, 6.55 mmol) in THF (3 mL) was added to the phosphide solution slowly. The resulting solution was refluxed for 20 h, and degassed water (30 mL) was added. The organic layer was separated, dried and concentrated. The residue was chromatographed on silica gel (30 g) with elution of hexane, 5% ethyl acetate in hexane, and 10% ethyl acetate in hexane. The fraction of 10% eluent was collected and concentrated to give compound **2** as a clear, viscous liquid (1.84 g, 60%): ^{1}H NMR ($CDCl_3$) δ 7.53–7.00 (m, 20 H), 3.10 (s, 4 H), 2.36 (d, $J_{\text{P-C-H}}$ = 4 Hz, 2 H), 1.03 (s, 3 H); ^{31}P NMR δ −25.62. Anal. Calcd for $C_{29}H_{29}PS_2$: C, 73.69; H, 6.18. Found: C, 73.98; H, 6.39.

[2,2-Bis((phenylthio)methyl)-1-(diphenylphosphino)propane]palladium(II) Chloride (11). A solution of **2** (40.0 mg, 0.085 mmol) and $(PhCN)_2PdCl_2$ (32.6 mg, 0.085 mmol) in dichloromethane (5 mL) was stirred at room temperature for 30 min. After removal of solvent, the residue was recrystallized in dichloromethane and hexane to give the desired complex **11** as a yellow crystalline solid (50.0 mg, 84%): mp 182 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.10–7.80 (m, 5 H), 7.60–7.10 (m, 15 H), 2.95 (br, 4 H), 2.44 (d, $J_{\text{P-C-H}}$ = 12.3 Hz, 2 H), 0.85 (s, 3 H); ^{31}P NMR δ 17.74. Anal. Calcd for $C_{29}H_{29}PS_2PdCl_2$: C, 53.59; H, 4.50. Found: C, 53.55; H, 4.73.

[1,1,1-Tris((phenylthio)methyl)ethane]palladium(II) Chloride (13). This complex was prepared by a method similar to that used for **11**: orange crystalline solid; mp 202 °C dec; ^{1}H NMR δ 7.94–7.10 (m, 15 H), 3.13 (br m, 6 H), 1.16 (s, 3 H). Anal. Calcd for $C_{23}H_{24}S_3PdCl_2$: C, 48.13; H, 4.21. Found: C, 48.50; H, 3.89.

Results and Discussion

Starting with 1,1,1-tris(hydroxymethyl)ethane, the synthesis of a new tripodal ligand containing one phosphorus and two sulfur donors, **2**, is given in Scheme I. Triol **3** may easily transformed into the alcohol **4**.[4] In order to avoid the formation of phosphonium salt I, the incorporation of the phosphorus group was designed as the last step of the synthesis and the hydroxy function was protected as an ester. Treatment of **4** with benzoyl chloride in presence of pyridine in dichloromethane provided ester **5** in high yield. Compound **5** was then hydrolyzed by using 2 mol equiv of water in tetrahydrofuran with a catalytic amount of hydrochloric acid at reflux to give diol **6** quantitatively. Methanesulfonylation of **6** afforded **7**, which was converted by sodium thiophenolate in refluxing ethanol into sulfide **8** together with the minor hydrolyzed product **9**. Although compound **8** could be isolated in pure form by silica gel chromatography, the mixture of **8** and **9** was subjected to hydrolysis under basic condition to

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(1) For a recent review in tripodal phosphorus and sulfur ligands, see: (a) Sacconi, L.; Mani, F. In *Transition Metal Chemistry*; Melson, G. A., Figgis, B. N. Eds.; Marcel Decker: New York, 1982; Vol. 8, p 179. (b) Meek, D. W. In *Homogeneous Catalysis by Metal Phosphine Complexes*, Pignolet, L. H., Ed.; Plenum: New York, 1983; p 257. (c) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365.

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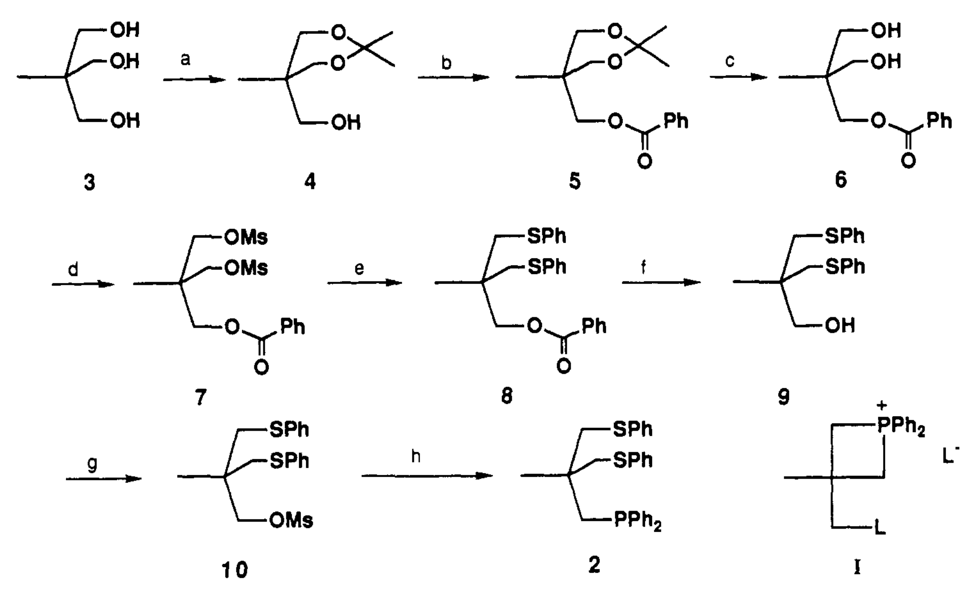
Scheme I. Preparation of Tripodal Ligand **2** (PS_2)



a. Acetone, TsOH b. PhCOCl, pyridine c. H_2O/THF, HCl d. MsCl, Et_3N
e. PhSNa, EtOH f. NaOH, H_2O g. MsCl, Et_3N h. Ph_2PLi, THF

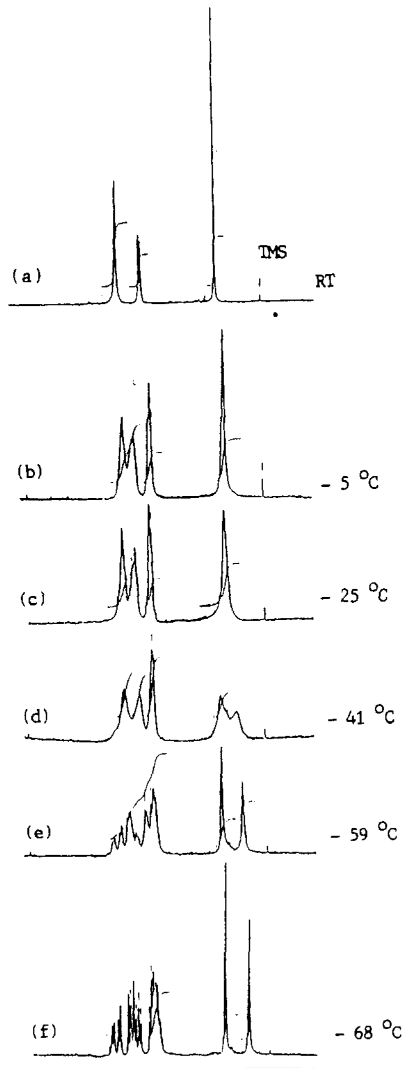
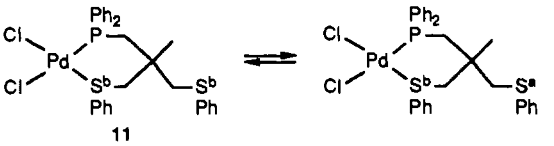


Figure 1. Variable-temperature ^1H NMR spectra of the aliphatic absorptions of **11** in CD_2Cl_2 solution.

give **9** as an exclusive product. Conversion of **9** into mesylate **10**, followed by the treatment of diphenylphosphide anion, produced the target ligand **2**, after anaerobic chromatography of the crude product on degassed silica gel using hexane/ethyl acetate as eluent. If we start from the ketal alcohol **4**, the total yield of the synthesis of **2** is 36%.

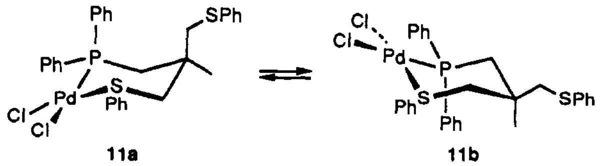
Molar equivalents of palladium(II) chloride and **2** were reacted in dichloromethane solvent with stirring under nitrogen atmosphere. Upon crystallization, the desired complex $(PS_2)PdCl_2$ (**11**) was obtained as a yellow crystalline solid (90% yield). Figure 1 shows variable-temperature ^1H NMR spectra of the aliphatic absorptions of **11** in CD_2Cl_2. At room temperature (Figure 1a), an absorption at δ 2.95 with integration of four protons appeared, which indicated that the two methylene units attached to the sulfur donors were equivalent. At lower temperatures, this peak separated into two broad signals (Figure 1b,c) suggesting that an intramolecular sulfur donor exchange was occurring around the metal center (eq 1).



(1)

11

As the temperature became much lower, a conformational interconversion process of the six-membered ring of **11** (eq 2) was



(2)

11a **11b**

observed as evidenced by the methyl signal splitting into two sets of broad peaks (Figure 1d,e). The axial and equatorial methyl absorptions were sharp and distinct at −68 °C (Figure 1f). The chemical shift at δ 0.47 was assigned as the methyl group at the equatorial position in the six-membered chair chelating ring, **11a**, whereas the δ 0.98 shift was assigned to the methyl group at the axial position, **11b**.[5] The intensity ratio of these two peaks is 45:55, which implies that the (phenylthio)methyl group slightly prefers the equatorial position. The interconversion barrier of the con-

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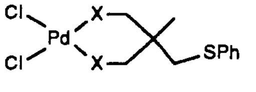
(5) The chemical shifts of equatorial methyl groups are ca. 0.5 ppm upfield than those of axial ones in 1,3-dioxane systems. Eliel, E. L.; Enanoza, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 355.

formational change was estimated to be ca. 13.3 kcal/mol.[6]

It would be of interest to compare this fluxional behavior with that of $(P_2S)PdCl_2$ (**12**)[7] and $(S_3)PdCl_2$ (**13**). There is no indication of **12** undergoing such displacement, but all three sulfur donors of **13** have similar exchange behavior. The fluxional behavior in **13** was confirmed similarly by variable-temperature ^1H NMR studies. The chemical shifts of all three methylene units attached to sulfur donors of **13** appeared as follows: (i) at 50°C, a broad peak, (ii) at room temperature, two broad overlapped peaks, and (iii) at lower temperature, a complicated splitting pattern.



12, X = PPh_2
13, X = SPh

Acknowledgment. We are grateful for financial support from the National Science Council (ROC), Grant NSC78-0208-M002-15.

Registry No. **2**, 129521-04-6; **4**, 3663-46-5; **5**, 129521-00-2; **6**, 69773-90-6; **7**, 129521-01-3; **9**, 129521-02-4; **10**, 129521-03-5; **11**, 129521-06-8; **13**, 129521-05-7; $(PhCN)_2PdCl_2$, 14220-64-5; PhCOCl, 98-88-4.

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(6) (a) The barrier was estimated from NMR technique, see: Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders Company, Philadelphia, PA, 1977; p 252. (b) Cf. Abel, E. W.; Orrell, K. G.; Bhargava, S. K. The Stereodynamics of Metal Complexes of S, Se and Te Containing Ligands. *Prog. Inorg. Chem.* **1987**, *32*, 1.

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Chemical Deposition of an Organozirconium Complex onto an Oxided Aluminum Surface: Using the "Quartz Crystal Microbalance" To Probe Microscopic Surface Acidity

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Received June 1, 1990

Surface modification of metal oxides by organometallic complex attachment (often to reactive hydroxyl groups) is well-known, but comparable treatment of metals, themselves, is less well established. An overlayer of a chemically reactive oxide on a metal can provide a "covalent" interface between the bulk metal and a target surface modification reactant. In this context, reproducible production of bound organometallic complexes on such modified metallic surfaces requires reproducible preparation of the reactive overlayer. A readily measured property of an oxided support is its total Brønsted acidity, related to the concentration of surface hydroxyl groups, usually determined by titration.[1] Differently prepared surfaces could have greatly different total acidities. Protolytic organometallic complex deposition procedures[2] on hydroxylated surfaces could depend, however, not on total acidity of the support but on *microscopic* (or local –OH group) considerations.

Table I. Kinetics Data for QCM-Monitored Depositions

deposition medium	hydroxylation method	rate const, 10^3 s^{-1}	areal loading,[a] ng/cm^2	areal concn,[a] nM/cm^2
pentane	steam	4.5	4700	20
gas phase	steam	3.7	4800	21
gas phase	D_2O steam	0.44	5000	21
gas phase	water	4.3	2200	10
gas phase	"atmosphere"	4.2	1300	6

[a] For the surface ligated fragment $Zr(C_5H_{11})_2$.

In principle, studying the stoichiometry of organometallic complex deposition onto an oxided metal surface could involve techniques similar to those for oxide surface modification, but, except for metal powders, low surface areas of metallic substrates and attendant low content, per unit weight, of reactive hydroxyl groups make titrimetric quantification of surface reactive sites difficult. Similarly, deposition kinetics can be difficult to ascertain: depositions could involve very small amounts of the organometallic reagent, the organic products could partition between the gas and solution phases, and spectroscopic probes are difficult to employ in situ.

Piezoelectric quartz can be made to oscillate at a resonant frequency that is determined by the cut and mass of a given crystal, and the "quartz crystal microbalance" (QCM) technique allows accurate determination of mass changes on an electrode deposited on such a crystal. Just as for a classical oscillator, a change in electrode mass results in a change in resonant frequency that can be easily and accurately measured. The QCM is, thus, ideal for monitoring surface reactions of target metals when they are used as electrodes. Furthermore, since time-dependent QCM measurements are readily obtained, reaction kinetics,[3] as well as stoichiometries, can be probed. In an effort to determine whether total surface or local (hydroxyl group specific) acidity determines reactivity of an oxided overlayer toward an organometallic reagent, we adapted a QCM to directly measure deposition rates of tetraneopentylzirconium onto variously oxidized and hydroxylated aluminum electrode surfaces of that device.

Results

The surface of aluminum metal, deposited on a standard gold on chromium electrode on a quartz crystal, was hydrolyzed according to three regimes of increasing vigor. In the first, the surface of the aluminum was simply exposed to ambient conditions of the laboratory; in the second, it was treated with water, and in the third, with steam. In a parallel experiment, bulk aluminum metal powder was treated according to two of these same procedures, and the content of surface hydroxyl groups obtained by each route was determined by methyllithium titration and quantitative measurement of evolved methane. Bulk aluminum powder titrated after atmospheric exposure showed an hydroxyl loading of 0.007 $mmol \cdot g^{-1}$, and steam-treated Al had a loading of 0.024 $mmol \cdot g^{-1}$. Quantitative analysis of the reaction of hydroxylated, powdered Al with $Zr(C_5H_{11})_4$ showed evolution of 2.0 equiv of neopentane per Zr. The QCM was used to determine the course of the reaction between the surface of an aluminum electrode and $Zr(C_5H_{11})_4$. In typical procedures, the zirconium reagent was transported to the Al electrode in one of two ways. One was deposition from the gas phase with constant flux of the $Zr(C_5H_{11})_4$; the other was deposition from solution. In all experiments, the resonance frequency of the crystal was measured vs time and related to the mass change at the surface.[4] De-

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(1) Methyllithium titration has been used to determine total hydroxyl concentration for metal oxides: Ward, M. D. Ph.D. Dissertation, Princeton University, 1981. Titrations also often employ substituted pyridines and may be able to differentiate between Brønsted and Lewis acid sites. See for example: Murrekk, L. L.; Dispenziere, N. C. *J. Catal.* **1989**, *117*, 275.

(2) Candlin, J. P.; Thomas, H. *Adv. Chem. Ser.* **1974**, *132*, 212. Ballard, D. G. H. *Adv. Catal.* **1974**, *23*, 263. Zakharov, V. A.; Dudchenko, V. K.; Paukshtis, E. A.; Karakchiev, L. G.; Yermakov, Yu. I. *J. Mol. Catal.* **1977**, *2*, 421. Zakharov, V. A.; Yermakov, Yu. I. *Catal. Rev.—Sci. Eng.* **1979**, *19*, 67. Schwartz, J.; Ward, M. D. *J. Mol. Catal.* **1980**, *8*, 465.

(3) Schumacher, R.; Pesek, J. J.; Melroy, O. R. *J. Phys. Chem.* **1985**, *89*, 4338. See also: Ward, M. D. *J. Phys. Chem.* **1988**, *92*, 2049.

(4) To interconvert frequency and mass, the following relationship is employed:

$$\Delta m = \frac{\Delta f}{(-2.26 \times 10^{-6}) f_0^2}$$

See: Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206. A review of QCM applications is available: Lu, C.; Czanderna, A. W., Eds.; *Applications of Piezoelectric Quartz Crystal Microbalances*; Elsevier: New York, 1984.

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