solvation of Co(TPPS)(py)$^{3-}$. It is interesting to note that the activation parameters associated with k_2^{py} are similar to those of the k_4^{py} path. Clearly $OH^- > py > H_2O$ in labilizing the trans ligand in $Co(TPPS)(H_2O)_2^{3-}$ when py is the entering ligand and H_2O is the leaving group. This same ordering is found in $Co(TMpyP)(H_2O)_2^{5+}$ and $Co(TCCP)(H_2O)_2^{3-}$ (Table V). However the relative differences are not as great as for $Co(TPPS)(H_2O)_2^{3-}$. The combined labilizing effects of the porphyrin and the trans ligand must wait additional information in order to be understood.

Acknowledgment. This research was supported by the Robert A. Welch Foundation, Houston, Texas. J.G.L. wishes to express his gratitude to the Robert A. Welch Foundation and the South African CSIR for financial support as well as the University of the Orange Free State, Bloemfontain, South Africa, for granting the leave.

Registry No. $CoTPPS(H_2O)_2^{3-}$, 58881-09-7; py, 110-86-1; $CoTPPS(py)H_2O^{3-}$, 77342-06-4; $CoTPPS(py)_2^{3-}$, 77342-07-5; $CoTPPS(OH)H_2O^{4-}$, 59366-37-9; $CoTPPS(OH)py^{4-}$, 77342-08-6; $CoTPPS(OH)_2^{5-}$, 77342-09-7; $Na_3Co(TPPS)(H_2O)_2$, 77342-10-0.

Notes

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Hydrolysis of Chlorodiphenylphosphine Complexes of Molybdenum and Palladium

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Coordination of the chlorodiphenylphosphine ligand to transition metals appears to stabilize the P–Cl bond toward hydrolysis, a normally facile process for the free ligand.[1] Under basic conditions, however, Kraihanzel has reported the successful hydrolysis of the cis isomer of bis(chlorodiphenylphosphine)molybdenum tetracarbonyl, $(CO)_4Mo(PPh_2Cl)_2$, to give an anionic product containing a P–O–H–O–P chelate ring (Figure 1).[2]

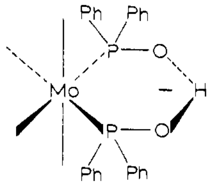


Figure 1.

Austin studied the hydrolysis of *cis*-$Cl_2Pd(PPh_2Cl)_2$ and reported the product to be *cis*-$Cl_2Pd(PPh_2OH)_2$ in which diphenylphosphinous acid, the thermodynamically unstable tautomer of diphenylphosphine oxide, was coordinated to the metal.[3,4]

We were interested in the hydrolytic reactivity of the trans isomer of $(CO)_4Mo(PPh_2Cl)_2$ and the resulting products. We also reinvestigated the hydrolysis of *cis*-$Cl_2Pd(PPh_2Cl)_2$ to confirm the identity of the reported compound. We detail here our findings that demonstrate the recurring formation of the same P–O–H–O–P chelate unit in both hydrolysis reactions.

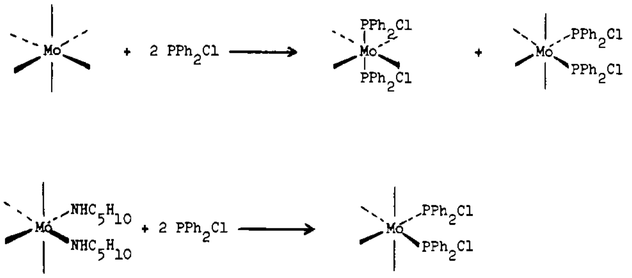
No straightforward synthesis of the trans isomer of $(CO)_4Mo(PPh_2Cl)_2$ has been available to our knowledge. Kraihanzel has isolated this complex as a minor product in the preparation of $(CO)_5MoPPh_2Cl$.[5] Direct substitution on $Mo(CO)_6$ with a slight excess of phosphine resulted in both cis and trans isomers of $(CO)_4Mo(PPh_2Cl)_2$. Careful recrystallization yielded the less soluble trans isomer in pure form as indicated by IR and ^{31}P NMR data (Table I). The cis isomer can be conveniently prepared from *cis*-$(CO)_4Mo$(piperidine)$_2$, a useful precursor to *cis*-$(CO)_4Mo$(phosphine)$_2$ complexes first prepared by Darensbourg (Scheme I).[6]

Table I. ^{31}P NMR Data for the Complexes

complex	chem shift,[a] ppm	solvent
cis-$(CO)_4Mo(PPh_2Cl)_2$	259.7	$CDCl_3$
trans-$(CO)_4Mo(PPh_2Cl)_2$	271.1	$CDCl_3$
cis-$(CO)_4Mo(Ph_2P\text{-}O\text{-}H\text{-}O\text{-}PPh_2)^-$	105.2	$Me_2SO\text{-}d_6$
$[(Ph_2P\text{-}O\text{-}H\text{-}O\text{-}PPh_2)PdCl]_2$	78.1	$CDCl_3$

[a] Referenced to external 85% H_3PO_4; proton decoupled.

Scheme I



Both *cis*- and *trans*-$(CO)_4Mo(PPh_2Cl)_2$ were found to be stable in neutral or acidic aqueous methanol solutions. We have confirmed Kraihanzel's report that under basic conditions the cis isomer hydrolyzed to give the anionic *cis*-$(CO)_4Mo(Ph_2P\text{-}O\text{-}H\text{-}O\text{-}PPh_2)^-$.[2]

Under identical conditions, the trans isomer gave the same product as supported by IR and ^1H and ^{31}P NMR as well as elemental analyses (eq 1 and 2).

A trans → cis rearrangement has therefore occurred during this reaction. Darensbourg has observed that for normal phosphine ligands, a slight thermodynamic preference for the trans isomer of $(CO)_4Mo$(phosphine)$_2$ exists.[7] This preference is readily overcome here due to the very favorable intramolecular proton bridging available only in the cis product. Many other examples of this P–O–H–O–P chelating unit have been reported. These include complexes of palladium,[8] platinum,[9] and ruthenium[10] in addition to molybdenum.

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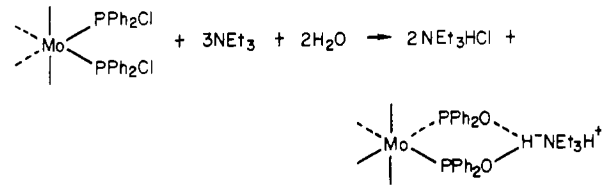
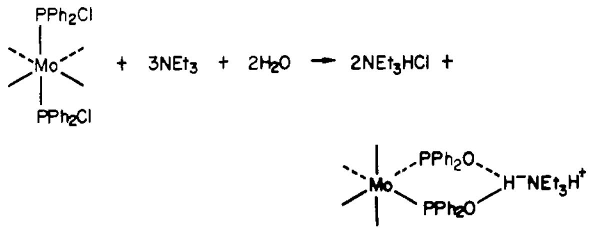


(1)



(2)

We found the palladium complex *cis*-$Cl_2Pd(PPh_2Cl)_2$ to be stable for short durations as a suspension in aqueous acetone. Prolonged exposure gave a greyish yellow suspension from which a light yellow crystalline product can be isolated. The identity of this compound was established by its IR, ^1H and ^{31}P NMR, and elemental analyses, as well as molecular weight determination. It was found to be the dimeric complex $[(Ph_2P\text{-}O\text{-}H\text{-}O\text{-}PPh_2)PdCl]_2$ (Figure 2).

This same compound was first reported by Carty as the hydrolysis product of *cis*-$Cl_2Pd(Ph_2PC{\equiv}CCF_3)_2$.[8] We also found that direct reaction of concentrated HCl with *cis*-$Cl_2Pd(PPh_2Cl)_2$ yielded the same product. We were not able to isolate the *cis*-$Cl_2Pd(PPh_2OH)_2$ complex described by Austin.[3] Furthermore, we would anticipate this complex, if formed, to readily dimerize and eliminate HCl and generate the isolated dimeric product.

Treatment of *cis*-$Cl_2Pd(PPh_2Cl)_2$ with aqueous THF or acetone in the presence of excess triethylamine resulted in the formation of an orange-yellow solid that analyzed as $[Pd(PPh_2O)_2]_n$. This solid has poor solubility in both polar and nonpolar solvents and is characterized by strong IR absorptions in the 995–1030-cm^{-1} region which can be attributed to metal bridging P–O ligands.[11] The stoichiometry of this reaction was found to be

$$nCl_2Pd(PPh_2Cl)_2 + 4nNEt_3 + 2nH_2O \rightarrow 4nNEt_3HCl + [Pd(PPh_2O)_2]_n \quad (3)$$

It is likely that this solid contain polymeric units of the type(s) in Figure 3.

Treatment of this solid with concentrated HCl in acetone resulted in rapid dissolution and the formation of a yellow solution. The dimeric $[(Ph_2P\text{-}O\text{-}H\text{-}O\text{-}PPh_2)PdCl]_2$ complex was again the isolated product (Scheme II).

Thus it appears that the $R_2P\text{-}O\text{-}H\text{-}O\text{-}PR_2$ chelate ring may be the preferred hydrolysis product for bis PR_2Cl complexes of this type. Both trans and cis molybdenum complexes here yielded the identical cis product. It is well established that cis palladium complexes of the type $X_2Pd(phosphine)_2$ exist as cis/trans mixtures in solution.[12] Here too only the cis product containing the P–O–H–O–P chelating unit has resulted.

Experimental Section

All reactions were carried out under oxygen-free conditions in Schlenk glassware. Solvents were routinely distilled and degassed before use. Chlorodiphenylphosphine was vacuum-distilled and kept under dry nitrogen. Molybdenum hexacarbonyl was vacuum-sublimed.

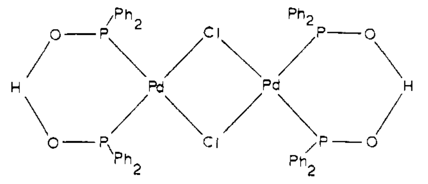


Figure 2.

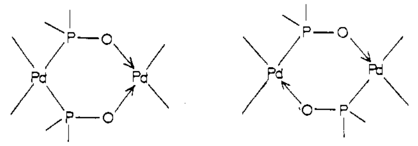
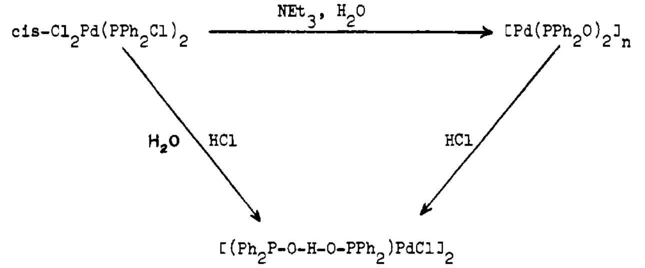


Figure 3.

Scheme II



Elemental analyses and osmometric molecular weight determination were performed by Schwarzkopf Analytical Laboratories, Woodside, NY. Infrared spectra were recorded as Nujol mulls or in $CHCl_3$ on a Perkin-Elmer 337 spectrometer. ^1H and ^{31}P NMR spectra were obtained with a JEOL-FX90Q-FT spectrometer using deuterium lock.

Synthesis of *trans*-$(CO)_4Mo(PPh_2Cl)_2$. An amount of 4.1 g (15.6 mmol) of $Mo(CO)_6$ was refluxed with 5.86 mL (35.9 mmol) of PPh_2Cl in 20 mL of toluene. After 1 h, the dark brown solution was filtered through Celite. The filtrate was concentrated under vacuum to about 5 mL and 20 mL of hexane added. After the solution was chilled in an ice bath, the brown, flocculent precipitate was filtered off and dried under vacuum. This was redissolved in 4 mL of CH_2Cl_2 and followed by a large volume of methanol. The resulting solid was isolated and dried. Anal. Calcd: C, 51.8; H, 3.10. Found: C, 51.95; H, 3.04.

Synthesis of *cis*-$(CO)_4Mo(PPh_2Cl)_2$. The *cis*-$(CO)_4Mo(piperidine)_2$ complex was prepared as reported by Darensbourg.[6] We found the reaction yielding the desired piperidine complex to proceed more satisfactorily under gentle reflux. Although the yield was only 30–40%, the resulting product was purer in quality. An amount of 0.80 g (2.1 mmol) of *cis*-$(CO)_4Mo(piperidine)_2$ and 0.8 mL of PPh_2Cl were stirred under reflux in CH_2Cl_2. After 0.5 h, the reaction mixture was concentrated in volume and redissolved in 4 mL of toluene. This was filtered through Celite and the Celite washed with additional toluene. The filtrate was concentrated and 8 mL of hexane added. After filtration and vacuum concentration until cloudy, 4 mL of CH_2Cl_2 was added followed by 20 mL of methanol. Chilling in ice yielded the cis product as yellow crystals. Anal. Calcd: C, 51.80; H, 3.10. Found: C, 51.94; H, 3.14.

Hydrolysis of the *cis*- and *trans*-$(CO)_4Mo(PPh_2Cl)_2$. A solution of 1.00 g (1.54 mmol) of either complex in 5 mL of water, 5 mL of triethylamine, and 10 mL of THF was stirred at room temperature for 0.5 h. The pale yellow solution was evaporated to dryness and the residue washed with three 10-mL portions of water and one of ethanol. Filtration and vacuum-drying yielded 980 mg of white solid. This can be recrystallized from CH_2Cl_2/hexane. Anal. Calcd for the cis product ($[NEt_3H][(CO)_4Mo(Ph_2P\text{-}O\text{-}H\text{-}O\text{-}PPh_2)]$): N, 1.96; C, 57.23; H, 5.22. Found: N, 2.27; C, 56.97; H, 5.27. Found for the trans product: N, 2.23; C, 56.97; H, 5.41. IR absorptions for both products include carbonyl stretches at 2003, 1917, and 1890 cm^{-1}. ^{31}P NMR data consisted of a single resonance (proton decoupled) at 105.2 ppm relative to external 85% H_3PO_4.

Synthesis of *cis*-$Cl_2Pd(PPh_2Cl)_2$. An amount of 330 mg (0.855 mmol) of $(PhCN)_2PdCl_2$ was stirred with 0.32 mL (1.8 mmol) of

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PPh_2Cl in 5 mL of toluene. The orange suspension rapidly turned yellow. After 0.5 h, 5 mL of hexane was added and the bright yellow product filtered off, washed with hexane, and vacuum-dried. The yield was 520 mg (98%).

Hydrolysis of *cis*-$Cl_2Pd(PPh_2Cl)_2$. (a) A sample of the complex was suspended in aqueous acetone (1:1) and stirred for 2–3 days at room temperature. The greyish yellow solid was isolated and recrystallized from CH_2Cl_2/ethanol to give light yellow crystals. IR and ^1H and ^{31}P NMR data were identical with literature values.[8] Osmometric molecular weight determination gave 1062 (1090.1 theory). Anal. Calcd: C, 52.87; H, 3.89; Cl, 6.50. Found: C, 52.65; H, 3.82; Cl, 7.05. The product was therefore identified as $[(Ph_2P\text{–}O\text{–}H\text{–}O\text{–}PPh_2)PdCl]_2$.

(b) A sample of the complex was suspended in acetone. An equal volume of concentrated HCl was added slowly with stirring. After 1 h, the clear, yellow solution was concentrated and diluted with water. Filtation yielded the light yellow product of $[(Ph_2P\text{–}O\text{–}H\text{–}O\text{–}PPh_2)PdCl]_2$.

(c) An amount of 250 mg (0.4 mmol) of the complex was suspended in 10 mL of aqueous acetone (1:3). A total of 3 mL of triethylamine was added and the suspension stirred for 2 h. After reduction in volume, the reaction mixture was diluted with water to give a yellow-orange solid (180 mg). IR absorptions are as follows: 1100 (s), 1030 (s), 1020 (s), 995 (s), 735 (m), 705 (m), 683 (s) cm^{-1}. The aqueous filtrate was evaporated to dryness and washed with ether to give 220 mg (100% of theory) of NEt_3HCl. Anal. Calcd for $[Pd(PPh_2O)_2]$: C, 56.68; H, 3.93. Found: C, 56.99; C, 4.03.

Reaction of $[Pd(PPh_2O)_2]_n$ with HCl. To a suspension of the solid in acetone was added an equal volume of concentrated HCl. An immediate formation of a clear yellow-orange solution resulted. After volume reduction, the light yellow, water-insoluble solid was recrystallized from CH_2Cl_2/ethanol to give $[(Ph_2P\text{–}O\text{–}H\text{–}O\text{–}PPh_2)PdCl]_2$.

Acknowledgment. We are grateful to the National Science Foundation for an instrumental grant toward the purchase of the FT NMR spectrometer.

Registry No. *cis*-$(CO)_4Mo(PPh_2Cl)_2$, 42724-61-8; *trans*-$(CO)_4Mo(PPh_2Cl)_2$, 37834-17-6; $[NEt_3H][(CO)_4Mo(Ph_2P\text{-}O\text{-}H\text{-}O\text{-}PPh_2)]$, 66245-44-1; $[(Ph_2P\text{-}O\text{-}H\text{-}O\text{-}PPh_2)PdCl]_2$, 77071-72-8; $[Pd(PPh_2O)_2]_n$, 36560-97-1; *cis*-$Cl_2Pd(PPh_2Cl)_2$, 61567-62-2; $Mo(CO)_6$, 13939-06-5; *cis*-$(CO)_4Mo(piperidine)_2$, 65337-26-0; $(PhCN)_2PdCl_2$, 14220-64-5.

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Crystal and Molecular Structure of Tetramethylbis[μ-(phenylethynyl)]-digallium

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Received October 20, 1980

Our initial observation that the vinyl group stabilized the electron-deficient bridged dimeric molecule $Ga_2(CH{=}CH_2)_6$ lead us to postulate that the stabilization of this dimer resulted from metal–π-electron interactions.[1] This stimulated our group, and others, to explore the structures of a variety of compounds including $Al_2[trans\text{-}(\mu\text{-}CH{=}CHC(CH_3)_3)]_2(i\text{-}Bu)_4$,[2] $Al_2(c\text{-}Pr)_6$, $Al_2(\mu\text{-}C{\equiv}CPh)_2Ph_4$,[4] $Al_2(\mu\text{-}C{\equiv}CMe)_2Me_4$,[5] and $In_2(\mu\text{-}C{\equiv}CMe)_2Me_4$ as well as several studies on aromatic species.[7-9] These studies have shown that there are two distinct types of bridge bonds which may be formed. The first of these is that initially predicted from our studies[1] and involves the formation of a symmetrically bridged species. The second, and the subject of this report, involves an asymmetric bridge as first reported for $Al_2(\mu\text{-}C{\equiv}CPh)_2Ph_4$[4] and subsequently observed in $Al_2(\mu\text{-}C{\equiv}CMe)_2Me_4$[5] in the gas phase and for $In_2(\mu\text{-}C{\equiv}CPh)_2Me_4$.[6] We now report the structure of the phenylethynyl-bridged gallium analogue.

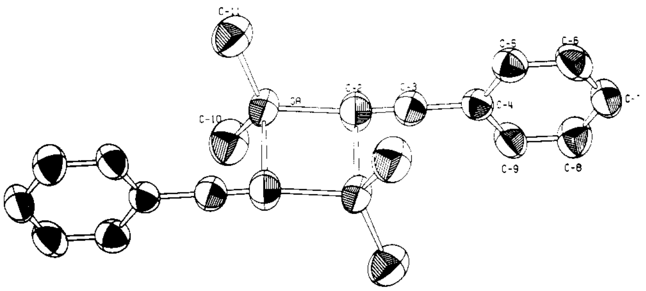

Figure 1. Molecular structure of $Ga_2(\mu\text{-}C{\equiv}CPh)_2Me_4$ with the atoms labeled.

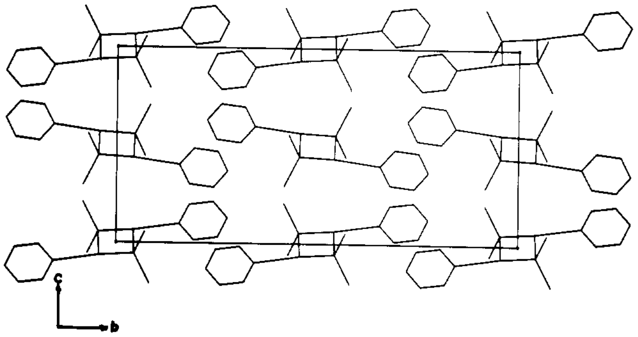

Figure 2. Projection along the *a* axis of $Ga_2(\mu\text{-}C{\equiv}CPh)_2Me_4$ showing the molecular packing.

Experimental Section

Synthesis and Crystal Selection of $Ga_2(\mu\text{-}C{\equiv}CPh)_2Me_4$. Tetramethylbis[μ-(phenylethynyl)]-digallium was prepared as described by Jeffrey and Mole.[10] The compound was recrystallized from a toluene–hexane mixed solvent which yielded well-defined prisms suitable for X-ray crystallography. The vessel containing the crystals was placed in an argon-filled drybox where the air-sensitive crystals were removed. Suitable crystals were then selected by viewing with a microscope (external to the drybox) and placed in 0.2-mm diameter thin-walled glass capillaries. These were initially plugged with silicon grease and then flame sealed on removal from the drybox.

Data Collection. A suitable crystal, selected by examination with a polarizing microscope, was mounted on a goniometer head with an epoxy adhesive and placed on a Syntex $P2_1$ diffractometer. The data were collected with use of Mo $K\bar{\alpha}$ radiation diffracted from a highly oriented graphite crystal in the parallel mode with a θ–2θ scan in the bisecting mode. The specific conditions, unit cell, and unit cell dimensions are given in Table I.

Solution and Refinement. The gallium atoms were initially located with the use of Patterson synthesis in three dimensions. Subsequent

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