Novel Reactions of Metal–Metal Bonds. Insertion of Isocyanides and Carbon Monoxide into the Palladium–Palladium Bond of Some Pd(I) Dimers

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Abstract: A new preparation of $Pd_2(dpm)_2Cl_2$ (dpm = bis(diphenylphosphino)methane) and $Pd_2(dam)_2Cl_2$ (dam = bis(diphenylarsino)methane) from bis(benzonitrile)palladium(II) chloride, dipalladium(0) tris(dibenzylideneacetone), and the appropriate diphosphine or diarsine is reported. $Pd_2(dpm)_2Cl_2$ readily undergoes metathesis with a variety of alkali metal salts to exchange the terminal ligands and form $Pd_2(dpm)_2X_2$ (X = Br, I, N_3, NCO, SCN, and NO_2). These new complexes have been characterized by elemental analyses and electronic, infrared, and proton magnetic resonance spectroscopy. The cyanate and nitrite complexes exist solely as the N-bound linkage isomers while the thiocyanate exists as two isomers, one with two S-bound thiocyanate ligands and the other with one S- and one N-bound ligand. Addition of carbon monoxide to $Pd_2(dpm)_2X_2$ and $Pt_2(dpm)_2X_2$ results in insertion into the metal–metal bond to form $Pd_2(dpm)_2(\mu\text{-}CO)X_2$ (X = Cl, Br, I, N_3, NCO, and SCN) and $Pt_2(dpm)_2(\mu\text{-}CO)X_2$ (X = Cl or I) which, except for X = I and SCN, have been isolated as solids. The bridging carbon monoxide may be readily removed by heating the solids under vacuum or by refluxing their dichloromethane solutions. The effect of the terminal anions on the qualitative relative equilibrium constants for the formation of $M_2(dpm)_2(\mu\text{-}CO)X_2$ is discussed. Isocyanides react with $Pd_2(dpm)_2X_2$ to yield three products, $Pd_2(dpm)_2(\mu\text{-}CNR)X_2$, $[Pd(dpm)_2(\mu\text{-}CNR)(CNR)X]X$, and $[Pd_2(dpm)_2(\mu\text{-}CNR)(CNR)_2]X_2$. The equilibria between these three forms may be shifted by addition of isocyanide or anion X.

Introduction

The phosphine and arsine bridged Pd(I) dimers $Pd_2(dpm)_2X_2$ (**1**, dpm = bis(diphenylphosphino)methane; X

1
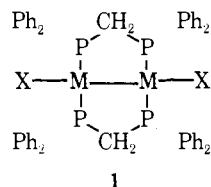
= Cl or Br) and $Pd_2(dam)_2Cl_2$ (dam = bis(diphenylarsino)methane), originally prepared by Colton and co-workers,[1,2] and their platinum analogues[3–5] contain unusually reactive metal–metal bonds. Crystal structures of two of these complexes reveal that the two metal atoms are connected by direct single bonds. The metal–metal bond length is 2.699 Å for **1** (M = Pd; X = Br)[2] and 2.652 Å for **1** (M = Pt; X = Cl).[5] The coordination geometry about each metal is approximately planar but the two metal coordination planes are twisted so that the dihedral angles between the planes are about 39°.

Carbon monoxide,[6,7] isocyanides,[2] and sulfur dioxide[8] insert into the metal–metal bond of **1** via eq 1. In the process the metal centers move about 0.5 Å apart and the formal metal–metal bond is broken. The structures of two molecules of type **2**, $Pd_2(dpm)_2(\mu\text{-}CNCH_3)(CNCH_3)_2{}^{2+}$ [6] and $Pd_2(dam)_2$-

2
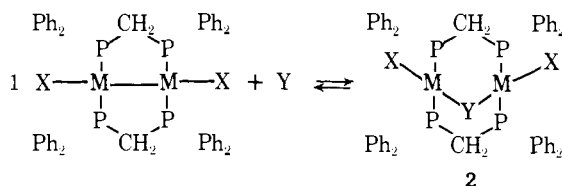
$(\mu\text{-}CO)Cl_2$,[7] have been determined crystallographically. One factor which may contribute to the reactivity of **1** is the presence of a metal–metal bond connecting two coordinatively unsaturated metal atoms. Generally the transition metal centers involved in metal–metal bonding are saturated 18-electron species. Major exceptions to this include dimeric Pd(I) and Pt(I) complexes which have two directly bonded, 16-electron, planar metal ions[9–17] and a number of tripalladium

or triplatinum complexes which may contain linear[19] or triangular M_3 units.[19–24]

Details of a new preparative route to **1** (M = Pd), exchange of its axial anions, and reactions with carbon monoxide and isocyanides are reported here.

Experimental Section

Preparation of Compounds. Methyl isocyanide,[25] *p*-tolyl isocyanide,[26] phenyl isocyanide,[27] $Pt_2(dpm)_2Cl_2$,[4] $Pt_2(dpm)_2I_2$,[4] $Pd_2(CH_3NC)_6(PF_6)_2$,[16] $Pd_2(p\text{-}CH_3C_6H_4NC)_6(PF_6)_2$,[17] $Pd(C_6H_5CN)_2Cl_2$,[28] $[Pd(CO)Cl]_n$,[29] and $Pd_2dba_3\cdot CHCl_3$[30] (dba = dibenzylideneacetone) were synthesized by the reported procedures. Cyclohexyl isocyanide (Aldrich), carbon monoxide (Matheson), bis(diphenylphosphino)methane (Strem), and bis(diphenylarsino)methane (Strem) were obtained from commercial sources and used without further purification. Reactions involving the use of $Pd_2dba_3\cdot CHCl_3$, $[Pd(CO)Cl]_n$, or CO were routinely carried out under prepurified nitrogen using deoxygenated solvents.

$Pd_2(Ph_2PCH_2PPh_2)_2Cl_2$. Method 1, a Modification of the Reported Procedure.[2] Bis(diphenylphosphino)methane (0.765 g, 1.99 mmol) was added to 0.332 g (1.95 mmol) of $[Pd(CO)Cl]_n$ in 70 mL of dichloromethane and the resulting suspension was refluxed for 2 h. The dark red solution was filtered to remove an insoluble solid and then concentrated under vacuum until the dark red product formed. Excess hexane was added to complete precipitation and the product was collected by filtration. The red compound was recrystallized from dichloromethane/hexane and vacuum dried. Highly variable yields of 50–90% were obtained by this procedure.

Method 2. $Pd_2dba_3\cdot CHCl_3$ (0.545 g, 0.527 mmol), $Pd(PhCN)_2Cl_2$ (0.412 g, 1.08 mmol), and $Ph_2PCH_2PPh_2$ (0.819 g, 2.13 mmol) were refluxed in 50 mL of dichloromethane for 30 min. The red solution was filtered and concentrated under vacuum to 10 mL. After precipitation by addition of excess methanol, the product was collected by filtration. Recrystallization from dichloromethane/methanol followed by vacuum drying afforded orange-red crystalline product in 80 ± 5% yield.

$Pd_2(Ph_2AsCH_2AsPh_2)_2Cl_2$. This rust-colored compound was synthesized by method 2 described above, using $Ph_2AsCH_2AsPh_2$ instead of $Ph_2PCH_2PPh_2$ and diethyl ether instead of methanol.

$Pd_2(Ph_2PCH_2PPh_2)_2Br_2$. To a solution of 0.226 g (0.215 mmol) of $Pd_2(Ph_2PCH_2PPh_2)_2Cl_2$ in 10 mL of dichloromethane, a solution of 0.203 g (1.97 mmol) of NaBr in 10 mL of aqueous methanol was added. The resulting solution was filtered and concentrated under vacuum until red-orange crystals formed. Aqueous methanol was

Table I. Characterization Data for New Palladium Compounds

compd[a,b]	color	mp, °C	yield, %	chemical analyses, %[c]					
				C	H	N	S	P	Cl
Pd₂dpm₂I₂·CH₂Cl₂	red-violet	225	94	46.24 (46.39)	3.35 (3.51)				
Pd₂dpm₂(SCN)₂·½(CH₃CH₂)₂O	orange	215–216	89	57.97 (57.15)	4.35 (4.35)		5.65 (5.65)		
Pd₂dpm₂(NCO)₂·½CH₂Cl₂	yellow	228–229	85	56.87 (56.90)	3.96 (4.09)	2.63 (2.53)			
Pd₂dpm₂(N₃)₂·½CH₃OH	orange-red	223–224	77	55.72 (56.07)	3.98 (4.29)	7.52 (7.77)			
Pd₂dpm₂(NO₂)₂·CH₃OH·½CH₂Cl₂	yellow-orange	199–200	94	53.25 (53.87)	4.09 (4.30)	2.43 (2.44)			
Pd₂dpm₂(μ-CO)Cl₂	orange-red	160 dec	84	56.59 (56.59)	4.30 (4.10)			11.14 (11.47)	
Pd₂dpm₂(μ-CO)Br₂	dark red	168 dec	88	52.65 (52.38)	3.98 (3.79)			10.23 (10.60)	
Pd₂dpm₂(μ-CO)(NCO)₂	dark yellow	165 dec	77	57.94 (58.21)	4.28 (4.06)	2.52 (2.56)		11.35 (11.35)	
Pd₂dam₂(μ-CO)Cl₂·³⁄₈CH₂Cl₂	dark red	168 dec	94	47.64 (47.90)	3.46 (3.50)				7.59 (7.57)
Pd₂dpm₂(μ-C₆H₁₁NC)Cl₂	yellow-orange	184–186	74	59.06 (58.93)	4.87 (4.77)	1.20 (1.21)		11.05 (10.76)	
Pd₂dpm₂(μ-C₆H₅NC)Cl₂	yellow-orange	195–196		59.47 (59.24)	4.35 (4.27)	.99 (1.21)			
Pd₂dpm₂(μ-p-CH₃C₆H₄NC)Cl₂	orange	219–220	83	59.70 (59.76)	4.67 (4.40)	1.51 (1.28)			
Pd₂dpm₂(μ-CH₃NC)Cl₂	yellow-orange	182–184	83	57.07 (57.11)	4.30 (4.33)	1.51 (1.28)			
Pd₂dpm₂(μ-CH₃NC)Br₂	red-orange	184–186	95	52.77 (52.82)	4.16 (4.01)	1.04 (1.18)			
Pd₂dpm₂(μ-CH₃NC)I₂	dark red	181–183	80	49.06 (48.93)	3.73 (3.71)	1.28 (1.10)		9.54 (9.71)	
Pd₂dpm₂(μ-CH₃NC)(SCN)₂	orange-red	183–186	95	56.84 (56.95)	4.17 (4.16)	3.92 (3.69)	5.65 (5.63)		
Pd₂dpm₂(μ-CH₃NC)(CH₃NC)I₂	yellow	176 dec	81	48.86 (49.23)	4.08 (3.83)	2.13 (2.13)		9.59 (9.40)	
Pd₂dpm₂(μ-CH₃NC)(CH₃NC)(SCN)₂	yellow	180 dec	95	57.42 (57.01)	4.37 (4.27)	4.59 (4.75)		5.42 (5.43)	
Pd₂dpm₂(μ-CH₃NC)(CH₃NC)₂(PF₆)₂	yellow	162–169	90	48.21 (48.22)	3.26 (3.83)	3.03 (3.01)			
Pd₂dpm₂(μ-p-CH₃C₆H₄NC)-(p-CH₃C₆H₄NC)₂(PF₆)₂	orange	195–197		54.50 (54.76)	4.32 (4.04)	2.50 (2.59)			

^{a} dpm = (C₆H₅)₂PCH₂P(C₆H₅)₂; dam = (C₆H₅)₂AsCH₂As(C₆H₅)₂. ^{b} Qualitative presence of solvent verified by NMR and/or IR spectroscopy. ^{c} Calculated values shown in parentheses.

added to complete precipitation and the product was filtered. Recrystallization from dichloromethane/aqueous methanol followed by vacuum drying yielded 0.227 g (93%) of product.

Pd₂(Ph₂PCH₂PPh₂)₂X₂ (X = I, SCN, NCO, N₃, or NO₂). These complexes were prepared using the procedure described for Pd₂(Ph₂PCH₂PPh₂)₂Br₂. A dichloromethane solution of Pd₂(Ph₂PCH₂PPh₂)₂Cl₂ was reacted with a three- to fourfold excess of the appropriate sodium or potassium salt dissolved in aqueous methanol. The products were isolated as described above, recrystallized from dichloromethane/aqueous methanol or dichloromethane/diethyl ether, and vacuum dried.

[Pd₂(Ph₂PCH₂PPh₂)₂(μ-CH₃NC)(CH₃NC)₂][PF₆]₂. Bis(diphenylphosphino)methane (0.431 g, 1.12 mmol) was added to 0.401 g (0.459 mmol) of Pd₂(CH₃NC)₆(PF₆)₂ dissolved in 20 mL of warm acetonitrile. The resulting solution was filtered and the product was precipitated with excess diethyl ether and collected. Purification was accomplished by dissolving the compound in a minimum of acetone containing 0.1 mL of methyl isocyanide, filtering, and precipitating the yellow compound with diethyl ether. After removal of the yellow crystals by filtration, they were vacuum dried (yield 0.576 g, 90%).

[Pd₂(Ph₂PCH₂PPh₂)₂(μ-p-CH₃C₆H₄NC)(p-CH₃C₆H₄NC)₂][PF₆]₂. This compound was prepared by the procedure described above, using Pd₂(p-CH₃C₆H₄NC)₆(PF₆)₂ instead of Pd₂(CH₃NC)₆(PF₆)₂. The orange, crystalline product was recrystallized from acetone/hot absolute ethanol and vacuum dried.

Pd₂(Ph₂PCH₂PPh₂)₂(μ-CH₃NC)Cl₂. Method 1. Methyl isocyanide was added to a suspension of 0.200 g (0.190 mmol) of

Pd₂(Ph₂PCH₂PPh₂)₂Cl₂ in 10 mL of acetonitrile until dissolution was complete. The solution was filtered and concentrated under vacuum. The yellow-orange product, after precipitation by the addition of diethyl ether, was collected and vacuum dried (yield 0.172 g, 83%).

Method 2. An acetonitrile solution of 0.100 g (0.0717 mmol) of Pd₂(Ph₂PCH₂PPh₂)₂(μ-CH₃NC)(CH₃NC)₂(PF₆)₂ was added to an acetonitrile solution of 0.063 g (0.143 mmol) of Ph₄AsCl·H₂O, and then filtered. About 100 mL of solution was concentrated to 5 mL on a rotary evaporator at elevated temperature to yield a yellow-orange solid which was collected by filtration, washed with acetonitrile and diethyl ether, and vacuum dried (yield 0.064 g, 82%).

Pd₂(Ph₂PCH₂PPh₂)₂(μ-RNC)Cl₂ (R = p-CH₃C₆H₄, C₆H₅, or C₆H₁₁). These compounds were synthesized by method 1 described above using p-tolyl isocyanide, phenyl isocyanide, or cyclohexyl isocyanide instead of methyl isocyanide.

Pd₂(Ph₂PCH₂PPh₂)₂(μ-CH₃NC)X₂ (X = Br, NCO, or N₃). Similarly to the preparation of Pd₂(Ph₂PCH₂PPh₂)₂(μ-CH₃NC)Cl₂ these compounds were prepared by the addition of excess methyl isocyanide to a suspension of Pd₂(Ph₂PCH₂PPh₂)₂X₂ in 10 mL of acetonitrile. After filtration, the compounds were precipitated from solution with diethyl ether, collected, and vacuum dried.

[Pd₂(Ph₂PCH₂PPh₂)₂(μ-CH₃NC)(CH₃NC)X]X (X = I or SCN). These compounds were synthesized by the addition of excess methyl isocyanide to Pd₂(Ph₂PCH₂PPh₂)₂X₂ (X = I or SCN) in acetonitrile. When excess diethyl ether was added to their filtered solutions, the yellow salt complexes precipitated. The compounds were recrystallized from acetonitrile/diethyl ether with added methyl isocyanide. Vacuum

Table II. Infrared Spectra[a]

compd	ν(terminal anion), cm⁻¹	ν(Pd–Cl), cm⁻¹
Pd₂dpm₂Cl₂		249 (w)
Pd₂dpm₂(SCN)₂	2094 (s), 2102 (s)	
Pd₂dpm₂(NCO)₂	2206 (vs)	
Pd₂dpm₂(N₃)₂	2010 (vs), 2032 (vs)	
Pd₂dpm₂(NO₂)₂	1306 (s), 1350 (s)	

compd	ν(CO), cm⁻¹	ν(terminal anion), cm⁻¹	ν(Pd–Cl), cm⁻¹
Pd₂dpm₂(μ-CO)Cl₂	1705 (m)		258 (w)
Pd₂dpm₂(μ-CO)Br₂	1712 (m)		
Pd₂dpm₂(μ-CO)I₂[b]	1713 (m)		
Pd₂dpm(μ-CO)(SCN)₂[b]	1712 (m)	2080 (s)	
Pd₂dpm₂(μ-CO)(NCO)₂	1720 (m)	2180 (vs), 2200 (vs)	
Pd₂dam₂(μ-CO)Cl₂	1723 (m)		234 (w)

compd	ν(μ-CN), cm⁻¹	ν(terminal anion) cm⁻¹	ν(Pd–Cl), cm⁻¹
Pd₂dpm₂(μ-C₆H₁₁NC)Cl₂	1645 (m)		246 (w)
Pd₂dpm₂(μ-C₆H₅NC)Cl₂	1624 (m)		248 (w)
Pd₂dpm₂(μ-p-CH₃C₆H₄NC)Cl₂	1627 (m)		256 (w)
Pd₂dpm₂(μ-CH₃NC)Cl₂	1642 (m), 1677 (w)		248 (w)
Pd₂dpm₂(μ-CH₃NC)Br₂	1642 (m), 1672 (w)		
Pd₂dpm₂(μ-CH₃NC)I₂	1611 (sh), 1634 (m), 1669 (w)		
Pd₂dpm₂(μ-CH₃NC)(SCN)₂	1644 (m), 1679 (w)	2073 (vs)	
Pd₂dpm₂(μ-CH₃NC)(NCO)₂	1648 (m), 1679 (w)	2192 (vs)	
Pd₂dpm₂(μ-CH₃NC)(N₃)₂	1634 (m), 1675 (w)	2205 (w)	

compd	ν(μ-CN), cm⁻¹	ν(terminal CN), cm⁻¹	ν(terminal anion), cm⁻¹
Pd₂dpm₂(μ-CH₃NC)(CH₃NC)I₂	1647 (w), 1674 (m)	2226 (s)	
Pd₂dpm₂(μ-CH₃NC)(CH₃NC)(SCN)₂	1645 (m), 1686 (m)	2208 (s)	2053 (vs), 2086 (vs)
Pd₂dpm₂(μ-CH₃NC)(CH₃NC)₂(PF₆)₂	1649 (w), 1680 (m)	2216 (s), 2224 (s)	
Pd₂dpm₂(μ-p-CH₃C₆H₄NC)(p-CH₃C₆H₄NC)₂(PF₆)₂	1655 (w), 1680 (m)	2173 (s), 2181 (s)	

[a] Recorded as mineral oil mulls. [b] CH₂Cl₂ solution.

drying slowly converted these salts to their molecular form: Pd₂(Ph₂PCH₂PPh₂)₂(μ-CH₃NC)X₂.

Pd₂(Ph₂PCH₂PPh₂)₂(μ-CH₃NC)X₂ (X = I or SCN). From the salt solutions described above, these compounds were isolated as follows: about 100 mL of a filtered acetonitrile solution was concentrated on a rotary evaporator at elevated temperature to 3 mL. If necessary, the process was repeated until significant precipitation was apparent. After refrigeration for several hours, the precipitate was collected by filtration, washed with ice-cold acetonitrile and diethyl ether, and vacuum dried.

Pd₂(Ph₂PCH₂PPh₂)₂(μ-CO)X₂ (X = Cl or Br). About 0.10 mmol of Pd₂(Ph₂PCH₂PPh₂)₂X₂ was dissolved in 10 mL of dichloromethane and filtered. Carbon monoxide was slowly bubbled into the solution for 30 min. The product which precipitated was filtered, washed with diethyl ether, and vacuum dried (yield 0.090 mmol, 90%).

Pd₂(Ph₂PCH₂PPh₂)₂(μ-CO)(NCO)₂. Using Pd₂(Ph₂PCH₂PPh₂)₂(NCO)₂, this compound was prepared as described above and isolated by precipitation with diethyl ether. The product was filtered, washed, and vacuum dried.

Pd₂(Ph₂AsCH₂AsPh₂)₂(μ-CO)Cl₂. This compound was synthesized and isolated as described for Pd₂(Ph₂PCH₂PPh₂)₂(μ-CO)(NCO)₂, using Pd₂(Ph₂AsCH₂AsPh₂)₂Cl₂ instead of the phosphine compound.

Physical Measurements. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer. Electronic spectra were recorded on a Cary 17 spectrophotometer. Proton magnetic resonance spectra were recorded on a JEOL-MH-100 spectrometer with tetramethylsilane as an internal standard. Conductivities were determined by the use of an Industrial Instruments conductivity bridge with 10⁻³ M acetonitrile solution.

Results

Preparation of Pd(I) Dimers. Pd₂(dpm)₂Cl₂ has been synthesized previously by the reaction of [Pd(CO)Cl]ₙ with dpm.[2]

However, we have found that the methods of forming [Pd(CO)Cl]ₙ give highly variable yields. Moreover, the reaction of this poorly defined polymer with dpm gives a byproduct of low solubility which decreases the yield of Pd₂(dpm)₂Cl₂. Consequently a new route to this Pd(I) dimer was sought. Since other Pd(I) dimers (e.g., Pd₂(CNCH₃)₆²⁺,[15,16] Pd₂(CNR)₄X₂[10]) are readily prepared by the reaction of suitable Pd(II) and Pd(0) complexes, a similar route to Pd₂(dpm)₂Cl₂ was examined. Reaction of Pd(PhCN)₂Cl₂, Pd₂(dba)₃ (dba = dibenzylideneacetone) and dpm in refluxing dichloromethane produces Pd₂(dpm)₂Cl₂ in 80% yield. The arsine complex Pd₂(dam)₂Cl₂ was prepared analogously. It is important to note that this preparation of Pd₂(dam)₂Cl₂ leads to a product which is free of carbon monoxide.

The terminal anionic ligands of these dimers may be readily exchanged by metathesis with alkali metal salts in methanol/dichloromethane solution. In this fashion new complexes with terminal iodide, thiocyanate, cyanate, azide, and nitrite ligands have been obtained. The bromide complex, which was previously prepared from [Pd(CO)Br]ₙ, may also be obtained in this manner. Physical and spectroscopic data relating to the characterization of these complexes are reported in Tables I–III. These complexes are indefinitely stable in air as solids and most, except the nitrite, are stable in dichloromethane for at least 1 week. These complexes crystallize as solvates. In every case that a solvate is reported, the presence of a particular solvent species in the lattice has been verified both by elemental analysis and by qualitative spectroscopic (infrared or ¹H NMR) observation.

The nitrite, cyanate, and thiocyanate complexes are capable

Table III. Electronic Spectra

compd	solvent	λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1}) at 25 °C
Pd$_2$dpm$_2$Cl$_2$	CH$_2$Cl$_2$	416 (7550), 347 (16 800), 293 (25 900)
Pd$_2$dpm$_2$Br$_2$	CH$_2$Cl$_2$	428 (10 600), 364 (17 500), 301 (23 100), 285 sh (21 300), 258 sh (29 400)
Pd$_2$dpm$_2$I$_2$	CH$_2$Cl$_2$	488 (13 000), 439 (11 900), 394 (11 900), 313 (20 000), 280 sh (23 900), 262 sh (28 500)
Pd$_2$dpm$_2$(SCN)$_2$	CH$_2$Cl$_2$	426 (14 600), 303 (21 200), 259 sh (30 400)
Pd$_2$dpm$_2$(NCO)$_2$	CH$_2$Cl$_2$	394 (7390), 326 sh (13 500), 290 sh (36 300)
Pd$_2$dpm$_2$(N$_3$)$_2$	CH$_2$Cl$_2$	428 (19 900), 305 sh (19 700), 287 sh (25 000), 265 sh (28 100)
Pd$_2$dpm$_2$(NO$_2$)$_2$	CH$_2$Cl$_2$	434 (11 500), 362 (9300), 316 sh (13 800), 294 sh (22 000)
Pd$_2$dam$_2$Cl$_2$	CH$_2$Cl$_2$	428 (6400), 370 (14 800), 306 sh (19 700), 254 sh (29 000)
Pd$_2$dpm$_2$(μ-CO)Cl$_2$[a]	CH$_2$Cl$_2$	468 (0.37), 404 (0.20), 306 (0.47), 250 sh (1.00)
Pd$_2$dpm$_2$(μ-CO)Br$_2$[a]	CH$_2$Cl$_2$	481 (1.00), 410 (0.57), 309 sh (0.97), 258 sh (0.57)
Pd$_2$dpm$_2$(μ-CO)(SCN)$_2$[a]	CH$_2$Cl$_2$	439 (0.50), 300 sh (0.71), 259 sh (1.00)
Pd$_2$dpm$_2$(μ-CO)(NCO)$_2$	CH$_2$Cl$_2$	444 (10 500), 401 sh (7590), 292 sh (23 200)
Pd$_2$dam$_2$(μ-CO)Cl$_2$	CH$_2$Cl$_2$	494 (14 400), 385 sh (6100), 324 (14 500), 263 sh (31 400)
Pd$_2$dpm$_2$(μ-C$_6$H$_{11}$NC)Cl$_2$[b]	CH$_3$CN	436 (0.20), 381 (0.46), 299 sh (1.00)
Pd$_2$dpm$_2$(μ-C$_6$H$_5$NC)Cl$_2$[b]	CH$_3$CN	433 (1.00)
Pd$_2$dpm$_2$(μ-p-CH$_3$C$_6$H$_4$NC)Cl$_2$[b]	CH$_3$CN	435 (0.45), 262 sh (1.00)
Pd$_2$dpm$_2$(μ-CH$_3$NC)Cl$_2$	CH$_3$CN	429 (13 100), 390 sh (7150), 299 sh (16 100)
Pd$_2$dpm$_2$(μ-CH$_3$NC)Br$_2$[b]	CH$_3$CN	440 (0.79), 384 (0.58), 306 (0.44), 260 sh (1.00)
Pd$_2$dpm$_2$(μ-CH$_3$NC)I$_2$[b]	CH$_3$CN	446 (0.63), 394 (0.62), 306 sh (1.00)
Pd$_2$dpm$_2$(μ-CH$_3$NC)(SCN)$_2$	CH$_3$CN	411 (13 800), 300 sh (16 500), 262 sh (33 500)
Pd$_2$dpm$_2$(μ-CH$_3$NC)(NCO)$_2$	CH$_3$CN	409 (14 500), 256 sh (35 200)
Pd$_2$dpm$_2$(μ-CH$_3$NC)(N$_3$)$_2$	CH$_3$CN	420 (6550), 260 sh (29 600)
Pd$_2$dpm$_2$(μ-CH$_3$NC)(CH$_3$NC)I$_2$	CH$_3$CN	456 (15 500) 392 sh (5740), 270 sh (30 300)
Pd$_2$dpm$_2$(μ-CH$_2$NC)(CH$_3$NC)(SCN)$_2$	CH$_3$CN	418 (13 800), 306 sh (13 800), 260 sh (33 100)
Pd$_2$dpm(μ-CH$_3$NC)(CH$_3$NC)$_2$(PF$_6$)$_2$	CH$_3$CN	462 sh (2560), 430 sh (4940), 381 (9650), 309 sh (18 900), 256 sh (34 300)
Pd$_2$dpm$_2$(μ-p-CH$_3$C$_6$H$_4$NC)-(p-CH$_3$C$_6$H$_4$NC)$_2$(PF$_6$)$_2$	CH$_3$CN	455 (14 800)

[a] The compound was generated in solution by purging the parent solution with CO gas. Values listed as ϵ_{max} are relative absorbance values.
[b] The compound has very low solubility. Values listed as ϵ_{max} are relative absorbance values.

of existing as linkage isomers. By comparison with Pd(II) complexes[31] the nitrite and cyanate anions would be expected to be nitrogen bonded and infrared measurements confirm this. The nitrite complex has both N–O stretching vibrations at frequencies (1350 and 1306 cm^{-1}) which are higher than those of free nitrite, and which are indicative of metal binding through nitrogen.[31] The cyanate complex has infrared absorptions for ν_a(NCO), 2206 cm^{-1}, and ν_s(NCO), 1310 cm^{-1}, which are typical for nitrogen-bound cyanate.[32] Linkage isomers of the thiocyanate complex have been isolated as solids. When Pd$_2$(dpm)$_2$(SCN)$_2$ is crystallized from dichloromethane solution by the addition of methanol, orange crystals (λ_{max} 445, 364, 342, 309, 289, 264, 241 nm as a Nujol mull) are obtained. These exhibit C–N stretching vibrations at 2102 and 2094 cm^{-1} which are within the range expected for S-bound thiocyanate. No band ascribable to the C–S stretch is observed. However, phenyl absorptions obscure the region from 780 to 690 cm^{-1} in which S-bound thiocyanate would have an absorption band. We assign structure **3** to this solid. When

3   4
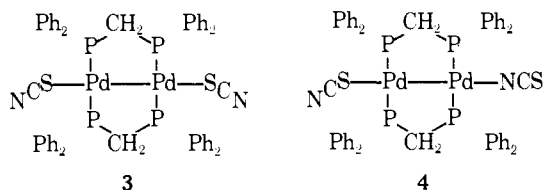
crystallization is induced by the addition of diethyl ether to a dichloromethane solution of Pd$_2$(dpm)$_2$(SCN)$_2$, a yellow-orange, crystalline solid (λ_{max} 378, 311, 298, 262, 240 nm as a Nujol mull) is obtained. This solid shows C–N stretching vibrations at 2102 and 2050 cm^{-1} with a shoulder at 2094 cm^{-1}, and a C–S stretching vibration at 808 cm^{-1}. The vibrational features at 2050 and 808 cm^{-1} are characteristic of N-bound thiocyanate, while the higher energy C–N stretching frequency is indicative of the presence of the S-bound form. We assign structure **4** to this solid. The alternative possibility,

that this solid consists of a mixture of **3** and the isomer with only N-bound thiocyanate ligands, is rejected because the relative intensity of the 2102- and 2050-cm^{-1} bands was constant in a number of independent preparations. Moreover, the C–N stretching doublet of **3** consists of a slightly weaker band at 2102 cm^{-1} and a stronger feature at 2094 cm^{-1} while the isomer we assign as structure **4** exhibits a strong absorption at 2102 cm^{-1} and a weak shoulder at 2094 cm^{-1}. In dichloromethane solution Pd$_2$(dpm)$_2$(SCN)$_2$ shows only a single C–N stretch at 2087 cm^{-1} and probably exists solely with two S-bound thiocyanate ligands.

Reactions with Carbon Monoxide. When carbon monoxide is bubbled into solutions of Pd$_2$(dpm)$_2$X$_2$ (X = Cl, Br, I, N$_3$, SCN, or NCO) or Pd$_2$(dam)$_2$Cl$_2$ the infrared spectrum indicates, through the presence of an absorption in the range 1725–1700 cm^{-1}, that carbon monoxide binds to these complexes. The electronic spectra of the complexes are also altered by the addition of carbon monoxide. The uptake of carbon monoxide is reversed by either purging the solutions with nitrogen or by refluxing their dichloromethane solutions. (The adduct Pd$_2$(dam)$_2$(μ-CO)Cl$_2$ is more resistant to decarbonylation and requires refluxing in benzene solution to revert to Pd$_2$(dam)$_2$Cl$_2$.) Solid carbonyl adducts have been isolated for the chloride, bromide, and cyanate complexes. These solids may be readily decarbonylated by heating at 78 °C under vacuum. The carbonyl adduct of Pd$_2$(dpm)$_2$(N$_3$)$_2$ undergoes further reactions (vide infra) which prevent its isolation as a pure solid. Attempts to isolate Pd$_2$(dpm)$_2$(μ-CO)(SCN)$_2$ produced only crystalline Pd$_2$(dpm)$_2$(SCN)$_2$. The carbonyl adduct of Pd$_2$(dpm)$_2$I$_2$ is observed to form under 1 atm of carbon monoxide in dichloromethane solution but rapidly decarbonylates if the partial pressure of carbon monoxide is lowered. No solid adduct could be isolated.

These qualitative observations relating to the stability of the carbonyl bridged complexes suggest that the equilibrium constants for formation of **2** (Y = CO) via eq 1 decrease in the order Pd$_2$(dam)$_2$Cl$_2$ > Pd$_2$(dpm)$_2$(NCO)$_2$ ~ Pd$_2$(dpm)$_2$Cl$_2$

~ $Pd_2(dpm)_2Br_2$ > $Pd_2(dpm)_2(SCN)_2$ > $Pd_2(dpm)_2I_2$. Similar carbonyl bridged complexes are formed by the platinum analogues. $Pt_2(dpm)_2Cl_2$ reacts with carbon monoxide to form $Pt_2(dpm)_2(\mu\text{-}CO)Cl_2$. This complex has previously been formulated[5] as containing a four-electron-donating bridging carbonyl but in the context of more recent results[6,7] it must have a structure analogous to that of $Pd_2(dam)_2(\mu\text{-}CO)Cl_2$. $Pt_2(dpm)_2(\mu\text{-}CO)Cl_2$ is decarbonylated in refluxing chloroform solution. In contrast, $Pt_2(dpm)_2(\mu\text{-}CO)I_2$ is stable in dichloromethane solution only under 1 atm of carbon monoxide and has not been isolated.

When $Pd_2(dpm)_2(N_3)_2$ is treated with carbon monoxide in dichloromethane solution, rapid carbonyl insertion into the metal–metal bond to form $Pd_2(dpm)_2(\mu\text{-}CO)(N_3)_2$ is followed by slower conversion of the azide ligand to cyanate and nitrogen so that $Pd_2(dpm)_2(\mu\text{-}CO)(NCO)_2$ is the ultimate product. The orange solid that is obtained after purging a dichloromethane solution of $Pd_2(dpm)_2(N_3)_2$ with carbon monoxide for 30 s has the following characteristic infrared bands: $\nu(NCO)$, 2200 m; $\nu(NNN)$, 2017 vs; and $\nu(\mu\text{-}CO)$, 1692 cm^{-1}. When the product is isolated after 3 h of purging with carbon monoxide the following bands are seen: $\nu(NCO)$, 2200, 2180; $\nu(NNN)$, 2030; and $\nu(\mu\text{-}CO)$, 1720 cm^{-1}. After 6 h of purging the solid product has infrared absorption characteristic of $Pd_2(dpm)_2(\mu\text{-}CO)(NCO)_2$ ($\nu(NCO)$, 2200, 2180; $\nu(\mu\text{-}CO)$, 1720 cm^{-1}) with a weak band at 2030 cm^{-1} due to some residual azide. The solid at this stage also has the same electronic spectrum (in dichloromethane solution) as the product formed by treating $Pd_2(dpm)_2(NCO)_2$ with carbon monoxide. The conversion of coordinated azide into cyanate is not unique to these carbonyl bridged dipalladium complexes. There exist several examples of mononuclear azide complexes, e.g., $(Ph_3P)_2Pd(N_3)_2$, which are converted to the corresponding cyanate complexes by reaction with carbon monoxide.[33,34]

The preparation of the diphosphine and diarsine bridged complexes from $[Pd(CO)Cl]_n$ produces not only the metal–metal bonded complexes **1** but also carbonyl bridged complexes. The initial addition of bis(diphenylphosphino)methane to $[Pd(CO)Cl]_n$ in dichloromethane produces a solid which contains bridging CO groups ($\nu(CO)$ 1715, 1705 cm^{-1}). This solid gradually dissolves to produce $Pd_2(dpm)_2Cl_2$, but because it dissolves so slowly, we believe that it contains other polymeric species in addition of $Pd_2(dpm)_2(\mu\text{-}CO)Cl_2$. Initially it was reported that the reaction of bis(diphenylarsino)methane with $[Pd(CO)Cl]_n$ produced $Pd_2(dam)_2Cl_2$.[1] However, recent crystallographic results have indicated that the product isolated was $Pd_2(dam)_2(\mu\text{-}CO)Cl_2$ and it has been suggested that $Pd_2(dam)_2Cl_2$ may not exist because of unfavorable effects due to the large bite distance of this diarsine ligand.[7] Our results clearly show that both $Pd_2(dam)_2Cl_2$ and $Pd_2(dam)_2(\mu\text{-}CO)Cl_2$ exist. $Pd_2(dam)_2Cl_2$ has been made from $Pd_2(dba)_3$, $Pd(PhCN)_2Cl_2$, and dam under carbon monoxide free conditions. It is readily carbonylated at atmospheric pressure to yield $Pd_2(dam)_2(\mu\text{-}CO)Cl_2$. The product $Pd_2(dam)_2(\mu\text{-}CO)Cl_2$ is the most stable bridged carbonyl complex of palladium described here. Nevertheless it is decarbonylated to produce $Pd_2(dam)_2Cl_2$ when it is refluxed in benzene solution. Depending on the conditions employed the reaction of bis(diphenylarsino)methane with $[Pd(CO)Cl]_n$ can produce either $Pd_2(dam)_2Cl_2$ or $Pd_2(dam)_2(\mu\text{-}CO)Cl_2$.

Reactions with Isocyanides. Isocyanides react with $Pd_2(dpm)_2X_2$ with insertion of an isocyanide into the metal–metal bond. Additionally, isocyanides may substitute for one or both of the terminal anionic ligands. A suspension of $Pd_2(dpm)_2X_2$ in acetonitrile reacts with excess methyl isocyanide to form a yellow solution. Addition of diethyl ether causes the precipitation of the molecular complexes $Pd_2(dpm)_2(\mu\text{-}CNCH_3)(X)_2$ when X is Cl, Br, N_3, or NCO. However, when the anions are iodide or thiocyanate, salts of composition

Table IV. Conductivity Data[a]

compd	Λ_M, ohm^{-1} cm^2 mol^{-1}
$Pd_2dpm_2(SCN)_2$	15
$Pd_2dpm_2(\mu\text{-}CH_3NC)(SCN)_2$	33
$Pd_2dpm_2(\mu\text{-}CH_3NC)(NCO)_2$	6
$Pd_2dpm_2(\mu\text{-}CH_3NC)(N_3)_2$	36
$Pd_2dpm_2(\mu\text{-}CH_3NC)(CH_3NC)I_2$	123
$Pd_2dpm_2(\mu\text{-}CH_3NC)(CH_3NC)(SCN)_2$	137
$Pd_2dpm_2(\mu\text{-}CH_3NC)(CH_3NC)_2(PF_6)_2$	277
$Pd_2dpm_2(\mu\text{-}p\text{-}CH_3C_6H_4NC)$ $(p\text{-}CH_3C_6H_4NC)_2(PF_6)_2$	269

[a] Solutions are 10^{-3} M in CH_3CN at 25 °C.

$[Pd_2(dpm)_2(\mu\text{-}CNCH_3)(CNCH_3)X]X$ with one terminal and one bridging isocyanide are formed. These two salts may be converted into $Pd_2(dpm)_2(\mu\text{-}CNCH_3)(SCN)_2$ and $Pd_2(dpm)_2(\mu\text{-}CNCH_3)I_2$ by repeated vacuum evaporation of acetonitrile solutions at elevated temperatures. The neutral complexes $Pd_2(dpm)_2(\mu\text{-}CNCH_3)X_2$ may be converted into the cations $Pd_2(dpm)_2(\mu\text{-}CNCH_3)(CNCH_3)_2{}^{2+}$ by treatment with an excess of methyl isocyanide and silver hexafluorophosphate. This cation may also be prepared by addition of bis(diphenylphosphino)methane to the Pd(I) dimer, $Pd_2(CNCH_3)_6{}^{2+}$. The cation $Pd_2(dpm)_2(\mu\text{-}CNCH_3)$-$(CNCH_3)_2{}^{2+}$ may be converted into $Pd_2(dpm)_2(\mu\text{-}CNCH_3)X_2$ (X = Cl or Br) by treatment with tetraphenylarsonium chloride or tetrabutylammonium bromide followed by vacuum evaporation to remove the volatile, uncoordinated isocyanide. When a stoichiometric amount of isocyanide is added to a solution of $Pd_2(dam)_2Cl_2$, the arsine ligand is displaced by isocyanide and no insertion of isocyanide into the metal–metal bond occurs. $Pd_2(dpm)_2Cl_2$ also reacts with other isocyanides to form $Pd_2(dpm)_2(\mu\text{-}CNR)Cl_2$ (R = C_6H_5, p-$CH_3C_6H_4$, and C_6H_{11}).

The infrared spectra of the neutral complexes exhibit an infrared band in the region 1680–1620 cm^{-1} due to the bridging isocyanide ligand. In this region, the methyl isocyanide complexes have a second weak band whose origin is uncertain. The structural data available for $Pd_2(dpm)_2(\mu\text{-}CNCH_3)(CNCH_3)_2{}^{2+}$ [6] do not present a cause for the additional band and we suspect that this absorption is an overtone or combination band. The cationic complexes have terminal isocyanide stretching vibrations in the 2225–2170-cm^{-1} region as well as bands due to the bridging isocyanides. The conductivity data for these complexes are presented in Table IV. The 1:1 salts have Λ_M of ca. 130 while the 1:2 salts have an Λ_M of ca. 270 cm^2 mol^{-1} ohm^{-1}. In acetonitrile solution some of the $Pd_2(dpm)_2(\mu\text{-}CNCH_3)X_2$ complexes have unexpectedly large conductivities which probably arise through substitution of the halide ligands by acetonitrile.

For those isocyanide complexes with sufficient solubility, the ^{1}H NMR chemical shift data for the isocyanide ligands appear in Table V. The phenyl resonances and broad methylene resonance of the phosphine ligands are also observed, but are relatively uninformative. The observation of only a single ligand resonance for $Pd_2(dpm)_2(\mu\text{-}CNR)(CNR)_2{}^{2+}$ (R = CH_3 or p-$CH_3C_6H_4$), which have both terminal and bridging isocyanides, indicates that a facile mechanism for ligand interchange may exist. This has been verified by low-temperature ^{1}H NMR studies. For $Pd_2(dpm)_2(\mu\text{-}CNCH_3)(CNCH_3)_2{}^{2+}$ in acetone-d_6 the single peak observed at 30 °C at 3.05 ± 0.05 ppm separates into two peaks at 3.3 ± 0.1 and 2.8 ± 0.1 ppm with relative intensities of 2:1 at −80 °C.

Discussion

The principal reactions described above are summarized in Chart I. Clearly the most unusual reaction of these dimeric
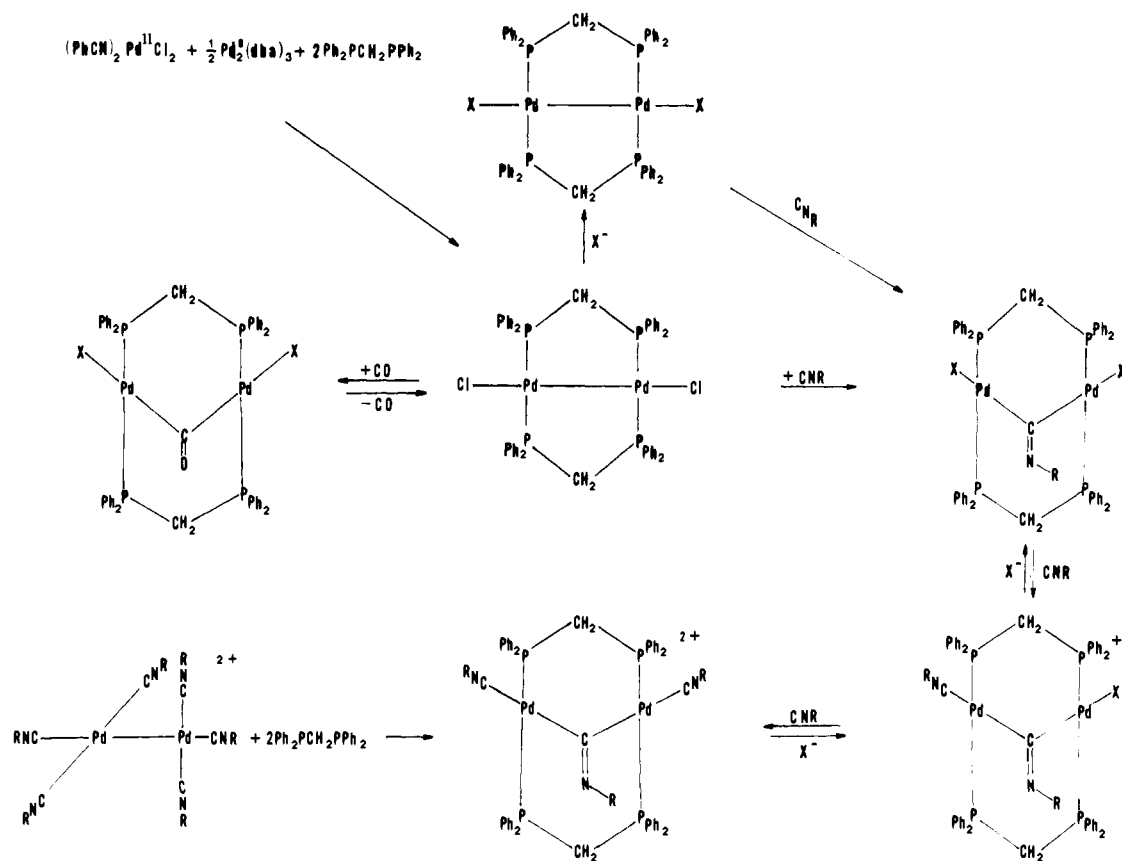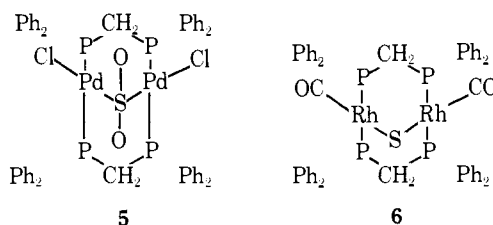
Chart I

Table V. Proton Magnetic Resonance Data

| compd[a] | RNC[b] | |
	CH₃	C₆H₄
Pd₂dpm₂(μ-CH₃NC)- (CH₃NC)₂(PF₆)₂	3.05 3.3 (2), 2.8 (1)[c] 2.83[d]	
Pd₂dpm₂(μ-p-CH₃C₆H₄NC)- (p-CH₃C₆H₄NC)₂(PF₆)₂	2.22	6.88 (AB quartet)
Pd₂dpm₂(μ-CH₃NC)(CH₃NC)- (SCN)₂	2.82	
Pd₂dpm₂(μ-CH₃NC)(CH₃NC)(I)₂	2.98	
Pd₂dpm₂(μ-CH₃NC)(NCO)₂	2.70	

[a] In acetone-d_6 at 30 °C, except where noted. [b] Chemical shift in parts per million. [c] In acetone-d_6 at −80 °C, relative intensities in parentheses. [d] In acetonitrile-d_3 at 30 °C.

palladium complexes is the facile insertion of carbon monoxide and isocyanide into the Pd–Pd bond. The structures of the insertion products are supported by the spectroscopic data reported here and by the crystallographic results for Pd₂(dpm)₂(μ-CNCH₃)(CNCH₃)₂²⁺ [6] and Pd₂(dam)₂(μ-CO)Cl₂[7] reported earlier. A drawing of Pd₂(dpm)₂(μ-CNCH₃)(CNCH₃)₂²⁺ is shown in Figure 1. The cation consists of two palladium ions with approximately square geometry linked by two bridging bis(diphenylphosphino)methane ligands and a bridging isocyanide. The coordination planes of the two palladium ions meet at the bridging isocyanide. The dihedral angle between these two planes is 106° and the palladium–palladium distance of 3.215 Å is 0.516 Å longer than the bonding palladium–palladium distance in **1**. The structure of Pd₂(dam)₂(μ-CO)Cl₂ also contains similar features; in this case the two planar Pd centers are separated by 3.274 Å. The overall geometry of these complexes is similar to that found
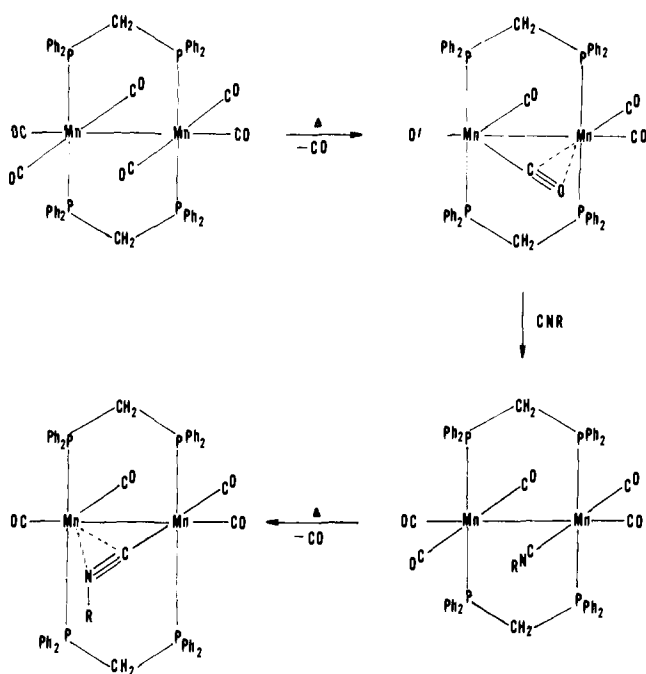
for two other dpm bridged complexes, Pd₂(dpm)₂(μ-SO₂)Cl₂ (**5**) [8] and Rh₂(dpm)₂(μ-S)(CO)₂(**6**).[35] For electron book-

keeping, if the bridging isocyanide acts as a one-electron donor to each palladium ion, then a 16-electron count is reached for each metal without necessitating a formal Pd–Pd bond. The metal–metal distances in these four A-frame complexes are effectively nonbonded distances. Nevertheless, some significant direct overlap of metal orbitals may occur in such A-frame structures. We have previously shown that planar Rh(I) ions which are placed directly facing one another with a separation of 2.8–3.4 Å can have direct overlap of metal orbitals that manifests itself in the electronic spectra of the complexes and which alters the chemical reactivity of these rhodium ions.[36,37]

Based on these structural results, the geometries of the other bridged isocyanide and carbonyl complexes are assigned by analogy and similarity of physical characteristics. The possibility of carbon monoxide acting as a bridging ligand between metal atoms not directly bonded has been discussed before, particularly in intermediates in a variety of chemical reactions.[38-41] However, all other examples of bridging carbonyl or isocyanide ligands involve a direct metal–metal bond.[42-44] A factor which may contribute to the novel carbon monoxide and isocyanide insertion reactions described here is the unsaturated nature of the palladium ions in **1** which allows the substrates access to the metal ions. However, coordination

Chart II

Figure 1. An ORTEP drawing of $Pd_2(dpm)_2(\mu\text{-CNCH}_3)(CNCH_3)_2{}^{2+}$ showing 50% thermal ellipsoids.

Figure 2. Idealized structural types for bis(diphenylphosphino)methane bridged binuclear complexes.

unsaturation alone is not sufficient to cause such insertions since a number of very similar Pd(I) complexes including $Pd_2(CNCH_3)_6{}^{2+}$, $Pd_2(CNCH_3)_4Cl_2$, and $Pd_2(CNCH_3)_4$-$(PPh_3)_2{}^{2+}$ do not react with carbon monoxide or isocyanides to produce bridging carbonyl or isocyanide ligands.

Another important feature of the complexes is the presence of the flexible bridging bis(diphenylphosphino)methane ligand. This ligand is capable of bridging two planar metal ions in the three ways shown in Figure 2; the side by side dimers I, the A-frame complexes II, and the face to face dimers III. In terms of these idealized structures the insertion of carbonyl or isocyanide ligands into metal–metal bonds converts the side by side dimers I into the A-frame complexes II. The addition of sulfide to $Rh_2(dpm)_2(CO)_2Cl_2$ to form $Rh_2(dpm)_2(\mu\text{-S})(CO)_2$ (6) is an example of a conversion of a face to face dimer III into an A-frame II. These transformations occur with minimal steric inhibition due to the bridging nature of the diphosphine ligand. On the other hand, a lone bridging carbon monoxide or isocyanide with 2 Å M–C bond distances and a 120° M–C–M bond angle would place the two metal atoms only 3.5 Å apart. At that close proximity, ligand–ligand contacts for all but the smallest ligands would be a significant source of strain.

The bridging carbonyl and isocyanide ligands of these palladium complexes contrast strongly with observations on some related manganese complexes shown in Chart II. Thermolysis of $Mn_2(dpm)_2(CO)_6$ converts it into $Mn_2(dpm)_2(\mu\text{-CO})(CO)_4$ with a doubly bridging carbonyl which acts as a two-electron donor via the carbon lone pair to one manganese and as a two-electron donor through its CO π bond to the second manganese.[45,46] Consequently each manganese retains an 18-electron count and the Mn–Mn bond is not broken. A similar four-electron donating, doubly bridging isocyanide ligand is present in $Mn_2(dpm)_2(\mu\text{-}p\text{-CNC}_6H_4CH_3)(CO)_4$, which is derived from $Mn_2(dpm)_2(\mu\text{-CO})(CO)_4$ by the addition of p-tolyl isocyanide and subsequent thermolysis of the product $Mn_2(dpm)_2(CO)_5(p\text{-CNC}_6H_4CH_3)$.[47] Recent X-ray crystallographic results have confirmed the presence of this novel bridging isocyanide.[48] The comparison of the behavior of these palladium and manganese complexes reveals that the electronic preference of the metal can dictate the bonding mode
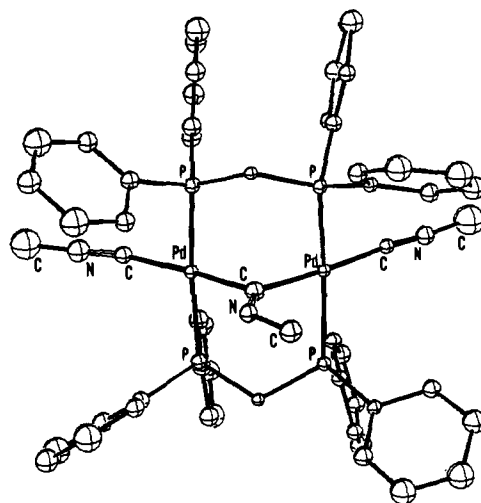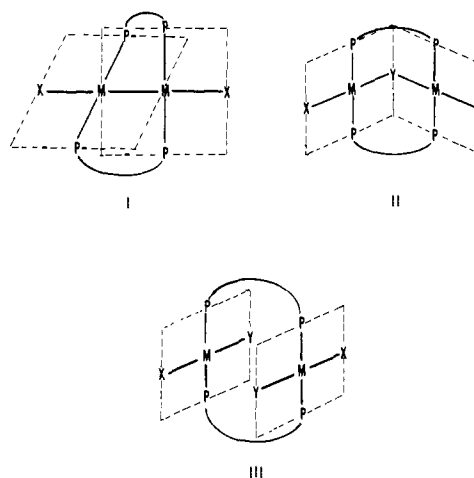
of a bridging carbonyl or isocyanide ligand in complexes with rather similar structures.

Finally it should be noted that the terminal ligands exercise control over the reactivity of metal–metal bonds in the dimeric $Pd_2(dpm)_2X_2$ and $Pt_2(dpm)_2X_2$ complexes. The data for chloride and iodide complexes are particularly germane. In both cases the equilibrium constants for the formation of the carbonyl bridged species decrease when the terminal anion is changed from chloride to iodide. At first sight this trend appears surprising since the higher trans effect of the iodide ligands should produce a weaker metal–metal bond in the iodide complexes than in the chloride complexes. This expectation is borne out in the Raman spectral data for the $Pt_2(dpm)_2X_2$ complexes. The Pt–Pt stretching frequencies and presumably the bond strengths decrease in the order $Pt_2(dpm)_2Cl_2 >$ $Pt_2(dpm)_2I_2$.[4] However, consideration of the trans effects in the product carbonyls suggests that the metal carbonyl bond should be weaker in $M_2(dpm)_2(\mu\text{-CO})I_2$ than in M_2-$(dpm)_2(\mu\text{-CO})Cl_2$ because of the greater trans effect of the iodide ligands. Thus the predicted trend of metal–metal bond strength in the reactants 1 and of metal–carbonyl bond strengths in the carbonyl bridged products 2 counterbalance one another so that $M_2(dpm)_2(\mu\text{-CO})I_2$ is less stable toward decarbonylation than is $M_2(dpm)_2(\mu\text{-CO})Cl_2$.

and Matthey Bishop Corp. for a loan of precious metal salts.

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Active Intermediates in the Reduction of Nitric Oxide by Ammonia over a CoY Zeolite

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Abstract: The reduction of nitric oxide by ammonia over a CoY zeolite has been studied using both conventional kinetic techniques and dynamic infrared spectroscopy. The $[Co^{II}(NH_3)(NO)_2]^{2+}$ complex was observed under steady-state reaction conditions, and the decay of the complex in the absence of gas-phase NO yielded turnover frequencies in good agreement with those obtained from the overall kinetic data. The nitrosyl ligands react with weakly coordinated NH_3 rather than with the more strongly coordinated ammonia. In agreement with this observation the order of the reaction with respect to NH_3 varied from approximately first order at low partial pressures of NH_3 to nearly zero order at higher partial pressures. A reaction order of 0.3 was observed for NO. A kinetic isotope effect of 1.5 is consistent with the breaking of an N–H bond in the rate-limiting step of the reaction. The overall reaction rate goes through a reversible maximum at 85 °C, and the decrease in activity at higher temperatures is attributed to a decrease in the number of complexes.

Introduction

The catalytic reduction of nitric oxide by ammonia over transition metal ions in zeolites has been demonstrated, and in the case of CuY zeolites a reasonable mechanism has been proposed.[1-3] Cobalt(II) ions in a Y-type zeolite are likewise active as a catalyst,[4] although the kinetics of the reaction over the two metal ions are different. With the CuY zeolite the reaction was first order with respect to nitric oxide partial pressure and the reaction was continuous at pressures approaching 500 Torr.[1] By contrast, over the CoY zeolite the reaction was <0.5 order with respect to nitric oxide, and partial pressures of nitric oxide greater than 10 Torr resulted in side reactions

which poisoned the catalyst. From a practical standpoint, this reaction has been proposed as a means of removing nitric oxide from stack gases,[5] and in this application the lower order in NO partial pressure is an advantage since the effluent streams may contain only low levels of nitric oxide.

In the present work attention has been given to the reactive intermediates in the catalytic process. The CoY zeolite was particularly promising for this investigation since several nitrosyl complexes in the zeolite have already been characterized by infrared spectroscopy,[6] and it was even suggested that the $[Co^{III}(NH_3)_n NO]^{2+}$ complex was an intermediate in the reaction scheme.[4]