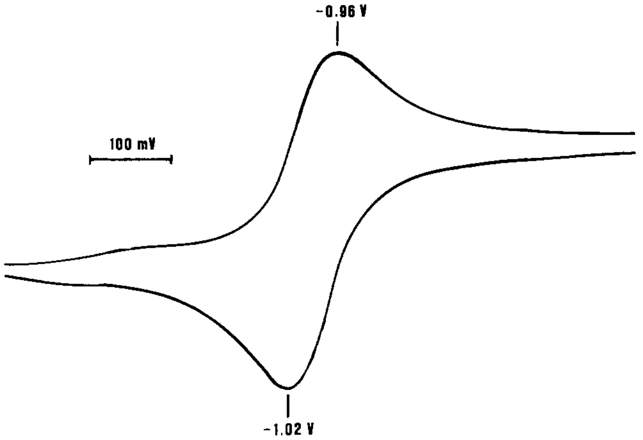

Figure 3. Cyclic voltammogram of 3 in CH_3CN with $N(C_4H_9)_4PF_6$ as the supporting electrolyte. Potentials shown are vs. SCE.

duction is illustrated in Figure 3. The reduction potential is -0.99 V vs SCE. The peak separation of 60 mV is consistent with a one-electron process. Electrochemical studies have demonstrated the general irreversibility of Ti(IV) reductions.[32] The metal–metal interaction present in 3 presumably results in the novel reversibility of this formally Ti(IV)–Ti(III) couple.

The synthetic route established here, and confirmed by the crystallographic data, provides a new and direct route to novel heterobimetallic species. Interactions between early and late transition metals are forced by the geometry of the "metalloligand" 1. Novel reactivity patterns are expected for such new heterobimetallic species and are exemplified by the novel electrochemical properties of compound 3. The nature of the product of the reduction of 3 as well as the chemistry of other complexes (specifically Rh) of the "metalloligand" 1 are the subject of current work. The result of these studies will be reported in due course.

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Registry No. 1, 95616-02-7; 2, 95616-03-8; 3, 95616-05-0; PSH, 3190-79-2; $(C_5H_5)TiCl(SCH_2CH_2P(C_6H_5)_2)$, 95616-06-1; $(C_5H_5)_2TiCl_2$, 1271-19-8; $Cu(CH_3CN)_4BF_4$, 15418-29-8; Cu, 7440-50-8; Ti, 7440-32-6; iodomethane, 74-88-4.

Supplementary Material Available: Tables S-I–S-IV listing temperature factors, hydrogen atom parameters, angles and distances associated with phenyl and cyclopentadienyl rings, and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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Synthesis of New CO Complexes of Palladium[1]

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The palladium(II) complexes $Pd(NO_2)_2L_2$ (L = PPh_3, $PMePh_2$, PMe_2Ph, PEt_3) react with CO to form $Pd_4(CO)_5L_4$. These reaction products have been characterized by IR and ^{31}P, ^1H, and ^{13}C NMR spectroscopy. $Pd_4(CO)_5(PPh_3)_4$ crystallized in the monoclinic space group $C2/c$ with $Z = 4$, $a = 24.957$ (5) Å, $b = 16.138$ (3) Å, $c = 17.758$ (3) Å, and $\beta = 103.47$ (2)°. The palladium atoms are at the corners of a distorted tetrahedron in which five of the six edges are bridged by the carbonyl ligands. The unbridged edge has a Pd–Pd distance of 3.209 (1) Å, indicating the absence of a metal–metal bond. The average bonding Pd–Pd distances are 2.753 (1) and 2.758 (13) Å. The average Pd–P distance is 2.318 (2) Å, and the average Pd–C–Pd angle is 82.0°. $Pd(NO_2)_2(PEt_2Ph)_2$ and $PdCl(NO_2)(PEt_2Ph)_2$ react with CO to form the novel Pd(I) dimer $Pd_2(CO)Cl_2(PEt_2Ph)_3$, which was also structurally characterized by X-ray crystallography. The compound crystallized in the monoclinic space group $P2_1/a$ with $Z = 4$, $a = 20.041$ (3) Å, $b = 11.353$ (3) Å, $c = 19.920$ (5) Å, and $\beta = 129.16$ (1)°. The molecule is dimeric with a Pd–Pd bond and is the first example of a semibridging carbonyl ligand in palladium complexes. Pd2 has roughly square-planar geometry with two phosphines, one chloride, and Pd1 comprising its coordination sphere. One phosphine, one chloride, Pd2, and the carbonyl ligand comprise the coordination sphere of Pd1. The semibridging carbonyl produces severe distortion in the coordination geometry of both Pd1 and Pd2. Some important distances and angles include Pd1–Pd2 = 2.6521 (3) Å, Pd1–C = 1.874 (3) Å, Pd2–C = 2.110 (3) Å, and Pd1–C–Pd2 = 83.3 (1)°.

Introduction

The synthesis of low-valent palladium complexes is of interest because of their importance in catalysis and organic synthesis.[2-5] Relatively few general methods for their preparation are available that permit their derivatization. Among them are the reduction of Pd(II) complexes with hydrazine and CO reduction of palladium acetate in acetic acid[6] in the presence of tertiary phosphine and isonitrile ligands. In our continuing studies of NO_2 ligands as oxidants, we have recently reported[7] the synthesis of $Pd_4(CO)_5(PMePh_2)_4$ from the reaction between CO and Pd-

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Table I. Elemental Analyses

compd	% anal. calcd (found)				
	C	H	N	O	Cl
$K_2[Pd(NO_2)_4]$			15.20	34.72	
			(14.90)	(35.50)	
trans-$Pd(NO_2)_2(PMePh_2)_2$	52.15	4.38	4.68	10.69	
	(52.24)	(4.36)	(4.42)	(10.39)	
trans-$Pd(NO_2)_2(PMe_2Ph)_2$	40.47	4.63	5.90		
	(40.58)	(4.93)	(5.65)		
trans-$Pd(NO_2)_2(PPh_3)_2$	59.80	4.15	3.87		
	(60.04)	(4.11)	(3.22)		
trans-$Pd(NO_2)_2(PEt_3)_2$	33.15	6.90	6.44		
	(33.19)	(7.10)	(6.23)		
trans-$Pd(NO_2)_2(PCy_3)_2$	56.96	8.70	3.69		
	(57.36)	(8.87)	(3.72)		
trans-$Pd(NO_2)_2(PEt_2Ph)_2$	45.24	5.65	5.28		
	(45.35)	(5.73)	(5.06)		
trans-$PdCl(NO_2)(PEt_2Ph)_2$	46.16	5.77	2.69		6.81
	(45.90)	(5.92)	(2.24)		(6.86)
$PdCl_2(PMePh_2)_2$	54.05	4.54			12.27
	(58.82)	(4.85)			(10.27)
$Pd_4(CO)_5(PMePh_2)_4$	50.08	4.39			
	(50.52)	(4.43)			
$Pd_4(CO)_5(PPh_3)_4$	57.26	3.71			
	(57.16)	(4.12)			
$Pd_2(CO)Cl_2(PEt_2Ph)_3$	46.18	5.95			8.75
	(45.95)	(5.56)			(8.49)

Table II. Spectroscopic Properties

compd	$\delta(P)^a$	$\delta(N)^b$	${}^2J_{P-N}{}^c$	$\delta(H)^d$	${}^2J_{P-H}{}^c$	$\delta(C)^e$	${}^1J_{P-C}{}^c$	$\nu_{asym}{}^f$	$\nu_{sym}{}^f$	δ^f	ρ^f
$Na_2[Pd(NO_2)_4]$		−2.0						$-NO_2$			
trans-$Pd(NO_2)_2(PMePh_2)_2$	5.3	−85.2	2.5	1.88	4	12.4	15	1398 s	1335 s	325 s	595 s
								(1370 s)	(1305 s)	(320 s)	(575 s)
trans-$Pd(NO_2)_2(PMe_2Ph)_2$		−86.3	2.9	1.67	4	12.4	15	1395 s	1325 s	823 s	585 s
								(1370 s)	(1305 s)	(820 s)	(565 s)
trans-$Pd(NO_2)_2(PPh_3)_2$								1415 s	1330 s	825 s	590 s
trans-$Pd(NO_2)_2(PEt_3)_2$		−87.2	2.9			14.6	13	1400 s	1330 s	820 s	590 s
								(1365 s)	(1310 s)	(818 s)	(570 s)
trans-$Pd(NO_2)_2(PCy_3)_2$											
trans-$PdCl(NO_2)(PEt_2Ph)_2$	15.9										
trans-$PdCl_2(PMePh_2)_2$	24.9			1.95							
trans-$PdCl_2(PEt_2Ph)_2$	16.3										

[a] The ${}^{31}P$ chemical shifts are reported with respect to 85% H_3PO_4. [b] The ${}^{15}N$ chemical shifts are referenced to aqueous $Na^{15}NO_3$. [c] The coupling constants are reported in Hz. [d] The ${}^1H$ chemical shifts are referenced to tetramethylsilane. [e] The ${}^{13}C$ chemical shifts are referenced to tetramethylsilane. [f] The infrared frequencies are in cm^{-1}. Frequencies in parentheses refer to ${}^{15}N$-substituted species.

$(NO_2)_2(PMePh_2)_2$. These studies have now been extended to the reactions of other $Pd(NO_2)_2L_2$ complexes with CO, which result in the formation of new Pd(I) and Pd(0) clusters. Prior to the present study, only six other Pd(0) carbonyl clusters have been reported.[6,8,9] The synthesis of new low-valent palladium complexes of CO from readily accessible Pd(II) complexes is described below.

Results and Discussion

The oxygen atom transfer reactions of $Ni(NO_2)_2L_2$ have been studied extensively.[10-14] The reaction of the nickel complexes with CO is associative and results in the quantitative formation of $Ni(NO)(NO_2)L_2$ and CO_2. These studies have been extended to palladium complexes to ascertain the role that the central metal plays in determining the products obtained from these interesting reactions. Palladium(II) complexes were selected because they are isostructural and isoelectronic with the nickel complexes. In addition, since relatively few palladium nitrosyl complexes had been reported,[15-17] it was hoped that the reaction between CO and $Pd(NO_2)_2L_2$ might prove to be a useful method for their synthesis.

Several $Pd(NO_2)_2L_2$ complexes with tertiary phosphines were prepared (Table I) and characterized by IR, ${}^{31}P$ NMR, and ${}^{15}N$ NMR spectroscopy (Table II) and structural methods.[18] The tertiary phosphines including PPh_3, $PMePh_2$, PMe_2Ph, PEt_2Ph, PEt_3, and PCy_3, were selected as ligands because of their range of donor properties, steric features, and solubility of their palladium derivatives. The $Pd(NO_2)_2L_2$ complexes were prepared from the reaction of $K_2Pd(NO_2)_4$ with the tertiary phosphine ligand in a water/acetone mixture:

$$K_2Pd(NO_2)_4 + 2L \rightarrow Pd(NO_2)_2L_2 + 2KNO_2 \qquad (1)$$

Due to the expense of $Na^{15}NO_2$, the ${}^{15}N$ derivatives were prepared from $PdCl_2L_2$:

$$PdCl_2L_2 + 2Na^{15}NO_2 \rightarrow Pd({}^{15}NO_2)_2L_2 + 2NaCl \qquad (2)$$

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The structures of $Pd(NO_2)_2(PEt_3)_2$ and $Pd(NO_2)_2(PMePh_2)_2$ have been determined by X-ray crystallography.[18] Each complex has trans geometry and possesses N-bonded nitro groups. The $^{31}P\{^1H\}$ and $^{15}N\{^1H\}$ NMR spectra of the ^{15}N-substituted (98%) $PMePh_2$, PMe_2Ph, PCy_3, and PEt_3 complexes indicate that the trans isomer with N-bonded nitro groups predominates in solution (Table II). Each ^{15}N-substituted complex has a ^{31}P and/or ^{15}N NMR spectrum that consists of a triplet due to coupling between the phosphorus ligands and the two equivalent $-NO_2$ groups. The $^2J_{N-P}$ coupling constants (2.5–2.9 Hz) are nearly identical for each of these complexes (Table II). In contrast to the corresponding nickel complexes, which are fluxional[11,19] at room temperature due to the rapid equilibrium between the $-NO_2$ and $-ONO$ isomers, the palladium nitro complexes have narrow resonances (1–2 Hz) and well-resolved coupling with ^{15}N. Also unlike the nickel complexes, only Pd–N-bonded species were detectable in the ^{31}P NMR spectra, indicating that $Pd-NO_2$ is the preferred bonding mode. The ^1H and ^{13}C NMR spectra were also useful in deducing the solution geometries of PdX_2L_2. Jenkins and Shaw[20] have shown that virtual coupling of the phosphorus nuclei in trans isomers of $PMeR_2$ complexes results in triplets in both the ^1H and ^{13}C NMR spectra of the methyl groups, while the cis isomers have the expected methyl doublets. The ^1H NMR spectra of the methylphosphine ligands ($PMePh_2$ and PMe_2Ph) are triplets with $^2J_{P-H}$ of 4 Hz, confirming the trans stereochemistry of these complexes.

The dinitro complexes have strong absorption bands in the infrared spectrum. ν_{asym} and ν_{sym} occur at frequencies higher than those in the spectrum of free nitrite ion as has been found previously for N-bonded NO_2 groups.[21] The lack of splitting of these IR bands is in agreement with trans geometry. The assignment of ν_{asym}, ν_{sym}, and δ vibrations was confirmed by ^{15}N substitution (Table II). In addition to these three vibrations of the $-NO_2$ ligands, a medium to strong band in the 585–645-cm^{-1} region was also observed to shift by ca. 20 cm^{-1}. The shift is too large for a Pd–N vibration. Burmeister and Timmer[22] have assigned the band in this region to ρ_{wag}, which is in accord with its large ^{15}N isotopic shift.

The $PdCl_2L_2$ complexes were prepared as described by Grim et al.[23] Comparison of the spectroscopic properties with those previously reported indicates that these $PdCl_2L_2$ complexes are mixtures of cis and trans isomers. However, in most cases, reaction 2 produces good yields of the trans isomers, and consequently, it was not necessary to separate the cis and trans isomers of $PdCl_2L_2$. The ^{31}P NMR spectrum of $PdCl(NO_2)(PEt_2Ph)_2$ substituted with ^{15}N consists of a doublet with $^2J_{P-N}$ similar to that of *trans*-$Pd(NO_2)_2L_2$ and indicates that the chloro nitro complex also has trans geometry. ^{31}P peaks due to traces of $PdCl_2(PEt_2Ph)_2$ and $Pd(NO_2)_2(PEt_2Ph)_2$ were also present.

The reaction between CO and $Pd(NO_2)_2L_2$ (L = $PMePh_2$, PMe_2Ph, PPh_3, PEt_3) at ambient temperature proceeds according to reaction 3. The progress of reaction 3 was followed with ^{31}P NMR spectroscopy, which showed that as many as seven distinct phosphorus-containing species appeared during the course of this reaction (ca. 10 h). Thus far, two types of complexes from these reactions have been isolated and characterized: the tetranuclear cluster and PdL_4 (L = $PMePh_2$). The complex with ν_{CO} = 1740 cm^{-1}, which was reported earlier,[7] has been isolated as a tan solid but decomposed under vacuum, N_2, CO, and CO_2. Consequently, its structure and composition remain unknown, although its infrared spectrum and instability are consistent with a CO_2 complex analogous to $Ni(PCy_3)_2(CO_2)$.[24] In an attempt to isolate the postulated CO_2 intermediate, the palladium tricyclohexylphosphine complex was prepared and treated with CO, and the reaction was monitored by infrared spectroscopy. The infrared spectrum showed that a new band developed at 1738 cm^{-1} upon addition of CO to a dichloromethane solution of $Pd(NO_2)_2(PCy_3)_2$. However, the starting material was the only solid that was isolated from this solution.

$$Pd(NO_2)_2L_2 + CO = Pd_4(CO)_5L_4 + N_2O + CO_2 + PdL_4 + \ldots \quad (3)$$

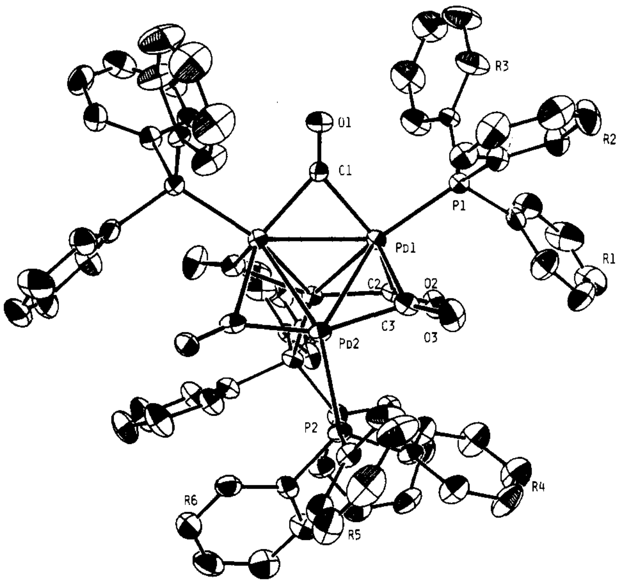

Figure 1. Molecular structure and numbering scheme for $Pd_4(CO)_5(PPh_3)_4$. The hydrogen atoms are omitted for clarity.

Although both Pd(II)–NO_2 and Ni(II)–NO_2 complexes are reduced to Pd(0) and Ni(0) by CO, all of the nitrogen originally present as $-NO_2$ in the palladium complexes is converted to N_2O, with no direct evidence for the formation of palladium nitrosyls, in marked contrast with the nickel analogues, which form nickel nitrosyls quantitatively. The reduced palladium products are also dependent upon the tertiary phosphine ligand in $Pd(NO_2)_2L_2$. Moreover, one tertiary phosphine ligand is lost upon reduction of $Pd(NO_2)_2L_2$ to $Pd_4(CO)_5L_4$ and is ultimately incorporated into the byproduct PdL_4, while both tertiary phosphine ligands are retained in the coordination sphere of nickel. The reactions of the palladium complexes are also much slower (10 h) than those of their nickel counterparts (0.5 h). The origin of these dramatic differences has not been established, but it seems plausible that unstable and reactive palladium nitrosyl complexes are responsible. Andrews and co-workers[15] have shown that $[Pd(NO)Cl]_x$ is formed from the reaction between olefins and $PdCl(NO_2)(CH_3CN)_2$. Thus, it is possible that the initial reaction of CO with $Pd(NO_2)_2L_2$ forms a palladium nitrosyl complex, which subsequently reacts to form N_2O and the Pd(0) species. The ^{31}P NMR spectra of these reacting solutions show that a single palladium species is formed during the first 0.5 h of the reaction, and infrared spectra of these same solutions exhibit several bands in the 1700-cm^{-1} region of the spectrum. Reaction between CO and $Pd(NO_2)_2L_2$ substituted with ^{15}N did not produce shifts in these IR bands, and consequently, they are not due to PdNO groups.

The structures of two $M_4(CO)_5L_4$ (M = Pt, L = PMe_2Ph; M = Pd, L = $PMePh_2$) complexes have been reported previously,[7,25] but only as communications. The crystals of these two complexes were small, and the quantity and quality of data were limited. Consequently, the structure of $Pd_4(CO)_5(PPh_3)_4$ was determined

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Table III. M-M Distances (Å) and Dihedral Angles (deg) in M_4 Clusters

atom 1	atom 2	Pd-PPh_3	Pd-$PMePh_2$	Pt-PMe_2Ph
M1	M1	2.753 (1)	2.750 (2)[a]	2.790 (7)
M1	M2	2.748 (1)		2.750 (6)
M1′	M2	2.767 (1)		2.754 (6)
M2	M2	3.209 (1)	3.365 (2)	3.543 (8)
dihedral angle		84	93	96.8

[a] Only the average Pd-Pd distance was given in the paper.[7]

Table IV. Crystallographic Data at 24 °C[a]

mol formula	$Pd_4(CO)_5(P(C_6H_5)_3)_4$
mol wt	1614.82
cryst shape	diamond
cryst dimens, mm	0.13 × 0.11 × 0.10
cryst system	monoclinic
space group	*C2/C*
cell dimens[b]	
a, Å	24.957 (5)
b, Å	16.138 (3)
c, Å	17.758 (3)
β, deg	103.47 (2)
V, Å^3	6956 (2)
Z	4
d_{obsd},[c] g cm^{-3}	1.52
d_{calcd}, g cm^{-3}	1.542
radiation, Å	0.710 69
monochromator	graphite crystal
data colln method	Wyckoff scan
scan, deg min^{-1}	19.5
scan range *ω*, deg	1.2
scan to bkgd time	2:1
decompn of stds	not significant
2*θ* limit, deg	50
no. of unique data (*h*,*k*,±*l*)	4543
no. of data used in the calcns ($I > 2.5\sigma(I)$)	3097
abs coeff (*μ*), cm^{-1}	11.44

[a] The standard deviation of the least significant figure is given in parentheses in this and other tables. [b] Cell dimensions were obtained from a least-squares refinement of setting angles of 25 reflections in the 2*θ* range 17–30°. [c] Density was determined by flotation in a solution of potassium iodide.

from crystals of suitable size and quality (Figure 1). The cluster is tetrameric with the palladium atoms located at the corners of a distorted tetrahedron. Five of the six edges are bridged by carbonyl ligands. The unbridged edge has a nonbonded Pd2–Pd2′ distance of 3.209 (1) Å. The three other independent Pd–Pd distances include Pd1–Pd1′ = 2.753 (1) Å, Pd1–Pd2 = 2.748 (1) Å, and Pd1′–Pd2 = 2.767 (1) Å. The dihedral angle formed by the two planes, Pd1,Pd1′,Pd2 and Pd1,Pd1′,Pd2′, is 84°, which is 14° larger than the corresponding dihedral angle of a regular tetrahedron (70.5°). Comparison of this dihedral angle for the three complexes that have been structurally characterized shows a flattening of the tetrahedron along the 2-fold axis with the larger nonbonded M–M distance accompanied by a larger dihedral angle. Although comparison of the metrical details of the three structures should be viewed with caution because of the limited accuracy of the previous structure determinations, the nonbonded M–M distance does not correlate with the steric bulk of the phosphine but rather with its basicity (Table III), with the more basic phosphine producing the larger dihedral angle.

There have been numerous discussions of the bonding–structure relationships in transition-metal carbonyl clusters (see the reviews by Lauher,[26] Teo,[27] and Hoffmann[29] and references therein, for example). However, the metal framework of $M_4(CO)_5L_4$ appears not to have been discussed specifically, even though it has been known since 1969.[25] The number of electrons predicted for a *regular* tetrahedral array of transition-metal atoms with their attendant ligands is 60 from any of the theories or rules thus far developed.[26–29] Indeed, there are numerous tetrahedral M_4 clusters that conform to the 60-electron rule,[28] including $Ni_4(CO)_6(P(C_2H_4CN)_3)_4$.[30] For this reason, several attempts were made to prepare $Pd_4(CO)_6L_4$ by reaction with excess CO. Examination of these solutions by ^{31}P NMR spectroscopy revealed only broad signals that are temperature dependent. Unfortunately, it was not possible to determine whether the fluxional character of these solutions was due to the formation of $Pd_4(CO)_6L_4$ or to some other interesting process. In any case, the only compounds that have been isolated from these solutions have the composition $Pd_4(CO)_5L_4$. This fact combined with the flattening of the tetrahedron with increasing ligand basicity has led us to conclude that molecular orbitals that lie along the open tetrahedral edge are *σ* antibonding with respect to a sixth CO ligand.

The average C–O distance is 1.152 (9) Å, and the individual distances do not differ from each other significantly. The average Pd–C–Pd angle is 82.2°, and the individual angles also do not differ significantly. There are statistical differences in the Pd–C–O angles (131.7–146.5°), but they are relatively small. On the other hand, there are significant differences in the Pd–C distances (1.988 (10)–2.230 (8) Å). The origin of these large differences in the Pd–C bonds does not appear to be associated with the steric effects of the phenyl rings, and consequently they are likely due to electronic effects. The two independent Pd–P distances are identical (2.318 (2) Å). No other important structural features are unusual in any respect.

The reactions of $Pd_4(CO)_5L_4$ are still being investigated. Although the tetrameric species are relatively reactive, they appear to be the thermodynamically most stable species in the series of palladium carbonyl clusters that have been prepared thus far[6–9,31] since they are the end products of several reaction sequences. The red cluster[9] reported to be $Pd_3(CO)_3(PPh_3)_3$ with ν_{CO} 1840 cm^{-1} is probably the tetramer prepared in the present investigation. The colors and IR spectra reported for $Pd_3(CO)_3(PPh_3)_3$ and $Pd_4(CO)_5(PPh_3)_4$ are the same, and they cannot be differentiated by C and H analysis. A total of five different types of palladium(0) carbonyl clusters (Pd_3, Pd_4, Pd_7, Pd_{10}, and Pd_{12}) have now been reported, and three of them have been structurally characterized.[6–8] The Pd_7, Pd_{10}, and Pd_{12} complexes appear to have been investigated extensively, and the two interesting examples of their structures have been reported. Each of these clusters was prepared by reductive carbonylation of different Pd(II) complexes. The Pd_7 cluster was formed from the reaction of CO with $Pd(\eta^1,\eta^3\text{-}C_8H_{12})(PMe_3)$, while the Pd_{10} and Pd_{12} species were prepared from the reaction of $Pd(OAc)_2$ with CO in water/acetic acid.[6] Thus far, there is no evidence that any of these clusters can be interconverted.

The palladium(I) dimer, $Pd_2(CO)Cl_2(PEt_2Ph)_3$, was formed from the reaction of CO with $Pd(NO_2)_2(PEt_2Ph)_2$ in dichloromethane. Consequently, the solvent must be the source of the chloride ligand in the palladium(I) product. Even though the dichloromethane was purified by storing over sodium carbonate and distilled immediately prior to use, it was possible that the starting material, $Pd(NO_2)_2(PEt_2Ph)_2$, may have reacted with HCl or Cl_2 to form $PdCl(NO_2)(PEt_2Ph)_2$. To assess this possibility, *trans*-$PdCl(NO_2)(PEt_2Ph)_2$ was prepared from the reaction of $PdCl_2(PEt_2Ph)_2$ with $NaNO_2$ and its reaction with CO examined. This reaction also resulted in the formation of the Pd(I) dimer.

The structure of the dimer was determined by X-ray crystallography (Table VI). A perspective view showing the numbering scheme and molecular geometry is shown in Figure 2. Selected interatomic distances and angles for the non-hydrogen atoms are given in Table VII. Several least-squares planes of the two palladium atoms and their attendant ligand atoms are also listed.

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Table V. Selected Bond Distances and Angles for $Pd_4(CO)_5(PPh_3)_4$

	Distances (Å)		
	Pd–Pd		
Pd1–Pd1′	2.753 (1)	Pd1–Pd2′	2.767 (1)
Pd1–Pd2	2.748 (1)	Pd2–Pd2′	3.209 (1)
	Pd–P		
Pd1–P1	2.318 (2)	Pd2–P2	2.318 (2)
	Pd–C		
Pd1–C1	2.096 (9)	Pd1–C3	2.117 (8)
Pd1–C2	2.230 (8)	Pd2–C3	2.047 (9)
Pd2–C2′	1.99 (1)		
	C–O		
C1–O1	1.149 (13)	C3–O3	1.142 (9)
C2–O2	1.166 (9)		
	Angles (deg)		
	Pd–Pd–Pd		
Pd1–Pd2–Pd1′	59.89 (3)	Pd2–Pd1–Pd2′	71.16 (3)
Pd1′–Pd1–Pd2	60.39 (2)	Pd1–Pd2–Pd2′	54.69 (2)
Pd1′–Pd1–Pd2′	59.72 (2)/ 180.10	Pd1–Pd2′–Pd2	54.15 (2)/ 180.00
	P1 angles		
P1–Pd1–C1	97.0 (2)	P1–Pd1–Pd1′	145.65 (6)
P1–Pd1–C2	97.7 (2)	P1–Pd1–Pd2	145.07 (6)
P1–Pd1–C3	97.9 (3)	P1–Pd1–Pd2′	136.04 (6)
	P2 angles		
P2–Pd2–C2′	106.3 (2)	P2′–Pd2′–Pd1	157.21 (7)
P2–Pd2–C3	95.4 (3)	P2′–Pd2′–Pd2	121.00 (5)
P2–Pd2–Pd1	139.20 (6)		
	C1 angles		
Pd1′–Pd1–C1	48.9 (2)	Pd2′–Pd1–C1	98.7 (2)
Pd1′–C1–Pd1	82.1 (5)	Pd1–C1–O1	138.9 (2)
Pd2–Pd1–C1	99.3 (2)		
	C2 angles		
Pd2′–Pd1–C2	45.3 (2)	Pd1–Pd2–C2′	112.8 (2)
Pd1–Pd2′–C2	52.9 (2)	Pd2–Pd2′–C2	38.7 (2)
Pd1–C2–Pd2′	81.8 (3)	Pd1–C2–O2	131.7 (7)
Pd1′–Pd1–C2	105.0 (2)	Pd2′–C2–O2	146.5 (7)
Pd2–Pd1–C2	91.5 (2)		
	C3 angles		
Pd2–Pd1–C3	47.6 (2)	Pd1–Pd2′–C3′	107.0 (2)
Pd1–Pd2–C3	49.8 (2)	Pd2–Pd2′–C3′	94.4 (2)
Pd1–C3–Pd2	82.6 (3)	Pd1–C3–O3	135.5 (7)
Pd1′–Pd1–C3	105.4 (2)	Pd2–C3–O3	141.9 (7)
Pd2′–Pd1–C3	106.6 (2)		

The structure consists of two nonequivalent palladium atoms with a semibridging carbonyl group (Figure 2). The Pd2 coordination sphere is approximately planar with P2–Pd2–P3 = 170.51 (3)°, Cl2–Pd2–P2 = 92.11 (3)°, Cl2–Pd2–P3 = 91.63 (3)°, C1–Pd2–P2 = 89.21 (8)°, C1–Pd2–P3 = 90.29 (8)°, and C1–Pd2–Cl2 = 159.8 (1)°. Essentially square-planar geometry was found for Pd2 when P2, P3, Cl1, and the midpoint between Pd1 and C1 were designated as the four ligands for Pd2.

The coordination environment around Pd1 is strongly distorted from square-planar geometry with Pd2–Pd1–P1 = 154.42 (9)°, Cl1–Pd1–P1 = 100.98 (3)°, C1–Pd1–P1 = 102.4 (1)°, and C1–Pd1–Cl1 = 156.6 (1)°. The interaction between the carbonyl group and Pd2 distorts the coordination geometry at Pd1 by reducing the C1–Pd1–Pd2 angle from the 90° expected for square-planar geometry to 52.18 (9)°. If the midpoint of the Pd2–C1 bond, Cl1, and P1 are designated as the three ligands for Pd1, then nearly trigonal-planar geometry is found for Pd1. In spite of the severe distortion, Pd1 and its four ligands are essentially coplanar (rms deviations of plane 1 <0.091 (4) Å). The dihedral angle between the least-squares plane at Pd1 (plane 1) and the least-squares plane at Pd2 (plane 3) is found to be 88.7° and shows that the ligand planes of the two palladium atoms are mutually perpendicular.

Although there are enough ligands for each palladium atom in this dimer to be four-coordinate, the ligand environment is inherently unsymmetric because of its composition. Cotton[32] has pointed out that carbonyl ligands can be semibridging in inherently unsymmetrical environments as in the present case. The semibridging CO ligand has Pd–C distances that differ by 0.23 Å and has a Pd1–C–O angle of 151.7 (3)°. These structural parameters

Table VI. Crystallographic Data at 24 °C[a]

mol formula	$Pd_2(CO)Cl_2(PEt_2Ph)_3$
mol wt	810.3
cryst shape	rectangular needle
cryst dimens, mm	0.23 × 0.17 × 0.15
cryst system	monoclinic
space group	$P2_1/c$
cell dimens[b]	
a, Å	20.041 (3)
b, Å	11.353 (3)
c, Å	19.920 (5)
β, deg	129.16 (1)
V, Å^3	3515 (1)
Z	4
d_{obsd},[c] g cm^{-3}	1.47 (1)
d_{calcd}, g cm^{-3}	1.53
radiation, Å	(Mo Kα) 0.710 73
monochromator	graphite crystal
supplied power	50 kV, 25 mA
data collcn method	θ–2θ scan
scan, deg min^{-1}	variable determined as a function of peak intensity: shell 1, 5.0–29.3; shell 2, 2.0–29.3
scan range 2θ, deg	Mo Kα_1 – 1.0 to Mo Kα_2 + 1.0
ratio of total bkgd time to peak scan time std reflcns	0.5 (12,0,0), (060), (009) after every 197 readings
decompn of stds	not significant
2θ limit, deg	shell 1, 0–30; shell 2, 30–50
no. of unique data	5590
no. of data used in the calcns ($I > 3\sigma(I)$)	4527
abs coeff (μ), cm^{-1}	13.13 (Mo Kα)

[a] The standard deviation of the least significant figure is given in parentheses in this and other tables. [b] Cell dimensions were obtained from a least-squares refinement of setting angles of 25 reflections in the 2θ range 17–30°. [c] Density was determined by flotation in aqueous potassium iodide.

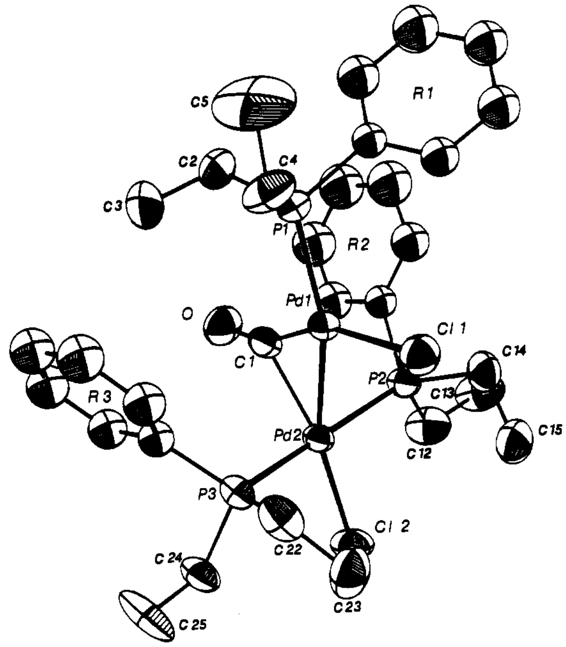

Figure 2. Molecular structure and numbering scheme for $Pd_2(CO)Cl_2(PEt_2Ph)_3$. The hydrogen atoms are omitted for clarity.

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Table VII. Geometrical Parameters for $Pd_2(CO)Cl_2(PEt_2Ph)_3$ [a]

Bond Distances (Å)

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Pd1	Pd2	2.6521 (3)	P3	C6	1.809 (3)	C16	C17	1.388 (4)
Pd1	Cl1	2.4132 (9)	P3	C22	1.814 (4)	C16	C21	1.374 (5)
Pd1	P1	2.2827 (8)	P3	C24	1.823 (3)	C17	C18	1.376 (6)
Pd1	Cl1	1.874 (3)	O	C1	1.156 (4)	C18	C19	1.360 (7)
Pd2	Cl2	2.3682 (8)	C2	C3	1.509 (6)	C19	C20	1.352 (7)
Pd2	P2	2.3338 (8)	C4	C5	1.486 (6)	C20	C21	1.359 (6)
Pd2	P3	2.3346 (8)	C6	C7	1.391 (4)	C22	C23	1.515 (6)
Pd2	C1	2.110 (3)	C6	C11	1.383 (5)	C24	C25	1.510 (5)
P1	C2	1.806 (4)	C7	C8	1.381 (5)	C26	C27	1.384 (5)
P1	C4	1.819 (4)	C8	C9	1.366 (6)	C26	C31	1.378 (5)
P1	C26	1.819 (3)	C9	C10	1.366 (5)	C27	C28	1.372 (5)
P2	C12	1.823 (3)	C10	C11	1.381 (5)	C28	C29	1.354 (5)
P2	C14	1.823 (4)	C12	C13	1.509 (6)	C29	C30	1.366 (6)
P2	C16	1.805 (3)	C14	C15	1.492 (5)	C30	C31	1.388 (5)

Bond Angles (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Pd2	Pd1	Cl1	104.48 (2)	Pd2	P2	C14	111.3 (1)	C6	C11	C10	121.1 (3)
Pd2	Pd1	P1	154.42 (3)	Pd2	P2	C16	114.8 (1)	P2	C12	C13	115.9 (3)
Pd2	Pd1	C1	52.18 (9)	C12	P2	C14	105.1 (2)	P2	C14	C15	113.5 (3)
Cl1	Pd1	P1	100.98 (3)	C12	P2	C16	102.8 (2)	P2	C16	C17	122.7 (3)
Cl1	Pd1	C1	156.6 (1)	C14	P2	C16	107.0 (2)	P2	C16	C21	118.3 (3)
P1	Pd1	C1	102.4 (1)	Pd2	P3	C6	116.7 (1)	C17	C16	C21	118.9 (3)
Pd1	Pd2	Cl2	155.56 (3)	Pd2	P3	C22	110.0 (1)	C16	C17	C18	118.9 (4)
Pd1	Pd2	P2	84.78 (2)	Pd2	P3	C24	115.0 (1)	C17	C18	C19	121.1 (4)
Pd1	Pd2	P3	88.21 (2)	C6	P3	C22	105.6 (2)	C18	C19	C20	119.8 (4)
Pd1	Pd2	C1	44.56 (9)	C6	P3	C24	103.3 (2)	C19	C20	C21	120.5 (5)
Cl2	Pd2	P2	92.11 (3)	C22	P3	C24	105.2 (2)	C16	C21	C20	120.8 (4)
Cl2	Pd2	P3	91.63 (3)	Pd1	C1	Pd2	83.3 (1)	P3	C22	C23	113.5 (3)
Cl2	Pd2	C1	159.8 (1)	Pd1	C1	O	151.7 (3)	P3	C24	C25	115.4 (3)
P2	Pd2	P3	170.51 (3)	Pd2	C1	O	125.0 (2)	P1	C26	C27	118.2 (2)
P2	Pd2	C1	89.21 (8)	P1	C2	C3	118.3 (3)	P1	C26	C31	123.7 (3)
P3	Pd2	C1	90.29 (8)	P1	C4	C5	113.0 (3)	C27	C26	C31	118.1 (3)
Pd1	P1	C2	111.5 (1)	P3	C6	C7	122.7 (3)	C26	C27	C28	121.2 (3)
Pd1	P1	C4	116.7 (2)	P3	C6	C11	119.1 (2)	C27	C28	C29	120.2 (4)
Pd1	P1	C26	114.01 (9)	C7	C6	C11	118.1 (3)	C28	C29	C30	120.0 (3)
C2	P1	C4	105.6 (2)	C6	C7	C8	119.9 (4)	C29	C30	C31	120.2 (4)
C2	P1	C26	103.5 (2)	C7	C8	C9	121.2 (4)	C26	C31	C30	120.3 (4)
C4	P1	C26	104.4 (2)	C8	C9	C10	119.5 (4)				
Pd2	P2	C12	114.9 (1)	C9	C10	C11	120.2 (4)				

Weighted Least-Squares Planes

Equation of plane:[b] $Ax + By + Cz - D = 0$

plane no.	A	B	C	D	atom[c]	x	y	z	dist, Å	esd, Å
1	0.3819	−0.9241	−0.0178	−3.9809	Pd1*	4.4109	6.0832	1.9326	0.010	0.000
					Pd2*	3.5718	5.7992	−0.5671	−0.004	0.000
					Cl1*	6.6189	7.0338	1.7235	−0.022	0.001
					P1*	4.1776	6.0203	4.2024	−0.062	0.001
					C1*	2.7976	5.3397	1.3400	0.091	0.004
					$\chi^2 = 6152$					
					O	1.7717	4.8434	1.5379	0.154	0.003
2	0.3804	−0.9247	−0.0172	−3.9902	Pd1*	4.4109	6.0832	1.9326	0.010	0.000
					Pd2*	3.5718	5.7992	−0.5671	−0.004	0.000
					Cl1*	6.6189	7.0338	1.7235	−0.025	0.001
					P1*	4.1776	6.0203	4.2024	−0.060	0.001
					$\chi^2 = 5519$					
					C1	2.7976	5.3397	1.3400	0.094	0.004
					O	1.7717	4.8434	1.5379	0.159	0.003
3	−0.9133	−0.4013	−0.0697	−5.5740	Pd2*	3.5718	5.7992	−0.5671	0.024	0.000
					Cl2*	3.7004	6.0132	−2.9220	−0.015	0.001
					P2*	2.7836	7.9825	−0.3255	−0.149	0.001
					P3*	4.6759	3.7431	−0.6269	−0.155	0.001
					$\chi^2 = 39\,738$					

dihedral angles between planes: 1-2 = 0.1°; 1-3 = 88.7°; 2-3 = 88.6°

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] A, B, C, and D are constants, and x, y, and z are orthogonalized coordinates. [c] Atoms in the plane are designated by asterisks.

compare favorably with those cited by Cotton for the Fe–C–Fe angle and differential distance in $C_4(CH_3)_2(OH)_2Fe_2(CO)_6$ of 165° and 0.55 Å, respectively. Both palladium atoms have formal oxidation states of I with a Pd–Pd bond, which accounts for its structure and observed diamagnetism. The palladium atoms are in reduced oxidation states, and some direct donation of electron density from Pd2 into the empty π orbital of the Pd1–CO ligand would produce the semibridging interaction observed between Pd2 and CO. The Pt_2CO unit in $Pt_2Br_2(\mu\text{-}CO)(PPh_3)_3$ recently reported by Goodfellow et al.[33] is similar to the present palladium complex in all essential details, and they have drawn similar conclusions regarding its structure.

Experimental Section

The palladium complexes were prepared from palladium powder (99.95%), which was obtained from Gallard-Schlessinger. A suspension of 3.0 g of Pd in 50–80 mL of distilled water was treated with Cl_2 until all of the palladium had dissolved. After being purged with N_2, the resulting deep red solution was filtered and 6.9 g of KNO_2 was added, producing a yellow solution from which 7.0 g (95%) of $K_2Pd(NO_2)_4$ was obtained by crystallization at 278 K. A solution of KCl (6.72 g) and $PdCl_2$ (4.0 g) in a minimum amount of water was heated to give an orange-brown solution. Cooling produced 5.9 g of crystalline K_2PdCl_4 (80%). The tertiary phosphine ligands were used as obtained from Strem Chemical, Newburyport, MA. Carbon monoxide was purchased from the Matheson Co. and was used as received. The solvents were analytical grade and were degassed by freeze–thaw procedures. The infrared spectra were obtained by using a Perkin-Elmer Model 983 infrared spectrometer. The ^{31}P and ^{13}C NMR spectra were obtained on a Bruker WM 250 NMR spectrometer operating at 101.2 and 62.9 mHz, respectively. The ^{15}N NMR spectra were obtained with the Bruker WH 90 located at Arizona State University. Elemental analyses were obtained from the University of Arizona Analytical Center and from Atlantic Research Laboratories, Atlanta, GA.

$Pd(NO_2)_2L_2$. The dinitro complexes (L = $PMePh_2$, PMe_2Ph, PPh_3, PEt_2Ph, PEt_3, PCy_3) were prepared according to the following general procedure. A solution of 2 mmol of $K_2Pd(NO_2)_4$ in 30 mL of water/acetone (30/5) was treated with 4 mmol of the ligand and stirred for 2 h. The initially homogeneous solution rapidly turned cloudy with formation of product. The precipitate was dissolved by addition of 20 mL of CH_2Cl_2 to the reaction mixture with stirring. The yellow dichloromethane solution was separated from the colorless aqueous layer, dried, and treated with 20 mL of hexane. In each case, the $Pd(NO_2)_2L_2$ complex crystallized on standing at 278 K. The pale yellow products were obtained in yields ranging from 85 to 90%. The elemental analyses are reported in Table I.

$PdCl_2L_2$. A solution of 2 mmol of K_2PdCl_4 in 30 mL of water/acetone (30/5) was treated with 4 mmol of the tertiary phosphine ligand ($PMePh_2$ or PEt_2Ph), and the mixture was stirred for 2 h, resulting in a yellow suspension. Additon of CH_2Cl_2 (20 mL) resulted in an almost colorless aqueous layer and a deep yellow dichloromethane layer. After the dichloromethane solution was separated and dried, 20 mL of hexane was added. The mixture was cooled to 278 K and allowed to stand for several hours, after which the $PdCl_2L_2$ complexes (Table I) were isolated as yellow needles in yields of 95%.

$PdCl(NO_2)(PEt_2Ph)_2$. Several procedures for preparing this complex were investigated. In no case was it possible to prepare the mixed-ligand complex spectroscopically free of the dichloride or dinitro derivative, but the following procedure produced materials of >95% purity (^{31}P NMR). A solution of 1 mmol of $PdCl_2L_2$ in 20 mL of dichloromethane was treated with a solution of KNO_2 (1 mmol) in 15 mL of H_2O, and the mixture was stirred for 4 h. Separation of the dichloromethane solution followed by drying, addition of 20 mL of hexane, and cooling to 278 K resulted in crystallization of the product (Table I).

$Pd_4(CO)_5(PMePh_2)_4$. A solution of $Pd(NO_2)_2(PMePh_2)_2$ (564 mg, 0.95 mmol) in oxygen-free dichloromethane (30 mL) was stirred vigorously under an atmosphere of CO for 12 h at 298 K. During this time, the intitially pale yellow solution turned deep red. The volume of the solution was reduced to 10 mL by evaporation under a stream of CO, and 30 mL of CO-saturated hexane was added. After the mixture was allowed to stand for 48 h under CO at 278 K, red crystals (222 mg) of $Pd_4(CO)_5(PMePh_2)_4$ formed, were collected by filtration, and were dried and stored under CO (Table I); ν_{CO} = 1840 cm^{-1}. The yellow mother liquor was allowed to stand at 243 K under N_2 overnight, which resulted in the deposition of yellow needles (78 mg). The infrared spectrum of the yellow complex exhibited no bands attributable to CO or NO_x, and its elemental analysis approximates that calculated for $Pd(PMePh_2)_4$. Anal. Calcd (found): C, 68.84 (71.13); H, 5.73 (6.32). The ^1H NMR spectrum of this compound indicated that hexane was present, but in quantities insufficient to account for the discrepancy in the elemental analyses.

$Pd_4(CO)_5(PPh_3)_4$. A suspension of $Pd(NO_2)_2(PPh_3)_2$ (200 mg, 0.276 mmol) in oxygen-free dichloromethane (30 mL) was stirred for 72 h under a CO atmosphere at 298 K. The resultant homogeneous red solution was filtered and the volume reduced to 5 mL under a stream of CO. Addition of CO-saturated hexane and cooling to 278 K resulted in the formation of deep red crystals of $Pd_4(CO)_5(PPh_3)_4$ (Table I).

Structural Studies

1. $Pd_2(CO)Cl_2(PEt_2Ph)_3$. Sample Preparation. A solution of $Pd(NO_2)_2(PEt_2Ph)_2$ (500 mg, 0.88 mmol) dissolved in 20 mL of dichloromethane was stirred with CO at 298 K for 48 h. The volume of the red-orange solution was reduced to 3 mL under CO. Addition of 20 mL of CO-saturated hexane followed by cooling to 273 K resulted in the formation of deep orange crystals of a size suitable for X-ray diffraction in 49% yield.

Data Collection and Structure Determination. Several crystals of $Pd_2(CO)Cl_2(PEt_2Ph)_3$ were mounted on glass fibers and coated with epoxy cement. One of them was mounted on a Syntex $P2_1$ autodiffractometer controlled by a Nova 1200 computer. The longest dimension of the crystal (201) was approximately parallel to the ϕ axis. Automatic centering, indexing, and least-squares routines[34] provided the cell dimensions, which are listed in Table IV along with other important crystallographic data. The intensity data for the $\pm h,k,l$ octants were collected under the conditions listed in Table IV. The data were reduced to F_o^2 and $\sigma(F_o^2)$ by published procedures. No correction for absorption was made. Lorenzt-polarization factors were calculated on the assumption of 50% mosaicity and 50% perfection of the monochromator crystal. The intensities of the 3 standard reflections were monitored after every 200 reflections and showed no significant variation in intensity (<2%) during data collection.

Neutral-atom scattering factors for the non-hydrogen atoms and corrections for the anomalous dispersion made for non-hydrogen atoms were taken from the tables of Cromer and Waber.[35] Hydrogen atom scattering factors were taken from the calculations of Stewart, Davidson, and Simpson.[36] The structure was refined by full-matrix least-squares techniques minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/[\sigma^2(F_o^2) + (\rho F_o^2)]$. The factor to prevent overweighting of strong reflections, ρ, was set equal to 0.03. The discrepancy indices, R_1 and R_2, are defined in the usual manner.

The structure was solved by direct methods in which the positions of the two palladium atoms, one phosphorus atom, and one chlorine atom were determined. The remaining 35 non-hydrogen atoms were located by successive isotropic refinements and difference electron density maps giving $R_1 = 0.079$ and $R_2 = 0.100$. All phenyl ring hydrogens were included as fixed contributions to the structure factors at idealized distances and angles. Successive difference electron density maps and refinement by counter-weighted full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms led to the location of the nine methyl hydrogen atoms, which were then included in subsequent refinements as fixed contributors. The positions of all hydrogen atoms are included as fixed contributors to the structure factors in the refinements. Final refinement using 4527 independent reflections[32] with $F_o^2 \geq 3\sigma(F_o^2)$ and $0.0° \leq 2\theta \leq 50.0°$ converged with $R_1 = 0.028$ and $R_2 = 0.035$ for 352 variables.[37] The standard deviation of an observation of unit weight defined by $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ was 1.58. The largest peak in the final electron density map was 0.48 e Å^3.

2. $Pd_4(CO)_5(PPh_3)_4$. Sample Preparation. Several attempts were made to obtain a suitable single crystal for X-ray diffraction studies, but attempts to collect data led to rapid crystal decomposition. Finally, a diamond-shaped crystal mounted in a glass capillary under CO pressure was found suitable for data collection.

Data Collection and Structure Determination. The lattice parameters were determined from the least-squares refinement of 21 independently centered reflections, $9° < 2\theta < 25°$. The ω-scan profiles of these reflections were extremely broad with the width at half-height being 1.2°. Since previous crystals decomposed very rapidly, a quick data collection was necessary. Data collection was carried out at room temperature with Mo Kα radiation by using a Wyckoff scan technique,[38] where only the

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(34) Programs used for centering of reflections, autoindexing, least-squares refinement of cell parameters, and data collection are in: "Syntex $P2_1$ Fortran Operation Manual"; Syntex Analytical Instruments: Cupertino, CA, 1975.

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(37) The 102, 011, 202, 200, 211, and 302 reflections were excluded from least-squares refinement due to a counter overflow that could not be properly scaled.

(38) The Wyckoff scan technique measures only the peak tops of the reflections and therefore may not be accurately measure intense broad reflections.

peak tops are sampled in ω (0.6° each side of Kα). One quadrant of data was collected $h,k,\pm l$ out to 45° in 2θ. The intensities of 2 standards were measured after every 98 reflections and showed no significant decay during the data collection period. The data was collected on a Syntex (Nicolet) $P2_1$ diffractometer equipped with a graphite-crystal monochrometer.

Solution and Refinement of the Structure. The structure determination and refinements were carried out with the Structure Determination Package[39] running on a PDP 11/34a computer. Phases provided by MULTAN were used to solve the structure with difference Fourier techniques used to locate the atoms not found in the E map. Isotropic refinement of the phenyl rings and anisotropic refinement of all other non-hydrogen atoms led to $R_1 = 0.061$, $R_2 = 0.064$ with a GOF of 2.4. Analysis of the weighting scheme and peak profiles lead to downweighting the more intense reflections by increasing the data stability constant (p)[40] from 0.03 to 0.06. The $I/\sigma(I)$ limit was set to 2.5 in order to maintain at least a 7:1 data to parameter ratio. All non-hydrogen atoms were refined isotropically for four cycles with hydrogen atoms added as fixed contributions to F_c at calculated positions. This led to the final tabulated results with $R_1 = 0.044$, $R_2 = 0.052$ and a goodness of fit value of 1.1.

Conclusions

The reactions of CO with $Pd(NO_2)_2L_2$ provide a general and useful synthetic method for preparing Pd(0) carbonyl clusters in high yield from air-stable, conveniently available starting materials. The fact that several different tertiary phosphine complexes undergo the same reaction allows the Pd(0) cluster to be derivatized. Other phosphine ligands such as PEt_2Ph led to the formation of unique Pd(I) dimers.

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Registry No. $K_2[Pd(NO_2)_4]$, 13844-89-8; *trans*-$Pd(NO_2)_2(PMePh_2)_2$, 73440-16-1; *trans*-$Pd(NO_2)_2(PMe_2Ph)_2$, 78520-98-6; *trans*-$Pd(NO_2)_2(PPh_3)_2$, 14409-50-8; *trans*-$Pd(NO_2)_2(PEt_3)_2$, 77010-09-4; *trans*-$Pd(NO_2)_2(PCy_3)_2$, 95464-58-7; *trans*-$Pd(NO_2)_2(PEt_2Ph)_2$, 77010-08-3; *trans*-$PdCl(NO_2)(PEt_2Ph)_2$, 95464-59-8; $PdCl_2(PMePh_2)_2$, 26973-01-3; $Pd_4(CO)_5(PMePh_2)_4$, 73956-31-7; $Pd_4(CO)_5(PPh_3)_4$, 85096-24-8; $Pd_2(CO)Cl_2(PEt_2Ph)_3$, 95464-60-1; *trans*-$PdCl_2(PEt_2Ph)_2$, 29484-77-3; $Na_2[Pd(NO_2)_4]$, 17031-23-1; K_2PdCl_4, 10025-98-6; Cl_2, 7782-50-5; Pd, 7440-05-3.

Supplementary Material Available: Positional and thermal parameters along with calculated and observed structure factors for $Pd_2(CO)Cl_2(PEt_2Ph)_3$ (Tables S-1–S-3) and for $Pd_4(CO)_5(PPh_3)_4$ (Tables S-4–S-6) (60 pages). Ordering information is given on any current masthead page.

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[39] Structure Determination Package (B. A. Frenz and Associates, Inc., College Station, TX 77840, and Enraf-Nonius, Delft, Holland).

[40] $w = 1/\sigma(F_o)^2 = 4F_o^2/[\sigma(F_o^2)^2 + (pF_o^2)^2]$.

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Multiple Bonds between Vanadium Atoms

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Opportunities are considered for extending the type of chemistry of vanadium(II) in which multiple bonds are formed between metal atoms in light of available experimental facts and molecular orbital calculations. The bond (2.200 Å) in $V_2(DMP)_4$ (DMP = 2,6-dimethoxyphenyl) is formulated as a $\sigma^2\pi^2\delta^2$ triple bond in an edge-sharing bioctahedron. It is argued that in some $V_2(XYZ)_4$ molecules $\sigma^2\pi^4$ triple bonds shorter than 2.20 Å should be stable provided the XYZ^- ligands are chosen to obviate rearrangement (such as that which occurs with $V_2(DMP)_4$) or further reaction. As a model system for both Fenske–Hall and Hartree–Fock calculations pertaining to $V_2(XYZ)_4$ molecules, $V_2(O_2CH)_4$ has been used. The two computations give orbital energies in excellent agreement. The calculations clearly indicate the stability of a $\sigma^2\pi^4$ V≡V bond. The failure of synthetic efforts to prepare $V_2(O_2CR)_4$ molecules is probably due to the even greater stability of $[V_3(\mu_3\text{-}O)(O_2CR)_6L_3]^n$ ($n = 0, 1+$) species. It is suggested that other XYZ ligands should be able to give isolable $V_2(XYZ)_4$ molecules. The bonding in the compound $V_2(PMePh_2)_4(H_2ZnH_2BH_2)_2$ is analyzed, and it is shown that a change in P–V–P bond angles could lead to the formation of a quadruple ($\sigma^2\pi^4\delta^2$) V–V bond.

Introduction

The ability of most of the d-block transition metal atoms to form metal–metal bonds of orders 2–4, based primarily on the overlap of d orbitals, is now well established.[2] If one examines the way in which the propensity for forming such bonds varies from element to element, one of the most conspicuous and important features of the pattern is that few such bonds are formed by the elements of the 3d series, i.e., Sc–Cu. Only chromium is known to form an extensive series of compounds, namely, those in which quadruple bonds occur.[2-4]

A question that naturally arises is whether the absence of compounds containing strong M–M bonds between atoms of other 3d metallic elements is to be ascribed to the inherent inability of these elements to form such compounds or simply to the failure of chemists to devise reactions and conditions suitable for isolating them. The answer to this question can be approached by both experimental and theoretical means. It is recognized, of course, that neither approach will ever lead to a proof of the negative, i.e., to proof that such bonds cannot under any circumstances exist. What we can hope to do by experiment is to achieve a proof of the positive, that is actually to isolate one or more such compounds, and thus show definitively that they can exist. This will always be the ultimate goal. In an effort to achieve it, however, we can seek guidance from theory as to the types of compounds that it is realistic to expect.

In this paper we shall do the following things: (1) We shall review some experimental facts that lead to the conclusion that vanadium is a 3d metal that holds promise of affording compounds with multiple metal–metal bonds. (2) We shall report a Hartree–Fock calculation on a model divanadium compound, $V_2(O_2CH)_4$, which provides further support for optimism regarding vanadium. (3) We shall relate the results of this calculation to some practical, experimental considerations. (4) We shall show that Fenske–Hall calculations on $V_2(O_2CH)_4$ give results in good

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