

with gas-tight syringes under N_2 , and frozen immediately in liquid N_2 . Room-temperature spectra were obtained with a flat cell under Ar. Estimates of spin concentrations were made by using known Mo(V) complexes ($K_3[Mo(CN)_8]$, $MoOCl(thiooxine)_2$)¹⁴ as standards. Estimates of g and A values were made by inspection of the measured spectra, using DPPH as standard.

Crystal Preparation. Crystals of the title compound $MoO_2(hbeH_2)$ were grown from dichloromethane. The compound crystallized as very thin rectangular plates. A plate was selected with dimensions in Table V and was mounted on the tip of a slim glass fiber with epoxy.

Crystallographic Data. The determination of the Bravais lattice and cell dimensions and the collection of intensity data were carried out with a Syntex P2₁ diffractometer equipped with a graphite monochromator. The cell constants were determined on the basis of the centering of 24 reflections with $9^\circ < 2\theta(Mo\ K\alpha) < 19^\circ$. After least-squares refinement of the setting angles, the crystal system and axis lengths were checked by using axial photographs. Several ω scans showed sharp Bragg peaks, width at half-height 0.27. The crystal and diffractometer data are listed in Table V. Data collection was carried out at room temperature with Mo $K\alpha$ radiation using a θ - 2θ scan technique. An octant of data was collected, hkl , out to $2\theta = 45^\circ$. The intensities of two standard reflections, measured every 98 reflections, showed no significant decay during data collection. The data revealed systematic absences unique to the nonstandard space group $Pcab$, which was transformed to the standard space group $Pbca$ prior to structure solution. The data were corrected for Lorentz and polarization effects and were also corrected for absorption by the Gaussian integration method.

Solution and Refinement. The structure determination and refinement were carried out with the SDP series of crystallographic programs on a PDP 11/34a computer.³⁰ MULTAN yielded the position

of the two independent molybdenum atoms. Subsequent difference Fourier techniques were used to locate the remaining independent non-hydrogen atoms of each molecule. Isotropic refinement of both molecules yielded $R_1 = 0.11$ and $R_2 = 0.13$. A difference map revealed the presence of a disordered dichloromethane molecule. The disorder model that was decided upon structurally resembles a staggered 1,2-dichloroethane molecule. However, the carbon-carbon bond is replaced by one carbon-chlorine bond from each of the disordered dichloromethane molecules. The solvent molecule was assigned an occupancy of 0.5 on the basis of a refinement of the occupancy factor of the chlorine atoms, which were not disordered with the carbon atoms. Refinement was continued with this disorder model and anisotropic thermal parameters for the molybdenum atoms and the oxo oxygen atoms. All the hydrogen atom positions were assigned an arbitrary isotropic thermal value of $B = 5.0 \text{ \AA}^2$.²³¹ These conditions gave final residual indices of $R_1 = 0.072$ and $R_2 = 0.071$ where refinement was based on the minimization of $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma(F_o)^2 + 0.25(cF_o)^2$ with $c = 0.03$. The highest peak from the final difference map was 1.1 e \AA^{-3} . The final fractional coordinates and thermal parameters of the refined atoms are listed in Table VII. The idealized hydrogen atom positions and a listing of the observed and calculated structure factors are available in the supplementary material.

Acknowledgment. The structure was determined in the Molecular Structure Laboratory of the University of Arizona, and we thank S. Merbs for assistance with portions of the structural studies. Financial support of this work by NIH Grant GM 08347 (J.T.S.) and ES 00966 (J.H.E.) is gratefully acknowledged.

Supplementary Material Available: Listings of calculated hydrogen atom positions, general temperature factor expressions, thermal parameters, and structure factors for $MoO_2(3-t-Bu-hbeH_2)$ (17 pages). Ordering information is given on any current masthead page.

(30) Computer program used for this analysis were: The Structure Determination Package (SDP) (B. A. Frenz & Associates, Inc., College Station, TX and Enraf-Nonius, Delft, Holland); MULTAN 80 (P. Main et al., University of York, York, England); ORTEP 2 (Johnson, C. K. Report ORNL-3794 Oak Ridge National Laboratory, Oak Ridge, TN). Both MULTAN 80 and ORTEP 2 are included in the SDP software.

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Contribution No. 6898 from the Arthur Amos Noyes Laboratory, California Institute of Technology, Pasadena, California 91125

Binuclear Complexes of Palladium(II) Containing 1,8-Diisocyano-*p*-menthane

CHI-MING CHE, FRANK H. HERBSTEIN, WILLIAM P. SCHAEFER, RICHARD E. MARSH, and HARRY B. GRAY*

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Well-characterized binuclear isocyanato complexes of palladium(II) are obtained with the bridging ligand 1,8-diisocyano-*p*-menthane (DMB). The ion $[Pd_2(DMB)_4]^{4+}$ reacts with X (Cl^- or Br^-) to give $[Pd_2(DMB)_4X]^{3+}$, where the X is positioned between the metal atoms, encapsulated in the complex. Reaction with I^- leads to an entirely different product, $Pd_2(DMB)_2I_4$, which has been characterized by X-ray crystallography: $Pd_2C_{24}N_4H_{36}I_4$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.766(4) \text{ \AA}$, $b = 15.123(8) \text{ \AA}$, $c = 9.703(2) \text{ \AA}$, $\beta = 93.93(2)^\circ$, and $Z = 2$. The Pd atoms are square-planar coordinated to two CN groups and two I atoms; the DMB ligands are disordered across a center of symmetry. The coordination planes of the Pd atoms are tilted 35° from the perpendicular to the Pd-Pd vector, and a fifth (axial) site is occupied by an I atom from the other half of the dimer. The Pd...Pd distance, $4.582(1) \text{ \AA}$, is such that the ion $[Pd_2(DMB)_4]^{4+}$ can accommodate a Br^- or Cl^- ion between the Pd atoms.

Introduction

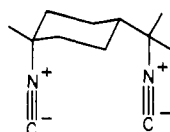
We have been studying for many years the spectroscopic and structural properties of d^8 -metal-isocyanide complexes.¹⁻³ Rhodium(I) and iridium(I) complexes have been extensively investigated, but studies involving nickel(II), palladium(II),

and platinum(II) have lagged because these divalent metals catalyze polymerization, hydrolysis, and dealkylation reactions of isocyanides.⁴⁻⁶ One method of avoiding these side reactions during synthesis is to use diisocyanide ligands that can bridge between two metal atoms to form binuclear species; one

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particularly good binucleating ligand of this type is DMB, or 1,8-diisocyanato-*p*-methane.^{7,8}



DMB

It has been shown that a binuclear Ni(II) complex of DMB, $[\text{Ni}_2(\text{DMB})_4]^{4+}$, is capable of encapsulating Cl^- or Br^- to form the stable species $[\text{Ni}_2(\text{DMB})_4\text{X}]^{3+}$; we have now extended this work and report here the preparation of some DMB compounds of Pd(II), including ones with encapsulated Cl^- and Br^- . We also report the synthesis and crystal structure of $\text{Pd}_2(\text{DMB})_2\text{I}_4$, in which iodide, instead of being encapsulated, has replaced two of the DMB linkages on each Pd atom.

Experimental Section

Materials. DMB was prepared and purified by standard procedures.⁸ $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$, $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$, and $\text{Pd}(\text{CH}_3\text{CN})_2\text{Br}_2$ were prepared by refluxing PdX_2 ($\text{X} = \text{Cl}$ or Br) in the appropriate nitrile solvent. Solvents were spectroscopic grade.

Physical Measurements. UV-vis spectra were recorded on a Cary 17 spectrophotometer. IR spectral measurements in the region 4000–500 cm^{-1} were made on a Beckman IR-4240, whereas far-IR spectra (500–50 cm^{-1}) were measured on a Perkin-Elmer 180 (Nujol mulls).

$[\text{Pd}_2(\text{DMB})_4\text{Cl}]\text{Y}_3$ ($\text{Y} = \text{ClO}_4$ or PF_6). A 0.5-g sample of DMB was slowly added to a well-stirred methanolic suspension of $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ (0.3 g in 20 mL of MeOH). A clear yellow solution formed (this was filtered if necessary) and excess LiClO_4 or KPF_6 (about 2 g) was added to the filtrate. A pale yellow solid precipitated on standing. This was filtered off, washed with a methanol-ether mixture (1:5), and dried under vacuum at room temperature; yield 80%. Anal. Calcd for $[\text{Pd}_2(\text{DMB})_4\text{Cl}][\text{ClO}_4]_3$: C, 44.07; H, 5.51; N, 8.57; Cl, 10.86. Found: C, 44.08; H, 5.59; N, 8.48; Cl, 10.77. IR $\nu(\text{C}\equiv\text{N})$: 2240 cm^{-1} (Nujol mull). Far-IR $\nu(\text{Pd}-\text{Cl})$: 201 cm^{-1} . Molar conductivity in nitromethane: 250 $\mu\Omega^{-1}$. UV-vis spectrum in CH_3CN , $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 360 br (890), 306 s (1.5×10^4).

$[\text{Pd}_2(\text{DMB})_4\text{Br}][\text{ClO}_4]_3$. This was prepared by essentially the same method as above except that $\text{Pd}(\text{CH}_3\text{CN})_2\text{Br}_2$ was used; yield 80%. Anal. Calcd for $[\text{Pd}_2(\text{DMB})_4\text{Br}][\text{ClO}_4]_3$: C, 42.62; H, 5.32; N, 8.29; Br, 5.91; Cl, 7.88. Found: C, 41.99; H, 5.62; N, 8.01; Br, 5.42; Cl, 7.90. IR $\nu(\text{C}\equiv\text{N})$: 2240 cm^{-1} (Nujol mull). Far-IR $\nu(\text{Pd}-\text{Br})$: 145 cm^{-1} (br).

$\text{Pd}_2(\text{DMB})_2\text{I}_4$. A methanolic solution of $[\text{Pd}_2(\text{DMB})_4\text{Cl}]^{3+}$ was prepared as described above. Excess sodium iodide (2 g) was added. The solution was left to stand for 1/2 h, during which time a yellowish orange solid precipitated. This was filtered off, washed with cold methanol and diethyl ether, and then recrystallized from CH_2Cl_2 ; yield 70–80%. Anal. Calcd for $\text{Pd}_2(\text{DMB})_2\text{I}_4$: C, 26.17; H, 3.27; N, 5.09; I, 46.12. Found: C, 26.32; H, 3.31; N, 5.07; I, 46.89. IR $\nu(\text{C}\equiv\text{N})$: 2200 cm^{-1} (nujol mull). UV-vis spectrum in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1}$): 402 sh, 352 (1600), 285 sh.

$[\text{Pd}_2(\text{DMB})_4][\text{ClO}_4]_4$. Treatment of $\text{Pd}(\text{NO}_3)_2$ (0.2 g) with excess DMB (0.4 g) in 20 mL of methanol gave a pale yellow solution. Addition of excess LiClO_4 resulted in the formation of a pale yellow solid in high yield (> 70%). The solid is unstable under UV light. Anal. Calcd for $[\text{Pd}_2(\text{DMB})_4][\text{ClO}_4]_4$: C, 42.0; H, 5.25; N, 8.17. Found: C, 42.04; H, 5.49; N, 8.37. In addition to strong peaks at 2240 cm^{-1} the IR spectrum (Nujol mull) of this solid showed the presence of several peaks in the 1550–1620- cm^{-1} region, thereby indicating the presence of a coordinated imino group.

X-ray Structural Determination of $\text{Pd}_2(\text{DMB})_2\text{I}_4$. Preliminary X-ray photographs indicated a monoclinic cell; systematic absences $h0l$, h and $l = 2n + 1$, and $0k0$, $k = 2n + 1$, indicate the space group $P2_1/n$, a special setting of $P2_1/c$ (No. 14) with equivalent positions $\pm (x,$

Table I. Crystal Data for $\text{Pd}_2(\text{DMB})_2\text{I}_4$ ($T = 21^\circ\text{C}$)

formula: $\text{Pd}_2\text{C}_{24}\text{N}_4\text{H}_{36}\text{I}_4$	$\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$
fw 1101.00	$\mu = 46.67 \text{ cm}^{-1}$
$a = 11.766 (4) \text{ \AA}$	cryst size: $\sim 0.09 \times 0.18 \times 0.30 \text{ mm}$ (10 sided, irregular)
$b = 15.123 (8) \text{ \AA}$	$d_x = 2.123 (1) \text{ g cm}^{-3}$
$c = 9.703 (2) \text{ \AA}$	space group $P2_1/n$ (No. 14)
$\beta = 93.93 (2)^\circ$	
$V = 1722.5 (10) \text{ \AA}^3$	
$Z = 2$	

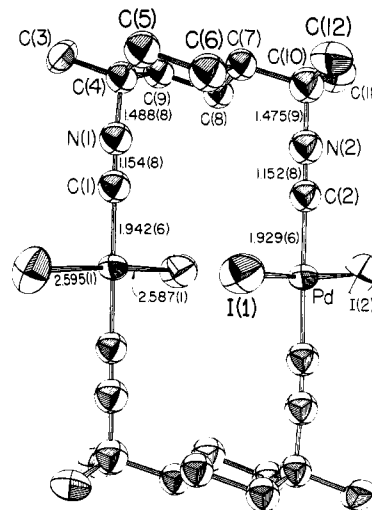


Figure 1. ORTEP drawing of the molecule showing important distances. Thermal ellipsoids are shown at the 50% probability level.

$y, z; 1/2 + x, 1/2 - y, 1/2 + z$). Cell dimensions were obtained by a least-squares fit to the setting angles of 15 reflections with $9^\circ < 2\theta < 26^\circ$. Crystal data are given in Table I.

Data were collected on a locally modified Syntex P2₁ diffractometer using graphite-monochromated Mo K α radiation. One set of data ($h, k, \pm l$) was collected with $3^\circ < 2\theta < 45^\circ$ at a scan speed of $2^\circ/\text{min}$, with background counted for half the scan time at each end of the θ - 2θ scan. A second set ($h, -k, \pm l$) was collected at a scan speed of $3^\circ/\text{min}$ in the 2θ range 3 – 55° . A total of 7288 intensities was measured, including four check reflections scanned every 96 reflections. These were corrected for Lorentz and polarization factors and for absorption by Gaussian integration over an $8 \times 8 \times 8$ grid (transmission factors fell into the range 0.54–0.68) and merged to give 4011 independent values, of which 3556 measured greater than zero and 2774 had $F_o^2 > 1.5\sigma(F_o^2)$. All 4011 reflections were used in the structure solution and refinement, which was by Patterson, Fourier, and full-matrix least-squares methods using the programs of the CRYM system. Scattering factors were taken from ref 9. The molecules crystallize on centers of symmetry and the DMB groups are disordered; the population parameter refined to 0.629 (8) for one orientation and $(1 - 0.629)$ for the other. The disorder results in some atoms (C4, C6, C8, and C10) of the two orientations being nearly superimposed. These were represented as single atoms, population 1.0, with isotropic temperature factors; the others were well separated and represented as partial atoms. The three methyl carbons of the DMB group with population 0.629 were given anisotropic thermal parameters, as were the Pd and the I atoms. Distances and angles involving the disordered atoms in the DMB group show large deviations from expected values; clearly our model does not represent the situation well. A final difference map showed excursions of $\pm 1.6 \text{ e \AA}^{-3}$ in the vicinity of I2 but nothing else greater than $\pm 1.0 \text{ e \AA}^{-3}$; in particular, there were no clues that suggested any different model for the carbon atoms of the DMB groups. Hydrogen atoms were included at calculated positions, assuming C–H distances of 0.95 \AA or were based on positions taken from difference maps. The final R index is 0.080 for all reflections with $F_o^2 > 0$ and 0.059 for those with $F_o^2 > 1.5\sigma(F_o^2)$ ($R = \sum |F_o - |F_c|| / \sum F_o$). The goodness-of-fit, $[\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, where $n = 4011 =$ number of reflections and $p = 125 =$ number of

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Table II. Final Atomic Parameters

atom	10 ⁴ x	10 ⁴ y	10 ⁴ z	B, Å ²	pop. ^a
Pd	6555.1 (4)	4100.6 (3)	4862.0 (5)	4.00 (1) ^b	
I1	4631.7 (4)	3808.6 (4)	3482.2 (5)	7.00 (1) ^b	
I2	8482.0 (4)	4266.3 (4)	6307.9 (6)	6.86 (1) ^b	
N1	7393 (5)	5174 (3)	2411 (6)	5.1 (1)	
N2	4318 (5)	6996 (4)	2753 (6)	5.4 (1)	
C1	7094 (5)	4766 (4)	3324 (7)	5.0 (1)	
C2	3982 (5)	6581 (4)	3633 (7)	4.6 (1)	
C3	8820 (9)	5269 (9)	730 (12)	7.1 (3) ^b	0.629 (8)
C4	7718 (5)	5723 (4)	1228 (7)	4.7 (1)	
C5	7970 (10)	6621 (7)	1777 (11)	5.6 (3)	0.629 (8)
C6	6830 (6)	7078 (5)	2289 (8)	6.1 (2)	
C7	5925 (8)	7055 (7)	1189 (10)	4.5 (2)	0.629 (8)
C8	5629 (5)	6144 (4)	654 (7)	4.8 (1)	
C9	6770 (9)	5696 (7)	186 (11)	4.9 (3)	0.629 (8)
C10	4759 (6)	7531 (5)	1636 (8)	5.8 (2)	
C11	3882 (12)	7574 (10)	513 (12)	8.4 (4) ^b	0.629 (8)
C12	5117 (12)	8396 (9)	2278 (14)	7.7 (3) ^b	0.629 (8)
C13	3823 (18)	8335 (15)	1341 (23)	7.1 (6)	0.371
C15	4695 (16)	6938 (12)	391 (19)	5.2 (4)	0.371
C17	6703 (14)	6498 (11)	991 (17)	4.4 (4)	0.371
C19	5791 (18)	7787 (15)	2066 (22)	6.6 (5)	0.371
C21	8796 (16)	6117 (13)	1556 (20)	5.5 (5)	0.371
C22	7561 (18)	5172 (14)	-56 (22)	6.5 (5)	0.371

^a Fractional occupancy; where no number is given, pop. = 1.0.

^b $B_{eq} = 8\pi^2 U_{eq}$; $U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*) \bar{a}_i \bar{a}_j]$; $\sigma(U_{eq}) = (1/6^{1/2}) \sigma(U_{ii}) / U_{ii} U_{eq}$.

Table III. Distances between Carbon Atoms

atom	atom	dist, Å	atom	atom	dist, Å
C3	C4	1.572 (14)	C4	C21	1.417 (20)
C4	C5	1.481 (13)	C4	C22	1.500 (22)
C5	C6	1.618 (13)	C4	C17	1.678 (17)
C6	C7	1.455 (12)	C17	C6	1.534 (18)
C7	C8	1.505 (12)	C6	C19	1.629 (23)
C8	C9	1.597 (12)	C19	C10	1.315 (23)
C9	C4	1.454 (12)	C10	C15	1.503 (20)
C7	C10	1.635 (12)	C15	C8	1.636 (19)
C10	C11	1.450 (15)	C8	C17	1.390 (17)
C10	C12	1.497 (15)	C10	C13	1.652 (23)

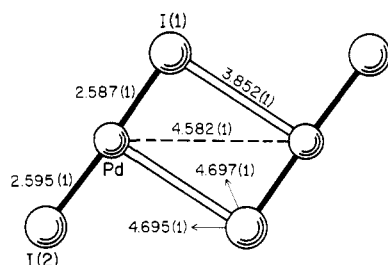


Figure 2. Drawing of the heavy atoms projected onto their plane.

parameters refined, is 1.70. Final values for the atomic parameters are given in Table II; important bond lengths and angles are listed in Tables III and IV (or shown in Figures 1 and 2).

Results and Discussion

We have shown that $[\text{Pd}_2(\text{DMB})_4]^{4+}$ can be obtained by the treatment of Pd(II) with an excess of diisocyanide ligand in aprotic solvents. The coordinated isocyanide group in the ClO_4^- salt is attacked readily by nucleophiles, resulting in the formation of coordinated imino species that exhibit infrared absorptions in the 1550–1620- cm^{-1} region. However, if the synthesis is carried out in the presence of 1 equiv of Cl^- or Br^- , the halide becomes encapsulated in the cation, forming the complex $[\text{Pd}_2(\text{DMB})_4\text{X}]^{3+}$; the presence of encapsulated halide greatly reduces the activating effect of Pd on the coordinated isocyanides (possibly by reducing the positive charge on the metal center), as evidenced by the absence of imino absorptions in the infrared spectra of $[\text{Pd}_2(\text{DMB})_4\text{X}]^{3+}$ species isolated

Table IV. Bond Angles in the Ordered Portion of the Molecule

atom	atom	atom	angle, deg
I1	Pd	C1	90.6 (2)
I1	Pd	C2	88.9 (2)
I2	Pd	C1	92.6 (2)
I2	Pd	C2	87.8 (2)
I1	Pd	I2	175.55 (2)
I1	Pd	I1'	91.53 (2)
I2	Pd	I1'	91.35 (2)
C1	Pd	C2	178.9 (3)
Pd	C1	N1	178.5 (6)
Pd	C2	N2	178.7 (6)
C1	N1	C4	176.9 (6)
C2	N2	C10	179.4 (6)

from various solutions. As with the binuclear Ni–DMB complexes,⁷ $[\text{Pd}_2(\text{DMB})_4]^{4+}$ shows a strong preference for Cl^- or Br^- over larger anions such as SCN^- in the encapsulation reaction.¹⁰

These results are quite different from those found in the $[\text{Rh}_2(\text{DMB})_4]^{2+}$ and $[\text{Ir}_2(\text{DMB})_4]^{2+}$ systems, where encapsulation of halide has not been observed.^{3,10,11} Since the binucleating-ligand bite and the metal–metal distances are comparable in all these complexes, it appears that the greater charge on the $[\text{Pd}_2(\text{DMB})_4]^{4+}$ and $[\text{Ni}_2(\text{DMB})_4]^{4+}$ ions is largely responsible for the encapsulation behavior.

The analytical data, conductivity measurements, and the far-infrared spectroscopic studies of $[\text{Pd}_2(\text{DMB})_4\text{Cl}][\text{ClO}_4]_3$ agree well with the chemical formulation. The observation of an intense $\nu(\text{Pd}-\text{Cl})$ stretch in the 201- cm^{-1} region (cf. $\nu(\text{Ni}-\text{Cl})$ 210 cm^{-1} in $[\text{Ni}_2(\text{DMB})_4\text{Cl}][\text{PF}_6]_3$)⁷ clearly shows that the chloride is in the bridging position. We have not been able to obtain good Raman spectra for $[\text{Pd}_2(\text{DMB})_4\text{X}][\text{Y}]_3$ species ($\text{X} = \text{Cl}, \text{Br}; \text{Y} = \text{ClO}_4$ or PF_6), because the sample decomposed during the measurements. Thus we do not know whether the halide in $[\text{Pd}_2(\text{DMB})_4\text{X}]\text{Y}_3$ bridges symmetrically or not. We are greatly interested in obtaining an X-ray crystal structure of a complex with an encapsulated halide, but so far satisfactory crystals have eluded us. The UV–vis spectrum of $[\text{Pd}_2(\text{DMB})_4\text{Cl}]^{3+}$ is remarkably similar to that of $[\text{Ni}_2(\text{DMB})_4\text{Cl}]^{3+}$. The intense band at 306 nm is assigned as the transition to the $d\sigma^*p\sigma$ ($p\sigma$ in this case is $p_z + \pi^*(\text{CNR})$)^{7,12} singlet state ($^1A_{1g} \rightarrow ^1A_{2u}$). Our finding that the band falls at a shorter wavelength than that ($\sim 320 \text{ nm}$)⁷ of the corresponding nickel complex accords with the expected metal-to-ligand charge-transfer character of the transition.

Structure of $\text{Pd}_2(\text{DMB})_2\text{I}_4$. The $\text{Pd}_2(\text{DMB})_2\text{I}_4$ molecule consists of two palladium atoms bridged by only two DMB groups, with two iodine atoms bonded to each palladium atom. The palladium atoms exhibit square-planar coordination, with two trans iodine atoms and two trans isocyanide units from DMB groups. Figure 1 is an ORTEP drawing of the molecule with population 0.629, showing some of the distances. Figure 2 is a drawing of the heavy atoms projected onto their plane. The average Pd–C distance (1.935 (15) Å) is normal for Pd–isocyanide complexes.¹³ The Pd–Pd distance within the cation is 4.582 (1) Å, which is slightly longer than M–M distances in other binuclear DMB complexes (for example, $d(\text{Ni}-\text{Ni}) = 4.33 \text{ Å}$ in $[\text{Ni}_2(\text{DMB})_2(\text{CN})_4]$ and $d(\text{Rh}-\text{Rh}) = 4.48 \text{ Å}$ ¹¹ in $[\text{Rh}_2(\text{DMB})_4]^{2+}$). Perhaps the most striking feature is that the Pd–Pd vector is not perpendicular to the I1–Pd–I2 line. Although the coordination planes of the Pd atoms are parallel, they are tilted such that I1 of one palladium lies close (3.852 (1) Å) to the second palladium atom (I1–Pd–Pd is 57.17 (1)°), thereby indicating the presence of a weak

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interunit Pd...I bonding interaction (Figure 2). The average Pd-I distance, 2.591 (1) Å, is comparable to those observed in other Pd(II)-I complexes: 2.492 (3) Å in the yellow form of *trans*-Pd(PPhMe₂)₂I₂¹⁴ and 2.58 (1) Å in *trans*-Pd-(PPh₃)₂I₂,¹⁵ where the palladium atoms have four nearest neighbors, and 2.638 (3) and 2.619 (3) Å in the red form of *trans*-Pd(PPhMe₂)₂I₂,¹⁴ where the palladium atom has five near neighbors.

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Registry No. [Pd₂(DMB)₄Cl][ClO₄]₃, 90857-67-3; [Pd₂(DMB)₄Cl][PF₆]₃, 90839-43-3; [Pd₂(DMB)₄Br][ClO₄]₃, 90839-45-5; Pd₂(DMB)₂I₄, 90839-46-6; [Pd₂(DMB)₄][ClO₄]₄, 90839-48-8.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen positional parameters, bond angles involving disordered atoms, and observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Chemistry of Sterically Crowded Aryloxy Ligands. 4.¹ Synthesis and Structure of Mixed Chloro Aryloxides of Tantalum

LINDA R. CHAMBERLAIN,[†] IAN P. ROTHWELL,^{*†} and JOHN C. HUFFMAN[†]

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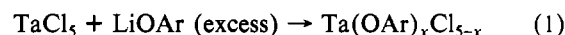
The reaction of tantalum pentachloride with a number of lithium 2,6-dialkylphenoxides has been investigated. The degree of substitution of OAr for Cl depends on the bulk of the alkyl substituents; for 2,6-dimethylphenoxide total substitution occurs to yield Ta(OC₆H₃Me₂-2,6)₅, while for the sterically very demanding 2,6-di-*tert*-butylphenoxide the disubstituted, mononuclear Ta(OC₆H₃-*t*-Bu₂-2,6)₂Cl₃ is given. Structural analysis of this compound shows a square-pyramidal arrangement about the tantalum with one aryloxy ligand occupying the apex and the other a basal position of the square pyramid. One of the *tert*-butyl groups of the basal aryloxy occupies the "open" site trans to the apical aryloxy, and one of the hydrogen atoms approaches within 2.67 Å of the metal center. The molecule crystallizes in space group C2/c with *a* = 17.477 (6) Å, *b* = 11.909 (3) Å, *c* = 28.319 (11) Å, β = 97.71 (1)°, *Z* = 8, and *d*_{calcd} = 1.587 g cm⁻³.

Introduction

Early-transition-metal alkoxides and phenoxides have been known for some time.^{2,3} In particular the pentaphenoxides of niobium and tantalum were first isolated as early as 1937 by Funk and co-workers.³ All of the mixed chloro phenoxides of these two metals, M(OPh)_xCl_{5-x} (M = Nb, Ta) have also been synthesized.⁴ It has been concluded, primarily on the basis of infrared spectral data and a comparison with the more extensively studied alkoxide chemistry, that all of these phenoxides are dimeric both as solids and in noncoordinating solvents and have phenoxide bridges.⁵ A common feature observed for the few structurally characterized early-transition-metal chloro phenoxides is the preference of μ-phenoxo rather than μ-chloro linkages.^{2,6,7} During our studies of the early-transition-metal organometallic chemistry associated with bulky aryloxides as ancillary ligands,⁸⁻¹¹ we have investigated the reaction of tantalum pentachloride with a number of 2,6-dialkylphenoxides to generate possible starting materials. The results of this study and their relevance to other areas of early-transition-metal chemistry are discussed in this paper.

Results and Discussion

Treatment of TaCl₅ with an excess of the lithium salts of various 2,6-dialkylphenoxides in benzene solvent leads to different degrees of substitution depending on the bulk of the alkyl substituents. With the relatively undemanding ligand 2,6-dimethylphenoxide (OC₆H₃Me₂-2,6) total substitution takes place to yield the white, crystalline Ta(OC₆H₃Me₂-2,6)₅ (I). However, with increasing alkyl bulk the degree of substitution drops off (eq 1). All of the partially substituted



OAr	<i>x</i>	
OC ₆ H ₃ Me ₂ -2,6	5	I
OC ₆ H ₃ Me- <i>t</i> -Bu-2,6	3	II
OC ₆ H ₃ - <i>i</i> -Pr ₂ -2,6	2	III
OC ₆ H ₃ - <i>t</i> -Bu ₂ -2,6	2	IV

compounds are yellow-orange solids, slightly soluble in hexane but more soluble in benzene or toluene. Mass spectral analysis of compounds I and IV shows a strong parent molecular ion with distinctive fragmentation due to loss of Cl (when present) or OAr. However, for compounds II and III, ions such as Ta(OC₆H₃Me-*t*-Bu-2,6)₄Cl⁺ and Ta(OC₆H₃-*i*-Pr₂-2,6)₃Cl₂⁺ were observed in low abundance. These we believe either to be indicative of the dimeric nature of these compounds in the solid state or else to be due to ligand exchange occurring within the mass spectrometer. Due to the low solubility of II and III solution molecular weight measurements were precluded.

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[†]Purdue University.

^{*}Indiana University.