Crystal and Molecular Structure of Anhydrous Tetraacetatodichromium

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Abstract: Tetraacetatodichromium has been prepared in crystalline form, apparently for the first time, by slow sublimation of the brown amorphous powder produced when water is removed under vacuum at 100 °C from the hydrate. The pale, yellow-brown crystals belong to the triclinic system and there is one molecule in the unit cell, which has the following dimensions: a = 7.583 (2), b = 8.688 (2), c = 5.178 (1) Å; α = 111.16 (2), β = 95.77 (2), γ = 98.16 (2)°; V = 310.7 (1) Å^3; d_{calcd} = 1.82 g/cm^3. The Cr–Cr distance of 2.288 (2) Å is significantly shorter than the distance of 2.362 (1) Å found in the hydrate. The crystal packing is qualitatively the same as that found in the isomorphous compounds $CrMo(O_2CCH_3)_4$ and $Mo_2(O_2CCH_3)_4$, but differs quantitatively in having very much shorter intermolecular O···Cr contacts (2.327 Å). However, this distance is greater than the Cr–OH$_2$ distance (2.272 Å) in the hydrate. It is suggested that there is a marked inverse correlation between Cr–Cr and Cr to axial ligand bond lengths and, therefore, that the Cr–Cr distance in a truly isolated $Cr_2(O_2CR)_4$ molecule might be very short.

The first dichromium tetracarboxylate compound, $Cr_2(O_2CCH_3)_4 \cdot 2H_2O$, was reported[1] in 1844, although, not surprisingly, the exact composition was not unambiguously established at that time. That the substance called "acetate de protoxyde de chrome", and described in this paper,[1] is what we now recognize to be $Cr_2(O_2CCH_3)_4 \cdot 2H_2O$ is evident from the method of preparation and the description of it, namely "petits cristaux rouge (et) brillants," which the action of air "transforme en une poudre verte." Upon calcination it afforded 41.8% Cr_2O_3, in tolerable agreement with the value of 40.4% calculated for $Cr_2(O_2CCH_3)_4 \cdot 2H_2O$.

An accurate determination of the crystal structure of the hydrate has been reported.[2] It showed, as expected, a bridged structure, with a water molecule axially coordinated to each chromium atom (Cr–O, 2.272 Å) and a Cr–Cr bond length (2.362 Å) intermediate between that in $Mo_2(O_2CCH_3)_4$[3] (2.093 (1) Å) where a quadruple bond exists between the metal atoms and that in $Cu_2(O_2CCH_3)_4 \cdot 2H_2O$[4] (2.614 Å) where there is no substantial metal-to-metal bond. We considered the possibility that the long distance of 2.36 Å observed in the hydrate, $Cr_2(O_2CCH_3)_4 \cdot 2H_2O$, might be caused by the competition of the water molecules for the same metal σ orbitals that are required to form a metal-to-metal σ bond. It was thus considered to be of interest to see whether an anhydrous $Cr_2(O_2CR)_4$ compound could be prepared in crystalline form and, if so, to see, by x-ray crystallography, whether the elimination of axial coordination results in a marked shortening of the Cr–Cr distance.

Added impetus to our work was given by arguments advanced in a recent publication,[5] purporting to show that no net metal–metal bonding interaction exists in $Cr_2(O_2CCH_3)_4(H_2O)_2$ despite the short (2.362 (1) Å)[2] metal–metal distance and the essential diamagnetism[6] of the compound. The arguments[5] were based on the photoelectron spectrum of gaseous $Cr_2(O_2CCH_3)_4$ interpreted in terms of an MO calculation upon $Cr_2(O_2CCH)_4(H_2O)_2$ using the atomic dimensions[2] for $Cr_2(O_2CCH_3)_4(H_2O)_2$.

Experimental Section

Synthesis and Crystallization of $Cr_2(O_2CCH_3)_4$. Anhydrous chromium(II) acetate powder was prepared by a standard method.[7] A small portion of the light brown product was sealed in an evacuated 11 × 70 mm glass tube. A few crystalline needles were obtained by sublimation at 225–230 °C for 12 days. The sublimation was carried out in a small muffle furnace and relied on the natural thermal gradients of the furnace. At only slightly higher temperature (240–245 °C) the sublimation was more rapid but yielded masses of very fine whiskers.

X-Ray Data Collection. The sublimation tube was opened under heavy, degassed mineral oil and a selected needle 0.05 × 0.05 × 0.5 mm was coated with epoxy, placed in a glass capillary, and mounted on a Syntex P$\bar{1}$ automated diffractometer. All data were collected at 20 ± 2 °C using Mo Kα radiation with a graphite-crystal monochromator in the incident beam. The automatic centering and indexing procedures followed have been described.[8] The triclinic cell parameters are the following: a = 7.583 (2), b = 8.688 (2), c = 5.178 (1) Å; α = 111.16 (2), β = 95.77 (2), γ = 98.16 (2)°; V = 310.7 (1) Å^3; d_{calcd} = 1.82 g/cm^3 for Z = 1 and a molecular weight of 340.18.

A total of 1076 unique reflections with $0° < 2\theta \leq 50°$ were collected using the θ–2θ scan technique with variable scan rates from 4.0 to 24.0°/min and a scan range from 2θ(Mo Kα_1) − 1.0° to 2θ(Mo Kα_2) + 1.0°. Intensities of three standard reflections measured after every 40 reflections showed no significant variation during data collection. Lorentz and polarization corrections were applied,[9] but absorption correction was deemed unnecessary, as μ = 18 cm^{-1} and transmission coefficients would range from ca. 0.86 to ca. 0.89.

Solution and Refinement of the Structure.[9] The structure was solved in the space group $P\bar{1}$ and refined using only those 688 reflections for which $F_o^2 > 3\sigma(F_o^2)$. The position of the chromium atom was determined using a three-dimensional Patterson function. These coordinates were refined by three cycles of least-squares refinement to give discrepancy indices

$$R_1 = \sum ||F_o| - |F_c|| / |F_o| = 0.280$$

$$R_2 = [\sum w(||F_o|/|F_c||)^2 / \sum w|F_o|^2]^{1/2} = 0.351$$

The function minimized during all least-squares refinements was $\sum w(|F_o| - |F_c|)^2$, where the weighting factor, w, equals $4F_o^2/\sigma(F_o^2)^2$. A value of 0.07 was used for p in the calculation of σ.[9]

A difference Fourier map revealed the positions of all the remaining non-hydrogen atoms. The positions of the non-hydrogen atoms were refined isotropically by five full-matrix least-squares cycles giving R_1 = 0.072 and R_2 = 0.090. These atoms were then refined anisotropically to convergence in three full-matrix least-squares cycles giving R_1 = 0.051 and R_2 = 0.064. The effects of anomalous dispersion were included in all structure factor calculations. An attempt to locate hydrogen atoms gave unsatisfactory results and was abandoned. The error in an observation of unit weight was 1.303. Tables of observed and calculated structure factor amplitudes are available.[10]

Results

The positional and thermal parameters are listed in Table I. The molecular structure of $Cr_2(O_2CCH_3)_4$ is shown in Figure 1. The axial site on Cr (trans to Cr′) is filled by an acetate oxygen atom from an adjacent molecule. The bond lengths and angles reported in Table II differ significantly from those of $Cr_2(O_2CCH_3)_4(H_2O)_2$ only in those parameters which involve the Cr–Cr′ and Cr–O axial vectors. Replacement of the water molecule in $Cr_2(O_2CCH_3)_4(H_2O)_2$ by the bridging

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0.4261 (2)	0.4613 (1)	0.1555 (2)	0.0098 (2)	0.0086 (1)	0.0154 (3)	0.0015 (3)	−0.0002 (4)	0.0103 (3)
O(1)	0.6536 (6)	0.5755 (5)	0.4453 (8)	0.0079 (9)	0.0121 (7)	0.015 (2)	−0.000 (1)	0.005 (2)	0.013 (2)
O(2)	0.7939 (7)	0.6499 (6)	0.1436 (9)	0.0125 (10)	0.0157 (8)	0.024 (2)	−0.003 (2)	0.004 (2)	0.021 (2)
O(3)	0.3343 (7)	0.6754 (6)	0.2683 (10)	0.0141 (10)	0.0128 (8)	0.029 (2)	0.011 (1)	0.013 (2)	0.018 (2)
O(4)	0.5201 (7)	0.2459 (6)	0.0306 (10)	0.0160 (10)	0.0091 (7)	0.031 (2)	0.006 (1)	0.013 (2)	0.017 (2)
C(1)	0.791 (1)	0.6443 (8)	0.383 (1)	0.012 (1)	0.0085 (9)	0.020 (3)	0.006 (2)	0.010 (3)	0.010 (2)
C(2)	0.963 (1)	0.7257 (10)	0.601 (1)	0.011 (1)	0.0157 (13)	0.028 (3)	0.001 (2)	−0.003 (4)	0.018 (3)
C(3)	0.378 (1)	0.7781 (9)	0.152 (1)	0.013 (1)	0.0095 (10)	0.021 (3)	0.005 (2)	−0.002 (3)	0.008 (3)
C(4)	0.302 (1)	0.9382 (10)	0.236 (2)	0.019 (2)	0.0097 (11)	0.048 (4)	0.012 (2)	0.003 (5)	0.010 (3)

[a] The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table II. Interatomic Distances (Å) and Angles (deg)

Intramolecular distances		Bond angles	
Cr-Cr	2.288 (2)	Cr'-Cr-O(1)	87.7 (1)
Cr-O(1)	2.033 (5)	Cr-Cr'-O(2)	89.9 (1)
Cr-O(2')	2.014 (5)	Cr'-Cr-O(3)	89.2 (2)
Cr-O(3)	1.988 (5)	Cr-Cr'-O(4)	89.1 (2)
Cr-O(4')	2.007 (5)	O(1)-Cr-O(2')	177.6 (2)
C(1)-O(1)	1.258 (8)	O(1)-Cr-O(3)	90.7 (2)
C(1)-O(2)	1.259 (8)	O(1)-Cr-O(4')	89.8 (2)
C(3)-O(3)	1.270 (8)	O(2')-Cr-O(3)	89.5 (2)
C(3)-O(4)	1.258 (8)	O(2')-Cr-O(4')	89.9 (2)
C(1)-C(2)	1.528 (9)	O(3)-Cr-O(4')	178.2 (2)
C(3)-C(4)	1.516 (10)	Cr-O(1)-C(1)	120.8 (4)
Intermolecular distance		Cr'-O(2)-C(1)	119.4 (5)
Cr-O(1')	2.327 (4)	Cr-O(3)-C(3)	119.2 (4)
Intermolecular angle		Cr'-O(4)-C(3)	118.6 (5)
Cr'-Cr-O(1')	164.6 (1)	O(1)-C(1)-O(2)	122.2 (6)
		O(3)-C(3)-O(4)	123.9 (6)
		O(1)-C(1)-C(2)	120.1 (6)
		O(2)-C(1)-C(2)	117.7 (6)
		O(3)-C(3)-C(4)	118.1 (6)
		O(4)-C(3)-C(4)	118.0 (6)

Table III. Selected Distances and Angles from Chromium(II) and Molybdenum(II) Carboxylates

Compound	M-M, Å	M-L, Å	M-M-L, deg
$Cr_2(O_2CCH_3)_4$	2.288 (2)	2.327 (4)	164.6 (1)
$Cr_2(O_2CCH_3)_4(H_2O)_2$	2.362 (1)	2.272 (3)	175.6 (1)
$Mo_2(O_2CCF_3)_4$[a]	2.090 (4)	2.72 (1)	161.0 (4)
$Mo_2(O_2CCF_3)_4(C_5H_5N)_2$[b]	2.129 (2)	2.548 (8)	171.0 (2)
$Mo_2(O_2CPh)_4$[c]	2.097 (1)	2.876 (2)	159.7 (1)
$Mo_2(O_2CPh)_4(MeOCH_2CH_2OMe)_2$[d]	2.100 (1)	2.663 (6)	169.9 (1)
$CrMo(O_2CCH_3)$[e]	2.050 (1)	2.548 (4)	161.2 (1)

[a] Reference 12. [b] Reference 13. [c] F. A. Cotton, M. Extine, and C. E. Rice, unpublished. [d] Reference 15. [e] Reference 11.

oxygen leads to a slight increase in the $Cr-O_{axial}$ distance. Additionally, formation of a four-membered ring containing two chromium atoms and two bridging oxygens forces the axial oxygen off the Cr-Cr' axis, as seen in the packing diagram in Figure 2. Presumably the observed angles represent a compromise between the "ideal" angles of Cr'-Cr-O(1)' = 180° and Cr-O(1)'-Cr' = 110-120°. Both the increase in the distance of the axial oxygen atom in $Cr_2(O_2CCH_3)_4$ and its displacement from the Cr-Cr' axis should work to strengthen the σ contribution to the Cr-Cr bond, and indeed the metal-metal distance observed here is 0.074 Å shorter than that in the hydrate. All these data are collected in Table III along with corresponding data for comparable dinuclear molybdenum carboxylates, and $CrMo(O_2CCH_3)_4$.[11]

Anhydrous $Cr_2(O_2CCH_3)_4$ is isomorphous with $Mo_2(O_2CCH_3)_4$ and $CrMo(O_2CCH_3)_4$. The unit cells previously used[3,11] for $Mo_2(OAc)_4$ and $CrMo(OAc)_4$ can be transformed to the cell chosen here for $Cr_2(OAc)_4$ by applying the transformation matrix

$$\begin{matrix} 0 & 0 & -1 \\ -1 & -1 & 0 \\ 0 & 1 & 0 \end{matrix}$$

and translating the origin by (½, ½, ½). The way in which the compounds are packed along the short cell dimensions (the c axis of the cell chosen for $Cr_2(O_2CCH_3)_4$) is illustrated in Figure 2. The intermolecular interactions shown are clearly strongest in the dichromium compound. A stereoscopic view of $Cr_2(O_2CCH_3)_4$ approximately along the c axis is presented in Figure 3, and this shows that there are no significant intermolecular interactions in the a and b directions. This is reflected macroscopically in the tendency of the crystalline needles to fray along their long dimension upon handling. The apparently open channel down the center of Figure 3 is, of

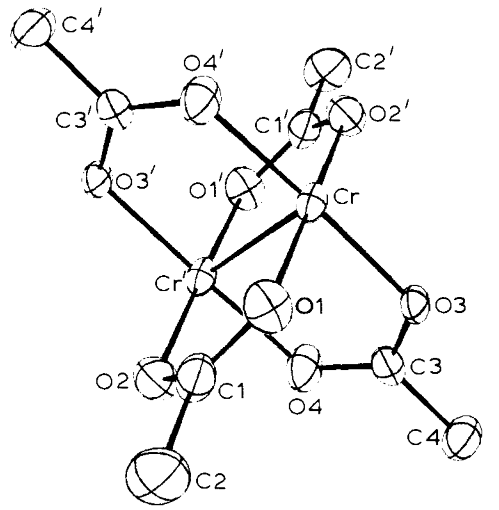

Figure 1. A convenient projection of the $Cr_2(O_2CCH_3)_4$ molecule. Ellipsoids of thermal motion enclose 50% of the electron density.

course, filled by the methyl hydrogen atoms. This figure will differ only slightly from those which could be produced for the corresponding views of the isomorphous $Mo_2(O_2CCH_3)_4$ and $CrMo(O_2CCH_3)_4$ and thus can be considered to depict any of the three structures.

Discussion

It is pertinent to compare the structure of anhydrous chromous acetate, which is the first structure to be reported for an unsolvated dichromium(II) tetracarboxylate, with the structure of $Cr_2(O_2CCH_3)_4(H_2O)_2$[2] and with those of the anhydrous acetates $Mo_2(O_2CCH_3)_4$[3] and $CrMo(O_2CCH_3)_4$.[11] Let us first compare the two dichromium compounds.

Although it might be argued that the difference in the Cr–Cr distances in these two cases is small from a chemical viewpoint, it is greater than the change in Mo–Mo distance which accompanies a much greater change in the axial ligand,[12,13] when $Mo_2(O_2CCF_3)_4$ and $Mo_2(O_2CCF_3)_4(py)_2$ are compared (see Table III). The data on these two molybdenum compounds show that an intrinsically strong Mo–Mo bond leads to weakly bound axial ligands due to a large metal-metal trans influence. This point has been reinforced in a more recent study.[14] Clearly the metal-metal trans influence is smaller in the chromium(II) dimers, so that the axial ligands are more strongly bound. In consequence, however, the Cr–Cr bonding and the Cr–Cr distance should be relatively sensitive to the basicity and positions of the axial ligands, and this is observed in the present case.

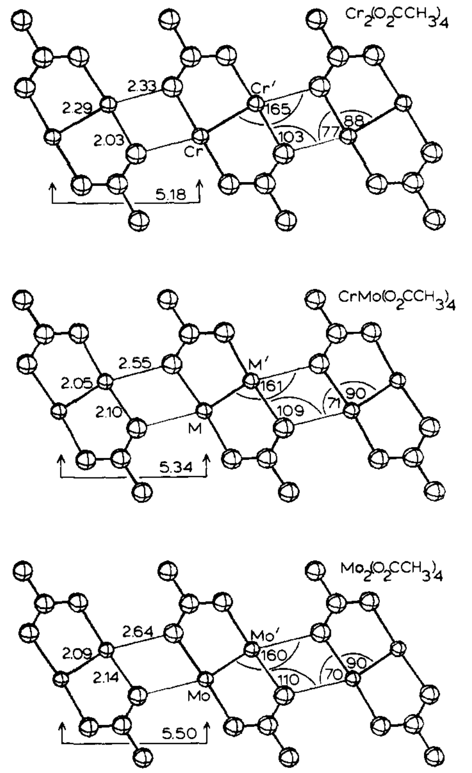

Figure 2. Packing of the anhydrous dimetal tetraacetates along the short cell axes whose dimensions are given. Acetates above and below the planes of projection have been omitted for clarity. Pertinent bond distances (Å) and angles (deg) are included.

The present results strongly suggest that the success claimed by Garner et al.[5] in correlating the photoelectron spectrum of gaseous $Cr_2(O_2CCH_3)_4$ with the MO treatment carried out on (hypothetical) $Cr_2(O_2CH)_4 \cdot 2H_2O$ using the structure parameters[2] for $Cr_2(O_2CCH_3)_4(H_2O)_2$ (including the Cr–Cr distance of 2.362 Å) is fortuitous. There seems little doubt that an isolated $Cr_2(O_2CCH_3)_4$ molecule would have a significantly shorter Cr–Cr distance than that observed in the crystalline hydrate, thus invalidating the comparison. Crystalline $Cr_2(O_2CCH_3)_4(H_2O)_2$ and gaseous $Cr_2(O_2CCH_3)_4$ may well be very different chemical entities, indeed. It cannot, therefore, be said that there is, as yet, any experimental evidence with which to test the MO calculation described by Garner et al.

Note Added in Proof: Photoelectron spectra have now been obtained of anhydrous, solid $Cr_2(O_2CCH_3)_4$ and they are substantially different from the spectrum in the gas phase, thus supporting our contention that it is unjustified to compare the

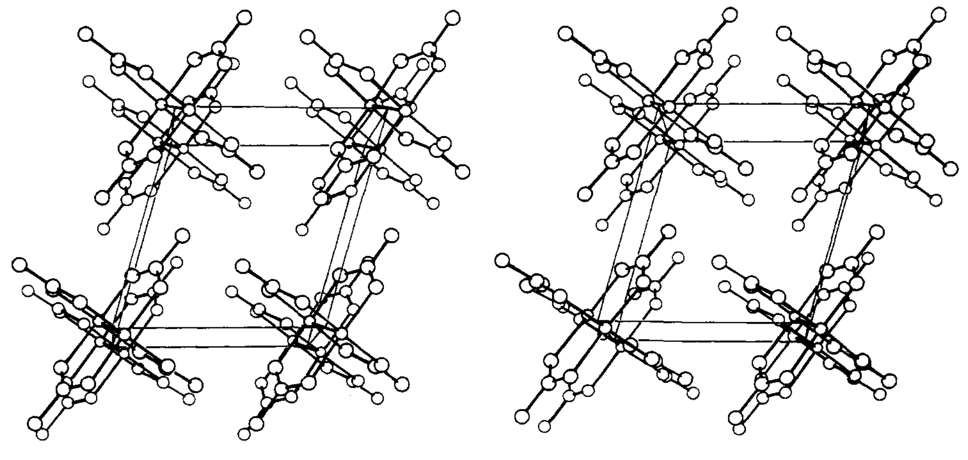

Figure 3. A stereoscopic view of eight molecules of $Cr_2(O_2CCH_3)_4$. The vertices of the unit cell are defined by the center of the Cr–Cr bond.

theoretical results for a molecule with the Cr–Cr distance and axial interactions characteristic of the solid state with the experimental spectrum given by isolated gaseous molecules. As for the calculation[5] per se, it appears to have given a qualitatively erroneous description of the ground state electronic structure because correlation energies were ignored. Inclusion of those effects of configuration interaction expected to be of greatest importance gives a ground state with appreciable Cr–Cr bonding, as recently shown by M. Benard and A. Veillard, *Nouv. J. Chem.*, **1**, 97 (1977). An SCF-Xα-SW calculation by G. G. Stanley and F. A. C., *Inorg. Chem.*, in press, gives a ground state with a clear-cut quadruple bond, albeit a weaker one than that in $Mo_2(O_2CCH_3)_4$.

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Supplementary Material Available: Listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of μ-Diphenylacetylene-bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I) and Related Analogues

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Abstract: The reaction of diphenylacetylene with palladium acetate in alcohols leads to the formation of μ-diphenylacetylene-bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I). Similar compounds of the general form $[(\mu\text{-}RC_2R')(\eta^5\text{-}Ar_3RR'C_5)_2Pd_2]$ are more readily prepared from the reaction of the acetylene RC_2R' with *endo*-alkoxytetraarylcyclobutenylpalladium acetate in alcohol. The formation of pentasubstituted cyclopentadienyl ligands from acetylenes is a novel reaction that involves an unusually facile cleavage of an acetylene triple bond. One-half of the acetylene cleaved is lost as the ortho ester $ArC(OR)_3$. A mechanism for this reaction is proposed. The molecules $[(\mu\text{-}RC_2R')(\eta^5\text{-}Ar_3RR'C_5)_2Pd_2]$ undergo bridge acetylene displacement reactions, react with NO to give $[(\eta^5\text{-}Ar_3RR'C_5)PdNO]$, and react with HX (X = Cl, Br) to give $[(\eta^5\text{-}Ar_3RR'C_5)_2Pd_2X_2]$ and $[(\eta^5\text{-}Ar_3RR'C_5)_2Pd_2HX]$. The latter compounds are tentatively formulated as bridging hydrido complexes.

Recent work by Maitlis and co-workers on the mechanism of the palladium(II) chloride induced cyclotrimerization of acetylenes to benzenes has demonstrated the intermediacy of cyclopentadienylmethyl complexes in the reaction pathway.[1,2] In several cases these complexes have been isolated and in others decomposition of these intermediates leads to the formation of benzenes and/or cyclopentadiene products. In this paper we report that under suitable conditions palladium complexes containing η^5-pentasubstituted cyclopentadienyl ligands may be isolated from the reaction of acetylenes with a variety of palladium compounds in alcoholic solutions.

Results and Discussion

(i) Synthesis and Structure of $[(\mu\text{-}PhC{\equiv}CPh)(\eta^5\text{-}C_5Ph_5Pd)_2]$. The reaction of diphenylacetylene with palladium acetate in methanol at 25 °C gave a dark green crystalline diamagnetic solid **1**. Microanalysis and molecular weight data (Table I) for the recrystallized compound **1** showed it to have the stoichiometry $Pd_2C_{84}H_{60}{\cdot}S$ (where S = $CHCl_3$ or C_6H_6 depending on the solvent used for the recrystallization). Attempts to ascertain the structure of **1** by chemical means proved fruitless and finally a crystal was grown (in benzene) suitable for x-ray diffraction studies. The molecular structure of **1** as determined by Nyburg and co-workers[3] is shown in Figure 1. The molecule contains a dinuclear Pd(I) unit, bridged orthogonally by a diphenylacetylene, and two pentaphenylcyclopentadienyl ligands each of which is bound to one of the Pd(I)'s. This structure is novel in several features: it is one of the few established stable formally Pd(I) species;[4–12] it is a rare example of an acetylene bridging two palladiums; and it represents a significant addition to the number of known cyclopentadienyl-palladium complexes.[2] Despite its novelty, complex **1** completes the occurrence of this structure for the nickel triad being analogous to the complex $[(\mu\text{-}PhC{\equiv}CPh)(\eta^5\text{-}C_5H_5Ni)_2]$[13] and related to the complex $[(\mu\text{-}C_5H_5C_5H_5)(\eta^5\text{-}C_5H_5Pt)_2]$.[14] The intermetallic Pd–Pd distance (2.64 Å) is significantly shorter than that found in the elemental metal (2.75 Å)[15] and is comparable to the Pd–Pd bond length reported by Allegra et al.[4] for the complexes $[(\eta^6\text{-}C_6H_6)\text{-}PdAlCl_3X]_2$ (2.57 Å; X = Cl or $AlCl_4$). The bridging acetylene has a carbon-carbon distance of 1.33 Å in close agreement with that observed in the nickel analogue $[(\mu\text{-}PhC{\equiv}CPh)((\eta^5\text{-}$