The molecule has approximate C_s symmetry, as clearly shown in Figure 1. The carbonyl ligand C(41)–O(41) which is associated principally with the tungsten atom [W(4)–C(41) = 1.91 (6) Å; W(4)–C(41)–O(41) = 154.2 (47)°] is oriented such as to suggest a weak interaction also with Os(2) [Os(2)···C(41) = 2.73 (6) Å; Os(2)···C(41)–O(41) = 128.1 (40)°]. The carbonyl ligand C(42)–O(42) is also associated primarily with the tungsten atom [W(4)–C(42) = 2.03 (5) Å]. This carbonyl ligand is also slightly bent [W(4)–C(42)–O(42) = 170.0 (41)°] and interacts slightly with Os(2) [Os(2)···C(42) = 2.95 (4) Å and Os(2)···C(42)–O(42) = 121.1 (35)°].

Weakly "semibridging" carbonyl ligands often act so as to distribute electron density more evenly around a metal cluster complex.[20,21] (Formal electron counting, assuming *neutral* metal atoms and ligands, gives 19 outer valence electrons at W(4), 18 electrons at Os(1) and Os(3), and 17 electrons at Os(2).) "Semibridging" carbonyl ligands across the W(4)–Os(2) vector are in the appropriate location to effectively donate electron density from W(4) to Os(2).

Acknowledgment. We thank Professor J. R. Shapley for providing the sample and for his continuing interest in these studies. This work was generously supported by the National Science Foundation through Grant CHE77-04981 to M.R.C.

Registry No. $(\mu\text{-H})_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$, 68297-92-7.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Molecules with an M_4X_4 Core. 10.[1] Failure of the 1:1:1 Tricyclohexylphosphine–Copper(I)–Chloride Complex to Form a Tetramer. Crystal Structure of Dimeric (Tricyclohexylphosphine)copper(I) Chloride, $[(P(cHx)_3)CuCl]_2$

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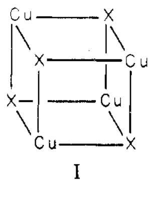
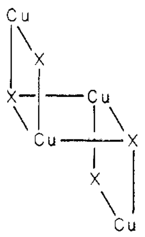
(Tricyclohexylphosphine)copper(I) chloride crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with a = 8.4977 (12) Å, b = 9.2667 (11) Å, c = 13.2797 (18) Å, α = 100.82 (1)°, β = 89.73 (1)°, γ = 113.66 (1)°, V = 937.9 (2) Å^3, ρ(obsd) = 1.32, and ρ(calcd) = 1.34 g cm^{-3} for Z = 1 (dimeric molecule). Diffraction data with 4.5° < 2θ < 40.0° (Mo Kα radiation) were collected with a Syntex $P2_1$ automated diffractometer, and the structure was solved via conventional Patterson, Fourier, and least-squares refinement techniques. All atoms (including hydrogens) were located directly, the final discrepancy indices being R_F = 4.9% and R_{wF} = 3.8% for those 1580 reflections with $|F_o| > \sigma(|F_o|)$. The complex exists as the *dimeric* species $[(P(cHx)_3)CuCl]_2$—in sharp contrast to the *tetrameric* "cubane" or "step" structures found for all previously examined phosphine–copper(I) halide complexes with a 1:1 ratio of monodentate tertiary phosphine to copper(I). The dimeric molecule has precise C_i symmetry. Each copper(I) atom is in trigonal-planar coordination to a phosphine ligand and two bridging chloride ions. Distances and angles within the coordination sphere are as follows: Cu–P = 2.183 (2) Å, Cu–Cl = 2.322 (2) Å, Cu–Cl′ = 2.285 (2) Å, ∠P–Cu–Cl = 127.40 (7)°, ∠P–Cu–Cl′ = 136.05 (7)°, ∠Cl–Cu–Cl′ = 96.56 (7)°. Angles at the bridging chloride ligands are *acute* (∠Cu–Cl–Cu′ = 83.44 (7)°) despite the absence of a metal–metal bond (Cu···Cu′ = 3.066 (1) Å); this is apparently due to intramolecular chlorine···chlorine repulsions (Cl···Cl′ = 3.439 (3) Å).

Introduction

The chemistry of monodentate tertiary phosphine complexes of the copper(I) halides has been surveyed by Lippard and Mayerle.[2] There is a remarkable diversity of stoichiometry, the phosphine-to-copper ratio varying through the range 4:1 in ionic $[L_4Cu^+]X^-$ complexes (L = PR$_3$, X = Cl, Br, I), 3:1 in L_3CuX complexes, 2:1 in $[L_2CuX]_2$ and L_2CuX complexes, 3:2 in the asymmetric $L_2Cu(\mu\text{-}X)_2CuL$ complexes, and 1:1 in $[LCuX]_4$ complexes. We have previously completed X-ray structural analyses of the tetrameric 1:1 complexes $[(PPh_3)CuCl]_4$,[3] $[(PPh_3)CuBr]_4$,[4] $[(PPh_3)CuI]_4$,[5] $[(PEt_3)CuCl]_4$,[6] $[(PEt_3)CuBr]_4$,[6] $[(PEt_3)CuI]_4$,[7] and $[(PMePh_2)CuI]_4$.[1] It has been established that the "cubane" structure (I) is destabilized relative to the "step" [otherwise termed



I



II

"chair"] structure (II) when large halogen atoms are accompanied by bulky phosphine ligands on the metal atom (i.e., only in $[(PPh_3)CuBr]_4$ and $[(PPh_3)CuI]_4$ of the complexes listed above). Teo and Calabrese[8] have analyzed steric interaction in $L_4M_4X_4$ tetramers and concluded: "As steric hindrance among the ligands increases, the following stereochemical variation inevitably occurs: symmetrical "cubane" → distorted "cubane" → ("cubane" ⇄ "chair" isomerization) → "chair"."

While we concur with this analysis, it is clearly not complete insofar as even the tetrameric chair form (II) is unstable with respect to dissociation if there are sufficiently bulky substituents. With this in mind we became interested in the tricyclohexylphosphine–copper(I)–halide system, which had previously been investigated by Moers and Op Het Veld.[9] While the reported work was not completely definitive, it was suggested[9] that the 1:1 species of stoichiometry $P(cHx)_3CuX$ (cHx = cyclohexyl) were *dimeric* rather than tetrameric.

We have now completed a single-crystal X-ray structural analysis of the 1:1 complex $[(P(cHx)_3)CuCl]_n$ and confirm that it is indeed dimeric (i.e., $n = 2$), thus defining a new structural type in these complex phosphine–copper(I)–halide systems. The present complex is of additional interest in that it represents a clear-cut example of trigonal-planar coordination geometry for d^{10} copper(I).

Collection and Correction of X-ray Data

The dimeric complex was synthesized by the method described by Moers and Op Het Veld.[9] The resulting white precipitate, after suitable ethanolic washing and air-drying (mp 215–220 °C), was found to be appreciably soluble only in 1,2-dichloroethane among common organic solvents. A portion of the precipitate was dissolved in deoxygenated 1,2-dichloroethane, and clear white crystals were obtained by slow evaporation of solvent under vacuum over a period of 5 days.

The crystal chosen for the structural analysis had the shape of a solid parallelepiped of dimensions 0.20 × 0.10 × 0.15 mm; it was jam-fit in a 0.2 mm diameter Lindemann glass capillary which was subsequently flushed with argon and flame-sealed. The capillary was fixed into an aluminum pin on a eucentric goniometer head, which was secured to the goniostat of a Syntex $P2_1$ four-circle automated diffractometer under the control of a Data General NOVA 1200 computer and disk storage system.[10] (This in-house computing system was used both for data collection and for all computations involving the solution and refinement of the crystal structure.) The crystal was centered accurately in a monochromated Mo K$\bar{\alpha}$ X-ray beam; its relative orientation and unit cell parameters were determined, and intensity data were collected as described previously.[11] Partial rotation photographs about all three axes indicated only triclinic crystal symmetry—i.e., the space groups $P1$ (C_1^1; No. 1) or $P\bar{1}$ (C_i^1; No. 2) are indicated. The successful elucidation of the structure shows that the centrosymmetric space group $P\bar{1}$ is the correct one.

The effects of absorption were corrected for by an empirical method. The close-to-axial $3\bar{1}0$ reflection ($2\theta = 14.46°$; maximum:minimum intensity ratio 1.141) was measured at 10° intervals of ψ (the azimuthal angle, corresponding to rotation of the crystal about its diffraction vector) from $\psi = 0$ to 350°; the resulting normalized "pseudotransmission curve" was used to correct the primary set of reflections. Data were then averaged (where appropriate) and corrected for Lorentz and polarization effects.

Table I. Experimental Data for the X-Ray Diffraction Study of $[(P(cHx)_3)CuCl]_2$

(A) Crystal Data

unit cell parameters[a]	cryst system: triclinic
$a = 8.4977\ (12)$ Å	space group: $P\bar{1}$
$b = 9.2667\ (11)$ Å	temp 25.8 (3) °C
$c = 13.2797\ (18)$ Å	$Z = 1$ (dimer)
$\alpha = 100.820\ (10)°$	mol wt 758.86
$\beta = 89.732\ (11)°$	ρ(obsd)[b] = 1.32 (1) g cm^{-3}
$\gamma = 113.658\ (9)°$	ρ(calcd) = 1.34 g cm^{-3}
$V = 937.9\ (2)$ Å^3	

(B) Intensity Data

radiation: Mo Kα ($\bar{\lambda}$ 0.710 73 Å)
monochromator: highly oriented graphite
reflections measured: $h, \pm k, \pm l$
max 2θ measured: 40.0°
min 2θ measured: 4.5°
scan type: θ(cryst)–2θ(counter)
scan speed: 2.0° min^{-1}
scan range: symmetrical, from $[2\theta(K\alpha_1) - 0.9]°$ to $[2\theta(K\alpha_2) + 0.9]°$
background measurement: stationary crystal/stationary counter at beginning and end of scan, each for half of the time taken for the scan
standard reflections: 3, measured every 47 data; percent variances from the mean: 2.50% for 007, 4.08% for $14\bar{2}$, and 3.28% for $4\bar{1}\bar{2}$
data set information: 2047 data collected, of which 123 were standard reflections; equivalent reflections were averaged,[c] yielding 1762 reflections in the primary data set; 1580 of these data had $|F_o| > \sigma(F_o)$ and were used in the structural refinement

(C) Data Treatment Parameters

"ignorance factor": $p = 0.015$, applied to $\sigma(F)$ as $[\{\sigma(F)\}^2 + \{pF\}^2]^{1/2}$
abs coeff: $\mu = 13.87$ cm^{-1} (see text)

[a] Determined by a least-squares fit of the setting angles of the unresolved Mo Kα peaks of 24 reflections with 2θ ranging from 20.2 to 30.8°. [b] Measured by neutral buoyancy in aqueous KI solution. [c] The agreement between the averaged, symmetry-equivalent reflections was $R(I) = 1.98\%$.

Solution and Refinement of the Structure

Calculations were performed on our in-house computer (vide supra) using our own modified version of the Syntex XTL conversational crystallographic program package.[12]

Analytical scattering factors for neutral copper, chlorine, phosphorus, carbon, and hydrogen atoms were taken from the compilation of Cromer and Waber;[13a] both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion[13b] were included for all nonhydrogen atoms. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the weights are defined in eq 1; here $\sigma(F)$ is the stochastic esd, propagated from $\sigma(I)$, and p is the

$$w = [\{\sigma(F)\}^2 + (pF)^2]^{-1} \qquad (1)$$

so-called "ignorance factor". Discrepancy indices (R_F and R_{wF}) and the "goodness-of-fit" (GOF) are defined in eq 2–4. In eq 4, NO

$$R_F = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|}\right] \times 100\ (\%) \qquad (2)$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2} \times 100\ (\%) \qquad (3)$$

$$\mathrm{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)}{\mathrm{NO} - \mathrm{NV}}\right]^{1/2} \qquad (4)$$

is the number of observations and NV is the number of variables.

A three-dimensional Patterson synthesis yielded the positions of the copper, chlorine, and phosphorus atoms and suggested strongly that the space group was $P\bar{1}$, since the $P_2Cu_2Cl_2$ section of the molecule had precise C_i symmetry. A Fourier synthesis, phased by the heavy atoms, led to the unambiguous location of all carbon atoms and confirmed the correctness of the centrosymmetric space group. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms converged with $R_F = 7.9\%$, $R_{wF} = 7.6\%$, and GOF = 2.536.

At this stage a difference-Fourier synthesis yielded the positions of all 33 hydrogen atoms of the unique tricyclohexylphosphine ligand, with individual peak heights ranging from 0.65 e Å^{-3} down to 0.27 e Å^{-3}. Hydrogen atoms were included in the model in idealized positions with d(C–H) = 0.95 Å[14] and sp^3 geometry about the attached carbon atoms; their isotropic thermal parameters were each set at ($B_{C(i)} + 1.0$) Å^2, where $B_{C(i)}$ is the equivalent isotropic thermal parameter of the attached carbon atom.

Inclusion of the hydrogen atoms led to a dramatic improvement in discrepancy indices—convergence was reached in two cycles

Table II. Final Positional Parameters (with Esd's) for $[(P(cHx)_3)CuCl]_2$

atom	*x*	*y*	*z*	*B*, Å^2
Cu	0.90572 (10)	0.06472 (9)	0.08317 (6)	
Cl	1.19384 (20)	0.11022 (21)	0.07139 (12)	
P	0.79233 (19)	0.16765 (17)	0.20927 (11)	
C(11)	0.7206 (7)	0.3193 (6)	0.1772 (4)	
C(12)	0.7185 (7)	0.4512 (7)	0.2653 (4)	
C(13)	0.6458 (9)	0.5596 (8)	0.2310 (5)	
C(14)	0.7351 (9)	0.6282 (8)	0.1415 (5)	
C(15)	0.7371 (9)	0.4996 (8)	0.0542 (5)	
C(16)	0.8132 (8)	0.3913 (7)	0.0896 (4)	
C(21)	0.6008 (7)	0.0165 (6)	0.2524 (4)	
C(22)	0.5157 (7)	0.0809 (7)	0.3414 (4)	
C(23)	0.3676 (8)	−0.0553 (7)	0.3760 (5)	
C(24)	0.2371 (8)	−0.1559 (7)	0.2884 (5)	
C(25)	0.3157 (8)	−0.2205 (7)	0.1985 (4)	
C(26)	0.4663 (7)	−0.0869 (7)	0.1630 (4)	
C(31)	0.9408 (7)	0.2669 (6)	0.3277 (4)	
C(32)	0.9722 (7)	0.1432 (7)	0.3769 (5)	
C(33)	1.0977 (8)	0.2267 (8)	0.4731 (5)	
C(34)	1.2651 (8)	0.3524 (8)	0.4505 (5)	
C(35)	1.2347 (7)	0.4750 (7)	0.4010 (5)	
C(36)	1.1113 (7)	0.3920 (7)	0.3040 (4)	
H(11)	0.6018	0.2565	0.1568	4.09
H(12A)	0.8333	0.5147	0.2940	4.73
H(12E)	0.6502	0.4016	0.3161	4.73
H(13A)	0.5265	0.4993	0.2108	5.99
H(13E)	0.6601	0.6456	0.2868	5.99
H(14A)	0.8505	0.7003	0.1644	6.28
H(14E)	0.6764	0.6848	0.1172	6.28
H(15A)	0.6223	0.4351	0.0257	5.97
H(15E)	0.8045	0.5494	0.0032	5.97
H(16A)	0.9314	0.4533	0.1117	4.97
H(16E)	0.8029	0.3067	0.0335	4.97
H(21)	0.6461	−0.0480	0.2795	3.81
H(22A)	0.4723	0.1507	0.3195	4.49
H(22E)	0.5995	0.1389	0.3977	4.49
H(23A)	0.4120	−0.1210	0.4024	5.80
H(23E)	0.3139	−0.0107	0.4283	5.80
H(24A)	0.1854	−0.0921	0.2664	5.58
H(24E)	0.1515	−0.2439	0.3113	5.58
H(25A)	0.3561	−0.2937	0.2183	5.40
H(25E)	0.2297	−0.2752	0.1429	5.40
H(26A)	0.4240	−0.0206	0.1354	4.62
H(26E)	0.5189	−0.1340	0.1112	4.62
H(31)	0.8876	0.3198	0.3753	3.76
H(32A)	1.0195	0.0851	0.3287	5.24
H(32E)	0.8657	0.0708	0.3955	5.24
H(33A)	1.0455	0.2768	0.5232	5.90
H(33E)	1.1210	0.1481	0.4992	5.90
H(34A)	1.3225	0.3012	0.4050	5.91
H(34E)	1.3350	0.4062	0.5130	5.91
H(35A)	1.1862	0.5326	0.4486	4.82
H(35E)	1.3416	0.5476	0.3831	4.82
H(36A)	1.1632	0.3403	0.2546	4.84
H(36E)	1.0896	0.4707	0.2768	4.84

Table III. Final Anisotropic Thermal Parameters (with Esd's) for $[(P(cHx)_3)CuCl]_2$[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	4.38 (5)	3.95 (4)	3.00 (4)	2.36 (3)	1.13 (3)	0.69 (3)
Cl	3.72 (9)	7.22 (11)	4.01 (9)	2.82 (8)	−0.23 (7)	−1.43 (8)
P	2.98 (8)	2.75 (8)	2.41 (7)	1.29 (7)	0.53 (6)	0.42 (6)
C(11)	2.8 (3)	3.2 (3)	3.3 (3)	1.2 (2)	0.8 (2)	0.9 (2)
C(12)	4.8 (3)	3.3 (3)	2.5 (3)	1.8 (3)	1.2 (2)	0.3 (2)
C(13)	7.2 (4)	4.1 (3)	5.2 (4)	4.2 (3)	1.9 (3)	1.2 (3)
C(14)	7.9 (5)	4.5 (4)	5.6 (4)	3.9 (4)	0.8 (4)	2.3 (3)
C(15)	7.4 (4)	5.2 (4)	3.8 (4)	3.4 (3)	0.7 (3)	1.7 (3)
C(16)	6.7 (4)	3.7 (3)	2.7 (3)	3.1 (3)	1.2 (3)	0.9 (3)
C(21)	3.3 (3)	2.9 (3)	2.5 (3)	1.2 (3)	0.4 (2)	0.7 (2)
C(22)	3.7 (3)	3.1 (3)	3.1 (3)	0.9 (3)	1.1 (3)	−0.0 (2)
C(23)	4.9 (4)	4.3 (4)	3.4 (3)	1.0 (3)	1.9 (3)	−0.1 (3)
C(24)	4.0 (4)	3.7 (3)	5.9 (4)	0.6 (3)	1.6 (3)	1.5 (3)
C(25)	4.2 (3)	3.8 (3)	3.4 (3)	1.0 (3)	0.3 (3)	0.3 (3)
C(26)	3.9 (3)	3.6 (3)	3.1 (3)	1.5 (3)	0.9 (3)	0.6 (3)
C(31)	3.3 (3)	3.0 (3)	2.1 (3)	1.5 (3)	0.5 (2)	0.0 (2)
C(32)	3.9 (3)	3.5 (3)	4.3 (3)	1.0 (3)	−0.5 (3)	1.0 (3)
C(33)	4.4 (4)	5.0 (4)	4.6 (4)	1.7 (3)	−0.4 (3)	1.8 (3)
C(34)	3.4 (3)	6.1 (4)	4.1 (3)	1.6 (3)	−0.5 (3)	0.8 (3)
C(35)	3.1 (3)	4.4 (3)	3.8 (3)	1.1 (3)	0.6 (3)	0.1 (3)
C(36)	3.9 (3)	3.6 (3)	3.1 (3)	1.3 (3)	0.5 (3)	0.8 (3)

[a] The anisotropic thermal parameters have units of Å^2 and enter the equation for the calculated structure factor in the form $\exp[-{}^1/_4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

$[(\Delta/\sigma)_{\max} < 0.005]$ with $R_F = 4.9\%$, $R_{wF} = 3.8\%$, and GOF = 1.261 for those 1580 reflections with $|F_o| > \sigma(F_o)$. With NO = 1580 and NV = 190, the data-to-parameter ratio is 8.32:1.

A final difference-Fourier synthesis had a peak of height 0.37 e Å^{-3} (at 1.121, −0.017, 0.091) as its most intense feature, thereby confirming the correctness and completeness of the structural analysis. There was no evidence for secondary extinction, and the worst disagreement between $|F_o|$ and $|F_c|$ was 4.5σ for the $2\bar{7}9$ reflection. The average value of $\sum w(|F_o| - |F_c|)^2$ showed no significant variation as a function of $|F_o|$, (sin θ)/λ, identity or parity of Miller indices, or sequence number; the weighting scheme is thus satisfactory.

Final values for positional and anisotropic thermal parameters are collected in Tables II and III.

Results and Discussion

The crystal consists of discrete molecular units of the *dimeric* species $[(P(cHx)_3)CuCl]_2$ which are separated by normal van der Waals distances. There are no abnormally short intermolecular contacts.

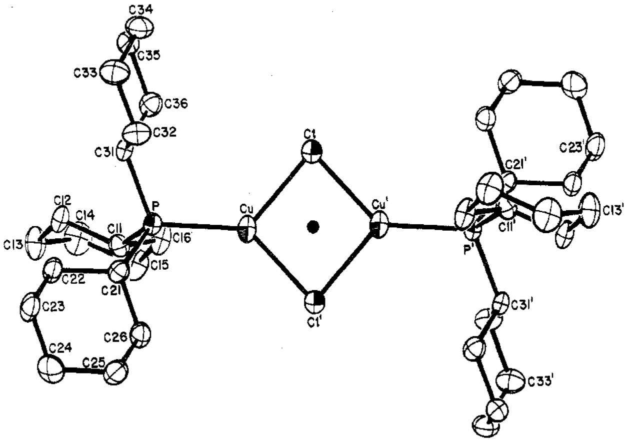


Figure 1. The $[(P(cHx)_3)CuCl]_2$ molecule projected onto its Cu-(μ-Cl)$_2$Cu plane [ORTEP-II diagram; 30% probability contours for thermal vibration ellipsoids; hydrogen atoms omitted]. The crystallographic center of symmetry is indicated by a solid circle.

The molecule is centered at (1, 0, 0), a site of crystallographic $\bar{1}$ (C_i) symmetry. The scheme used for labeling atoms is shown in Figure 1. Atoms of the defined basic asymmetric unit are labeled normally; those in the "other half" of the molecule, which are related to the principal set via the transformation $(x', y', z') = (2 - x, -y, -z)$, are labeled with a prime. Interatomic distances with their estimated standard deviations (esd's) are listed in Table IV; interatomic angles and their esd's are collected in Table V. A stereoscopic view of the entire dimeric molecule is provided as Figure 2.

Each copper(I) atom is in trigonal coordination to a tricyclohexylphosphine ligand (Cu–P = 2.183 (2) Å) and two bridging chloride ligands (Cu–Cl = 2.322 (2) Å and Cu–Cl′ = 2.285 (2) Å). Angles within the trigonal-planar coordination sphere are rather irregular—∠Cl–Cu–Cl′ = 96.56 (7)°, ∠P–Cu–Cl = 127.40 (7)°, and ∠P–Cu–Cl′ = 136.05 (7)°. However, as clearly shown in Table VI, the entire $P_2Cu_2(\mu\text{-}Cl)_2$ system is planar within the limits of experimental error. (The root-mean-square deviation from planarity is only 0.0025 Å.)

The central Cu(μ-Cl)$_2$Cu core of the molecule is *strictly* planar. The angle at copper is *obtuse* (∠Cl–Cu–Cl′ = 96.56 (7)°) whereas that at chlorine is *acute* (∠Cu–Cl–Cu′ = 83.44

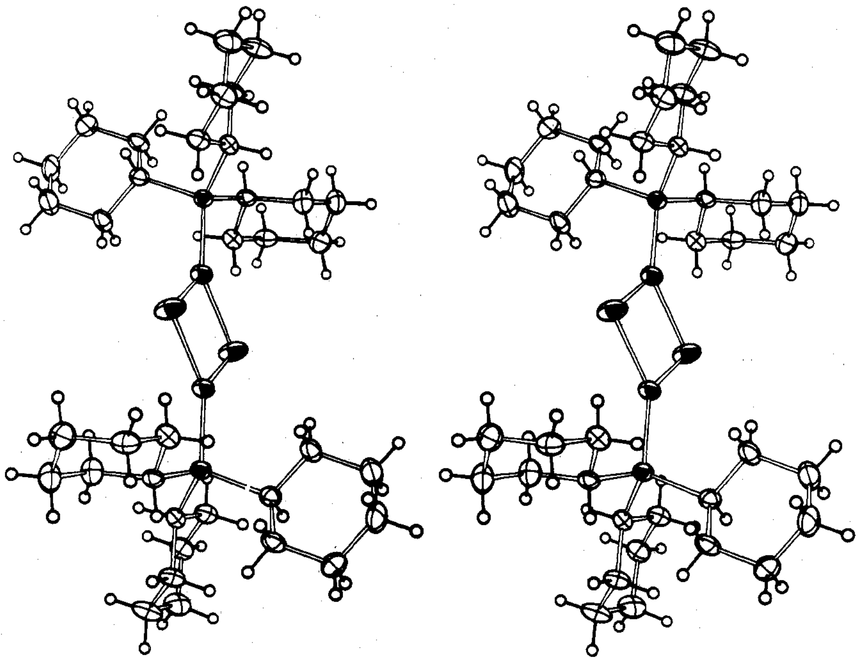


Figure 2. Stereoscopic view of the dimeric $[(P(cHx)_3)CuCl]_2$ molecule.

Table IV. Interatomic Distances (Å) and Esd's[a] for $[(P(cHx)_3)CuCl]_2$

(A) Distances within the $P_2Cu_2Cl_2$ Core			
Cu–Cl	2.322 (2)	Cu–Cl′	2.285 (2)
Cu···Cu′	3.066 (1)	Cl···Cl′	3.439 (3)
Cu–P	2.183 (2)		
(B) Phosphorus–Carbon Distances			
P–C(11)	1.856 (6)	P–C(31)	1.859 (6)
P–C(21)	1.844 (6)	mean[b]	1.853 ± 0.008
(C) Distances within Cyclohexyl Groups			
C(11)–C(12)	1.530 (8)	C(25)–C(26)	1.528 (9)
C(12)–C(13)	1.507 (10)	C(26)–C(21)	1.530 (8)
C(13)–C(14)	1.511 (10)	C(31)–C(32)	1.530 (8)
C(14)–C(15)	1.503 (10)	C(32)–C(33)	1.532 (9)
C(15)–C(16)	1.532 (10)	C(33)–C(34)	1.506 (10)
C(16)–C(11)	1.509 (8)	C(34)–C(35)	1.519 (10)
C(21)–C(22)	1.533 (8)	C(35)–C(36)	1.531 (9)
C(22)–C(23)	1.525 (9)	C(36)–C(31)	1.526 (9)
C(23)–C(24)	1.493 (10)	mean[b]	1.520 ± 0.012
C(24)–C(25)	1.508 (9)		

[a] Esd's, shown in parentheses, have been right-adjusted to the last digit of the preceding number. [b] The errors associated with the mean values were calculated from: $\sigma = [\Sigma_N(\chi_i - \overline{\chi})^2/(N-1)]^{1/2}$ where $\overline{\chi}$ is the mean value, χ_i is the value of the *i*th observation, and N is the number of observations in the set.

Table V. Intramolecular Angles (deg) and Esd's[a] for $[(P(cHx)_3)CuCl]_2$

(A) Angles within $CuCl_2$ Core			
Cl–Cu–Cl′	96.56 (7)	Cu–Cl–Cu′	83.44 (7)
(B) Angles Involving Phosphorus			
P–Cu–Cl	127.40 (7)	P–Cu–Cl′	136.05 (7)
Cu–P–C(11)	113.60 (19)	Cu–P–C(31)	113.24 (19)
Cu–P–C(21)	113.34 (19)	mean[b]	113.39 ± 0.18
C(11)–P–C(21)	105.4 (3)	C(21)–P–C(31)	103.9 (3)
C(11)–P–C(31)	106.5 (3)	mean[b]	105.3 ± 1.3
P–C(11)–C(12)	117.8 (4)	P–C(31)–C(32)	111.1 (4)
P–C(11)–C(16)	111.7 (4)	P–C(31)–C(36)	110.6 (4)
P–C(21)–C(22)	115.9 (4)	mean[b]	113.2 ± 3.0
P–C(21)–C(26)	111.9 (4)		
(C) Angles within Cyclohexyl Groups			
C(16)–C(11)–C(12)	110.7 (5)	C(24)–C(25)–C(26)	112.1 (5)
C(11)–C(12)–C(13)	112.9 (5)	C(25)–C(26)–C(21)	111.1 (5)
C(12)–C(13)–C(14)	111.7 (6)	C(36)–C(31)–C(32)	110.3 (5)
C(13)–C(14)–C(15)	112.2 (6)	C(31)–C(32)–C(33)	110.6 (5)
C(14)–C(15)–C(16)	112.0 (6)	C(32)–C(33)–C(34)	112.0 (6)
C(15)–C(16)–C(11)	111.4 (5)	C(33)–C(34)–C(35)	111.2 (6)
C(26)–C(21)–C(22)	110.2 (5)	C(34)–C(35)–C(36)	110.8 (5)
C(21)–C(22)–C(23)	111.4 (5)	C(35)–C(36)–C(31)	111.1 (5)
C(22)–C(23)–C(24)	111.0 (6)	mean[b]	111.4 ± 1.8
C(23)–C(24)–C(25)	112.3 (6)		

[a] See footnote *a* of Table IV. [b] See footnote *b* of Table IV.

(7)°). This observed geometry is clearly the resultant of a number of competing effects. The following points should be noted.

(1) The observed chlorine···chlorine contact is Cl···Cl = 3.439 (3) Å. This is slightly shorter than the expected sum of the van der Waals radii of two chlorine atoms (3.60 Å)[15] and shorter also than most of the Cl···Cl distances observed in the tetrameric "cubanelike" complexes $[(PEt_3)CuCl]_4$ (3.6567 (22) Å)[6] and $[(PPh_3)CuCl]_4$ (3.3925 (33)–3.7223 (26) Å; average 3.5762 Å).[3] Clearly, the present Cl···Cl contact is approaching the lower limit of its range of values.

(2) The observed copper(I)···copper(I) distance, Cu···Cu′ = 3.066 (10) Å, is clearly a nonbonding distance. We note here that considerably shorter nonbonding copper···copper distances have been observed in other species—viz., 2.7826 (24) Å in $[(AsEt_3)CuI]_4$[7] and 2.9272 (20) Å in $[(PEt_3)CuI]_4$.[7] The copper···copper distance thus *could* be shorter; this, in turn, would help to increase the chlorine···chlorine contact. Clearly some other factor also must be involved in determining bond angles in the Cu_2Cl_2 core. We believe this to be the following.

(3) It is found that ∠Cl–Cu–Cl′ is some 30–40° less than the other two trigonal angles (∠P–Cu–Cl and ∠P–Cu–Cl′). The observed geometry of the Cu_2Cl_2 system is therefore believed to result from the minimization of tricyclohexylphosphine···chlorine contacts.

Figure 3 shows the tricyclohexylphosphine ligand viewed down the P→Cu axis. Each of the carbocyclic cyclohexane rings takes up a chair conformation, with the phosphorus atom occupying an equatorial site at the 1-position on each ring. Fortuitously, Figure 3 shows three distinct views of the chair configuration—the ring defined by C(11)→C(16) shows the

Table VI

Pertinent Least-Squares Planes[a] and Esd's[b]

atom[c]	dev, Å	atom[c]	dev, Å
$P_2Cu_2Cl_2$ Plane			
$-0.1912X + 0.8752Y - 0.4444Z = -1.6247$			
Cu*	0.0022 (7)	Cu′*	−0.0023 (7)
Cl*	0.0004 (18)	Cl′*	−0.0005 (18)
P*	−0.0033 (15)	P′*	0.0033 (15)
Planes within Cyclohexyl Groups			
Plane Ia: $-0.9136X + 0.0077Y - 0.4066Z = -5.4389$			
C(11)*	0.000	C(16)*	0.000
C(12)*	0.000		
Plane 1b: $-0.6151X - 0.7448Y - 0.2585Z = -5.9499$			
C(12)*	0.004 (6)	C(16)*	−0.004 (6)
C(13)*	−0.005 (7)	C(11)	0.648 (6)
C(15)*	0.006 (8)	C(14)	−0.624 (7)
Plane Ic: $-0.9187X - 0.0027Y - 0.3948Z = -4.3406$			
C(13)*	0.000	C(15)*	0.000
C(14)*	0.000		
Plane IIa: $-0.1726X + 0.9072Y - 0.3836Z = -2.6225$			
C(21)*	0.000	C(26)*	0.000
C(22)*	0.000		
Plane IIb: $-0.8626X + 0.4423Y - 0.2455Z = -4.7390$			
C(22)*	0.007 (6)	C(26)*	−0.008 (6)
C(23)*	−0.010 (7)	C(21)	−0.670 (6)
C(25)*	0.008 (7)	C(24)	0.635 (7)
Plane IIc: $-0.1797X + 0.9088Y - 0.3766Z = -3.7910$			
C(23)*	0.000	C(25)*	0.000
C(24)*	0.000		
Plane IIIa: $0.1623X - 0.3899Y - 0.9065Z = -3.2616$			
C(31)*	0.000	C(36)*	0.000
C(32)*	0.000		
Plane IIIb: $0.8655X - 0.2657Y - 0.4246Z = 4.5792$			
C(32)*	−0.004 (7)	C(36)*	0.004 (6)
C(33)*	0.005 (7)	C(31)	−0.679 (6)
C(35)*	−0.004 (6)	C(34)	0.655 (7)
Plane IIIc: $0.1788X - 0.3867Y - 0.9047Z = -4.2947$			
C(33)*	0.000	C(35)*	0.000
C(34)*	0.000		

Dihedral Angles

planes	angle, deg	planes	angle, deg
Ia–Ib	131.40	IIb–IIc	130.50
Ib–Ic	132.01	IIIa–IIIb	128.98
IIa–IIb	130.12	IIIb–IIIc	129.92

[a] Equations of planes are expressed in orthonormal coordinates. [b] See footnote *a* of Table IV. [c] All atoms marked with an asterisk were given unit weight in the corresponding plane; all others are given zero weight.

chair viewed from the side of the C(12)–C(13)···C(15)–C(16) plane; the ring defined by C(21)→C(26) is viewed down the C(22)–C(21) and C(24)–C(25) bonds and clearly shows the mirror plane passing through C(23) and C(26); the ring defined by C(31)→C(36) is shown projected essentially onto its C(31)–C(32)···C(34)–C(35) plane and strongly indicates the S_6 axis of the chair conformation. The precise geometry of these rings is defined by the planes of Table VI.

The phosphorus–carbon distances range from P–C(21) = 1.844 (6) Å to P–C(31) = 1.859 (6) Å, averaging 1.853 ± 0.008 Å; the 18 independent carbon–carbon distances range from 1.493 (10) to 1.533 (8) Å, averaging 1.520 ± 0.012 Å. The Cu–P–C angles are all greater than the ideal tetrahedral value, with ∠Cu–P–C(11) = 113.60 (19)°, ∠Cu–P–C(21) = 113.34(19)°, and ∠Cu–P–C(31) = 113.24 (19)° (average 113.39 ± 0.18°), while the C–P–C angles are all smaller than the ideal tetrahedral value—viz., ∠C(11)–P–C(21) = 105.4 (3)°, ∠C(11)–P–C(31) = 106.5 (3)°, and ∠C(21)–P–C(31) = 103.9 (3)° (average 105.3 ± 1.3°).

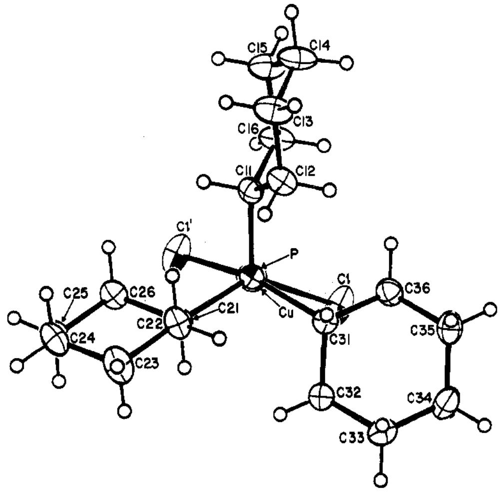


Figure 3. The $P(cHx)_3$ ligand, viewed down the P→Cu vector.

The present $[(P(cHx)_3)CuCl]_2$ molecule exists as a dimer, rather than as a tetramer, because of the steric bulk of the tricyclohexylphosphine ligands. The cyclohexyl rings form an approximately cylindrical mass at each end of the $P–Cu(\mu\text{-}Cl)_2Cu–P$ system, with hydrogen atoms pointing toward the chlorine atoms. (See Figure 3, where axial hydrogens on C(32), C(34), and C(36) and equatorial hydrogen atoms on C(16) and C(26) clearly act so as to hinder approach of other ligands to the copper atom; this shielding is also shown clearly in the stereoscopic view (Figure 2).) A cubane structure is clearly sterically forbidden, and even the step structure, which would require dimerization of the present dimer about only one of its Cu–Cl bonds, is apparently also unfavorable. It is worth noting that the occurrence of both *dimeric* $[(PR_3)CuX]_2$ and *tetrameric* $[(PR_3)CuX]_4$ cubanelike species parallels the observations of Holm et al.[16] on the $[Fe_2S_2(SR)_4]^{n-}$ and $[Fe_4S_4(SR)_4]^{n-}$ complexes (which are model systems for ferredoxin and high-potential iron–sulfur protein) but that the phosphine–copper–halide species show no well-defined redox behavior.

The present $[(P(cHx)_3)CuCl]_2$ molecule also represents one of a rather small group of complexes known to contain trigonally coordinated d^{10} Cu(I) atoms. Other Cu(I) complexes with this coordination geometry include $(PPh_3)_2CuBr$,[17] $[Cu(SPMe_3)_3^+][ClO_4^-]$,[18] $[Cu\{SCNH(CH_2)_2NH\}_3^+]_2[SO_4^{2-}]$,[19] $[Cu\{SC(NMe_2)\}_3^+][BF_4^-]$,[19] $[Cu(SPMe_3)Cl]_3$,[20] $Cu\{SC(NH_2)_2\}_2Cl$,[21] $[Cu(NC_5H_4Me)_3^+][ClO_4^-]$,[22] $Cu(2\text{-thiouracil})_2Cl$,[23] $NaCu(CN)_2{\cdot}2H_2O$,[24] $Na_2[Cu(CN)_3]{\cdot}3H_2O$,[25] and $(CH_2{=}CHCN)Cu_2Cl_2$.[26] Two of the four copper(I) atoms in the step structures $[(PPh_3)CuBr]_4$[4] and $[(PPh_3)CuI]_4$[5] are also trigonal planar as is one of the copper atoms in $[Cu_4\{SC(NH_2)_2\}_{10}^{4+}][SiF_6^{2-}]_2$.[27]

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Registry No. $[(P(cHx)_3)CuCl]_2$, 31168-43-1.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of a Tantalum–Benzylidyne Complex, Ta(η^5-C_5Me_5)(CPh)(PMe_3)$_2$Cl. Evidence for a Tantalum–Carbon Triple Bond

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The complex chloro(η^5-pentamethylcyclopentadienyl)bis(trimethylphosphine)benzylidynetantalum, Ta(η^5-C_5Me_5)(CPh)(PMe_3)$_2$Cl, has been studied via a single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with a = 10.5129 (12) Å, b = 13.8147 (16) Å, c = 18.1793 (21) Å, β = 102.945 (9)°, V = 2573.1 (5) Å^3, and ρ(calcd) = 1.531 g cm^{-3} for Z = 4 and mol wt 592.91. Diffraction data for $4.5° < 2\theta < 45°$ (Mo Kα radiation) were collected via a coupled θ–2θ scan routine on a Syntex $P2_1$ automated diffractometer. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms other than the hydrogen atoms of the η^5-C_5Me_5 ligand were located directly, the structure being refined to R_F = 4.1% and R_{wF} = 3.5% for those 3140 reflections with $|F_o| > \sigma(|F_o|)$. The molecule has a central tantalum atom surrounded in a "four-legged piano stool" arrangement by the η^5-C_5Me_5 ring and four monodentate ligands. The pseudo-trans Cl–Ta–C(1) and P(1)–Ta–P(2) angles are equivalent, with values of 125.54 (22) and 125.41 (7)°, respectively. The tantalum–benzylidyne linkage is 1.849 (8) Å in length—some 0.181 (10) Å shorter than the tantalum–neopentylidene linkage of 2.030 (6) Å in (η^5-C_5H_5)$_2$Ta(=CHCMe$_3$)Cl and 0.397 (14) Å shorter than the tantalum–methyl linkage of 2.246 (12) Å in (η^5-C_5H_5)$_2$Ta(=CH_2)(CH_3). The Ta–C(1)–C(2) angle of 171.75 (56)° and the C(1)–C(2) distance of 1.467 (10) Å are consistent with sp hybridization of C(1) and with the presence of a tantalum–benzylidyne triple bond.

Introduction

The first examples of terminal carbyne (or "alkylidyne") complexes of the transition metals were the species *trans*-X(OC)$_4$M≡CR (X = Cl, Br, I; M = Cr, Mo, W; R = Me, Ph), reported by Fischer and co-workers in 1973.[1] Structural studies on several of these group 6A complexes have appeared, and the results have been summarized in a recent article.[2]

Alkylidene and alkylidyne complexes of the group 5A elements niobium and tantalum have recently been synthesized by Schrock and co-workers.[3-11] X-ray structural analyses of the alkylidene species (η^5-C_5H_5)$_2$Ta(=CH_2)(CH_3)[8] and (η^5-C_5H_5)$_2$Ta(=CHCMe$_3$)Cl[12,13] have appeared previously. However, the only tantalum–alkylidyne derivative for which a crystal structure has been reported is the rather complex species [(Me_3CCH_2)$_3$Ta≡CCMe$_3$]Li(dmp) (dmp = *N,N'*-dimethylpiperazine),[10] in which there is, apparently, some interaction between the Li$^+$ ion and the α-carbon atom of the neopentylidyne system.

We now report the results of a single-crystal X-ray structural analysis of the tantalum–benzylidyne complex Ta(η^5-C_5Me_5)(CPh)(PMe_3)$_2$Cl. A brief account of this study has appeared previously.[14]

Experimental Section

(A) Collection and Processing of Diffraction Data. A crystalline sample of Ta(η^5-C_5Me_5)(CPh)(PMe_3)$_2$Cl was kindly supplied by Professor R. R. Schrock of the Massachusetts Institute of Technology. The complex forms orange-brown columnar crystals, which are extended along their b axes. The material may be handled in air for brief periods but decomposes to a white powder after some 24–36 h of exposure to the atmosphere.

Table I. Experimental Data for the X-ray Diffraction Study of Ta(η^5-C_5Me_5)(CPh)(PMe_3)$_2$Cl

(A) Crystal Parameters[a] at 24 °C

cryst system: monoclinic	β = 102.945 (9)°
space group: $P2_1/c$	V = 2573.1 (5) Å^3
a = 10.5129 (12) Å	Z = 4
b = 13.8147 (16) Å	mol wt 592.91
c = 18.1793 (21) Å	ρ(calcd) = 1.531 g cm^{-3}

(B) Measurement of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα ($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly oriented graphite, equatorial, $2\theta_{\text{mono}} = 12.2°$
reflections measd: $+h$, $+k$, $\pm l$
2θ range: 4.5–45°
scan type: coupled θ(cryst)–2θ(counter)
scan speed: 2.0°/min (in 2θ)
scan range: [2θ(Mo Kα_1) – 0.9]°–[2θ(Mo Kα_2 + 0.9]°
bkgd measurement: stationary crystal and counter at beginning and end of the scan, each measured for one-fourth of the scan time
standards: 3 every 97 reflections
reflections collected: 3625 total, yielding 3386 symmetry-independent data
absorption coeff: μ = 47.3 cm^{-1}
absorption cor: empirical (see text)

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of the 24 reflections of the forms $\{72\bar{4}\}$, $\{3,1,\overline{12}\}$, $\{19\bar{3}\}$, $\{284\}$, $\{2,2,10\}$, and $\{622\}$, all with 2θ = 25–30°.

A crystal of maximum orthogonal dimensions 0.13 × 0.23 × 0.41 mm, approximating a trapezoidal prism, was mechanically wedged

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