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Preparation and Structural Characterization of Tris(benzylcyclopentadienide)chlorouranium(IV), $U(C_5H_4CH_2C_6H_5)_3Cl$

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The compound tris(benzylcyclopentadienide)chlorouranium(IV), $U(C_5H_4CH_2C_6H_5)_3Cl$, has been prepared and the crystal and molecular structures have been determined from single-crystal, three-dimensional X-ray diffraction data collected by counter methods. The molecular structure consists of a uranium atom symmetrically bonded to the carbon atoms of three planar aromatic cyclopentadienide anions at an average U–C distance of 2.733 (1) Å and to one chloride ion at 2.627 (2) Å in a distorted tetrahedral geometry with approximately C_{3v} coordination symmetry. The uranium atom is located 0.428 Å above the plane defined by the centers of the three cyclopentadienide anions in contrast to a distance of 0.824 Å expected for tetrahedral geometry. The average C–C bond length in the three planar cyclopentadienide anions is 1.374 (2) Å. The average C–C bond distance for the three planar benzene rings is 1.359 (5) Å. Deep red trapezoidal prisms of $U(C_5H_4CH_2C_6H_5)_3Cl$ have the following crystal data: monoclinic space group $P2_1/n$, cell constants $a = 11.133$ (2), $b = 16.275$ (3), $c = 16.367$ (3) Å, $\beta = 100.45$ (2)°, $Z = 4$, $\rho_{obsd} = 1.68$, and $\rho_{calcd} = 1.68$ g/cm³. The structure has been refined by full-matrix, least-squares methods using 2964 independent reflections with $F^2 > 3\sigma(F^2)$ and a model which includes anisotropic thermal motion with fixed hydrogen positions to a standard unweighted R factor of 3.13%.

Introduction

Of the few lanthanide and actinide organometallic compounds which have been characterized structurally the majority have been the recently prepared complexes of the cyclooctatetraene dianion.[2] The first of these complexes to be prepared and also the first for which the π-sandwich structure was established was bis(cyclooctatetraenyl)uranium(IV), $U(C_8H_8)_2$.[3,4] The homologous thorium complex, $Th(C_8H_8)_2$,[5] has also been studied to compare its geometry with $U(C_8H_8)_2$.[6] More recently the structure of a substituted uranocene derivative, bis(1,3,5,7-tetramethylcyclooctatetraenyl)uranium(IV) has been determined[7,8] and found to contain two distinct conformations. Streitwieser and coworkers have characterized two homologous series of lanthanide(III) complexes with the cyclooctatetraene dianion:[9-11] $[Ln(C_8H_8)Cl\cdot 2C_4H_8O]_2$ and $K[Ln(C_8H_8)_2]$ (Ln = lanthanide). The crystal and molecular structures of the cerium members of both series have been completed and in both cases the C_8H_8 rings are symmetrically π bound.[12,13] A complex of U(III) with benzene, $U(C_6H_6)(AlCl_4)_3$, is known in which the benzene is symmetrically π bound to the uranium ion.[14] The remaining lanthanide or actinide π-sandwich compounds which have been the subjects of structural studies are complexes of the cyclopentadienide anion or the related indenide anion.

Table I. Summary of Crystal Data

Mol formula: $U(C_5H_4CH_2C_6H_5)_3Cl$
Mol wt: 739.147
Linear absorption coeff μ: 85.60 cm⁻¹
Obsd density:[a] 1.68 g/cm³
Calcd density: 1.68 g/cm³
Max crystal dimensions: 0.28 × 0.17 × 0.34 mm
Space group: monoclinic, $P2_1/n$
Molecules/unit cell: 4
Cell constants:[b] $a = 11.1329$ (13), $b = 16.2748$ (22), $c = 16.3674$ (20) Å; $\beta = 100.45$ (2)°; $\cos\beta = -0.1815$ (2)
Cell vol: 2916.3 Å³

[a] Density was measured by flotation in $CHBr_3$-CH_2ClCH_2Cl.
[b] Mo Kα_1 radiation, λ 0.70926 Å. Ambient temperature of 23°.

The structures of two lanthanide(III) complexes with the cyclopentadienide anion, tris(indenide)samarium[15] and the disordered tris(cyclopentadienide)samarium,[16] have been reported. The structure determination of tris(cyclopentadienide)chlorouranium(IV),[17] $U(C_5H_5)_3Cl$, was the first of an actinide(IV) π-sandwich complex. However, very little information can be derived from this structure since the carbon atom positions were not well determined. More recently the structure of tris(indenide)chlorouranium(IV), $U(C_9H_7)_3Cl$, has been reported and a substantial difference was found in the U–C bond lengths for individual carbon atoms in the five-membered ring of the indenyl anion.[18] Since it was not clear to what extent this asymmetry was due to the electronic structure of the indenyl anion as opposed to bonding effects in the uranium coordination, we have determined the crystal and molecular structure of a cyclopentadienide complex, $U(C_5H_4CH_2C_6H_5)_3Cl$.

In order to ensure a well-ordered crystal, a substituted

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Table II. Positional[a] and Anisotropic Thermal Parameters[b]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	0.16280(3)	0.23307(2)	0.27699(2)	75.0(3)	20.7(1)	43.1(2)	-0.42(18)	14.6(2)	-3.5(1)
Cl	-0.03206(20)	0.24819(11)	0.34543(16)	94.7(22)	34.0(11)	64.2(13)	2.0(10)	31.6(14)	-5.7(8)
C$_{11}$	0.2429(8)[c]	0.3389(6)	0.4111(7)	95(11)	43(5)	47(5)	-6(6)	5(6)	-12(4)
C$_{12}$	0.3051(10)	0.3607(6)	0.3488(7)	136(13)	38(5)	60(6)	-33(6)	16(7)	-16(4)
C$_{13}$	0.3831(11)	0.2995(11)	0.3349(10)	101(13)	98(8)	129(12)	-59(9)	59(10)	-72(9)
C$_{14}$	0.3688(13)	0.2404(7)	0.3907(14)	91(13)	54(6)	162(15)	16(8)	-50(11)	-26(8)
C$_{15}$	0.2808(13)	0.2608(8)	0.4373(7)	160(16)	74(7)	51(6)	-35(9)	-30(8)	7(5)
C$_{21}$	0.0990(8)	0.0700(4)	0.3034(6)	105(11)	18(3)	37(5)	-0.8(42)	3(6)	-2(3)
C$_{22}$	0.0796(10)	0.0815(5)	0.2192(6)	194(16)	24(4)	42(6)	-27(6)	20(8)	-10(3)
C$_{23}$	0.1935(16)	0.0918(6)	0.1993(10)	285(24)	16(4)	134(12)	-22(9)	156(15)	-23(6)
C$_{24}$	0.2819(11)	0.0907(7)	0.2643(14)	76(13)	28(5)	188(17)	4(6)	49(11)	-14(7)
C$_{25}$	0.2227(12)	0.0774(5)	0.3331(8)	150(16)	23(4)	86(8)	8(6)	-35(9)	7(4)
C$_{31}$	0.0479(17)	0.3568(8)	0.1825(8)	262(23)	54(6)	48(7)	41(10)	37(11)	27(5)
C$_{32}$	-0.0137(14)	0.2925(12)	0.1481(9)	215(22)	110(10)	49(7)	-31(13)	-16(10)	9(7)
C$_{33}$	0.0668(16)	0.2509(6)	0.1105(7)	274(24)	45(6)	38(5)	22(9)	37(9)	-0.2(4)
C$_{34}$	0.1787(11)	0.2850(9)	0.1217(8)	126(14)	80(8)	73(7)	4(8)	45(8)	21(6)
C$_{35}$	0.1682(15)	0.3595(8)	0.1702(8)	246(21)	55(6)	48(6)	-78(9)	-7(9)	19(5)
C$_{b10}$	0.1566(10)[c]	0.3905(7)	0.4480(8)	138(14)	90(7)	81(8)	-17(8)	26(9)	-48(6)
C$_{b11}$	0.2083(9)	0.4717(6)	0.4834(6)	115(12)	56(5)	53(6)	-8(6)	28(7)	-28(4)
C$_{b12}$	0.3300(11)	0.4779(6)	0.5245(7)	160(15)	43(5)	63(6)	9(6)	-12(8)	-17(5)
C$_{b13}$	0.3774(10)	0.5501(7)	0.5593(7)	152(15)	44(5)	70(7)	-4(7)	-24(8)	-7(5)
C$_{b14}$	0.3070(14)	0.6163(7)	0.5548(8)	219(21)	48(6)	69(8)	-12(9)	40(10)	-8(5)
C$_{b15}$	0.1889(12)	0.6132(7)	0.5138(8)	191(18)	44(5)	77(8)	30(8)	52(10)	4(5)
C$_{b16}$	0.1416(9)	0.5412(8)	0.4776(7)	86(11)	68(6)	76(7)	8(7)	28(7)	-5(5)
C$_{b20}$	0.0032(10)	0.0482(5)	0.3546(8)	211(17)	31(4)	97(8)	-8(6)	94(10)	-2(5)
C$_{b21}$	-0.0231(10)	-0.0434(5)	0.3570(8)	164(14)	33(4)	63(6)	-6(6)	79(8)	-3(4)
C$_{b22}$	0.0269(10)	-0.0908(7)	0.4233(7)	174(16)	56(6)	63(7)	-2(7)	48(9)	-4(5)
C$_{b23}$	-0.0023(12)	-0.1729(7)	0.4262(8)	225(19)	43(6)	72(8)	15(8)	61(10)	17(5)
C$_{b24}$	-0.0769(13)	-0.2076(7)	0.3634(10)	222(19)	39(5)	77(8)	-29(8)	64(10)	-1(5)
C$_{b25}$	-0.1285(12)	-0.1635(8)	0.2962(9)	207(19)	61(7)	86(9)	-41(9)	25(10)	-10(6)
C$_{b26}$	-0.1002(11)	-0.0812(7)	0.2921(8)	207(17)	48(6)	59(7)	12(8)	40(9)	10(5)
C$_{b30}$	-0.0357(25)	0.4162(15)	0.2168(15)	865(69)	272(23)	260(26)	413(37)	374(37)	208(22)
C$_{b31}$	-0.0852(11)	0.4872(8)	0.1790(9)	170(17)	102(9)	69(8)	91(10)	-4(9)	11(7)
C$_{b32}$	-0.0978(12)	0.4968(7)	0.0942(10)	207(19)	42(5)	96(10)	39(8)	10(11)	12(6)
C$_{b33}$	-0.1404(13)	0.5649(10)	0.0531(11)	178(19)	78(9)	119(12)	20(10)	4(12)	32(9)
C$_{b34}$	-0.1801(14)	0.6250(10)	0.0955(16)	138(19)	53(8)	199(20)	-11(9)	-14(17)	-10(11)
C$_{b35}$	-0.1707(14)	0.6208(11)	0.1783(13)	136(18)	82(10)	121(12)	-6(9)	-9(14)	-48(10)
C$_{b36}$	-0.1260(11)	0.5569(10)	0.2198(9)	95(14)	88(8)	96(9)	25(8)	-23(9)	-6(7)

[a] In fractional cell coordinates. [b] Anisotropic β values are multiplied by 10^4; the form of the thermal correction is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] The subscripts on the cyclopentadienide and benzyl carbon atoms specify first the ring number and then the atom number.

cyclopentadiene was chosen as a ligand. To minimize perturbation of the electronic structure of the cyclopentadienyl anion a saturated carbon substituent was desired, but one for which the side chain would promote ordered crystallization. The benzyl group was chosen for this purpose because of the crystallization energy usually released by the π-stacking forces between aromatic rings.

Tris(cyclopentadienide)chlorouranium(IV) and its derivatives previously have been prepared from uranium tetrachloride and a stoichiometric amount of either the sodium or potassium salt of an appropriately substituted cyclopentadiene, generated *in situ*.[19,20] The major drawbacks of this procedure include lack of careful control of stoichiometry and polymer formation resulting from the use of excess cyclopentadiene in the preparation of the alkali salt. Recently $U(C_5H_5)_3Cl$ has been prepared from uranium tetrachloride and a stoichiometric amount of thallous cyclopentadienide in a suitable solvent.[21] The thallous salt offers the experimental advantage of being a water- and air-stable solid; it allows careful control of stoichiometry and is capable of being readily purified by sublimation *in vacuo*.[22] This procedure was adopted in the preparation of $U(C_5H_4CH_2\text{-}C_6H_5)_3Cl$.

Experimental Section

All reactions on the vacuum line were carried out under an inert atmosphere of commercially available high-purity argon which was used without further purification. Transfer and handling of organometallic complexes was facilitated by the use of a Vacuum Atmospheres HE-193-2 inert-atmosphere glove box having an oxygen- and moisture-free recirculating argon atmosphere.

Proton nmr spectra were obtained on a Varian T-60 spectrometer. Ultraviolet-visible spectra were measured either with a Cary Model 14 spectrophotometer or with a Perkin-Elmer Model PE-202 spec-

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trophotometer. Mass spectra were recorded with an AEI-MS12 mass spectrometer.

Materials. Dried and degassed solvents were used in all syntheses and further characterizations. All solvents were dried by vacuum distillation from $LiAlH_4$, except $CHBr_3$ and $ClCH_2CH_2Cl$, which were distilled from Linde 4A molecular sieves. All solvents were deaerated under vacuum before use.

Benzylcyclopentadiene was prepared by the method of Hallam and Pauson[23] and Alder and Holzrichter,[24] using benzyl bromide instead of benzyl chloride. Characterization and purity of the product were established by uv and nmr spectra.

Thallous benzylcyclopentadienide was prepared by a procedure analogous to that for thallous cyclopentadienide.[25] The faintly yellow compound was purified by sublimation at 10^{-3} mm between 80 and 100°. In contrast with the unsubstituted thallous cyclopentadienide, the benzyl compound is air sensitive in the solid state.

Uranium tetrachloride was prepared by a literature procedure.[26]

$U(C_5H_4CH_2C_6H_5)_3Cl$. To a rapidly stirred slurry of 5.67 g (15.8 mmol) of thallous benzylcyclopentadienide in 150 ml of dimethoxyethane under argon was added, over a period of 5 min, a slurry of 1.00 g (2.63 mmol) of uranium tetrachloride in 100 ml of dimethoxyethane. The resulting deep red solution was stirred 5 hr at room temperature and filtered, and the filtrate was concentrated to dryness *in vacuo*. The reddish brown solid residue was sublimed *in vacuo* between 80 and 100° overnight to remove unreacted thallous benzylcyclopentadienide. The remaining solid was Soxhlet extracted under argon with cyclohexane until the recycling liquid was colorless. An amber cyclohexane solution was decanted from a reddish brown solid which had precipitated during the extraction. After this solid was dried *in vacuo*, it was recrystallized from heptane–toluene to afford dark red oxygen-stable crystals. These red crystals were identified as $U(C_5H_4CH_2C_6H_5)_3Cl$ from mass spectra.

Crystal Data. Crystals suitable for X-ray studies were obtained by controlled evaporation of a saturated cyclohexane–toluene solution of the complex under argon atmosphere at room temperature. The apparently oxygen-stable, but water-sensitive, crystals were mounted in thin-walled quartz capillaries with a small amount of Kel-F fluorocarbon grease as an adhesive under an argon atmosphere. A series of precession photographs showed monoclinic symmetry with the following systematic absences: $h0l, h + l \neq 2n$; $0k0, k \neq 2n$. Space group $P2_1/n$ (an alternate setting of $P2_1/c$, $C_{2h}{}^5$) is the only choice which is consistent with these conditions. The general positions are x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; and $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

Data Collection. The data crystal, a dark red trapezoidal block, was bounded by the following six planes: $10\bar{1}$, $0\bar{1}0$, $00\bar{1}$, $\bar{1}01$, 010, 101. The perpendicular distances to each of these planes from the intersection point of the $10\bar{1}$, $0\bar{1}0$, and $00\bar{1}$ planes which was defined as the crystal origin are 0.0, 0.0, 0.0, 0.0166, 0.0209, and 0.0204 cm. The crystal gave ω-scan widths at half-heights of 0.05, 0.06, and 0.07° for the 020, 002, and 200 reflections, respectively. The crystal in its capillary on a translation goniometer head was mounted with the $00\bar{1}$ axis approximately parallel to the ϕ axis of a Picker FACS-1 four-circle diffractometer.

The optimum crystal orientation matrix and unit cell constants were determined by least-squares refinement of the orientation and Bragg 2θ angles for 12 carefully centered reflections whose 2θ angles ranged from 39 to 43°.[27] The X-ray source and diffractometer parameters were kept identical with those used in intensity measurements. The final refined cell parameters and other pertinent crystal data are given in Table I.

Intensity data were collected in the θ–2θ scan mode using monochromatic Mo Kα radiation and a scintillation counter. The Bragg 2θ angle for the graphite monochromator crystal was 12.08° and the X-ray tube takeoff angle was 1.5°. The pulse height analyzer, centered on a Mo Kα peak, was set to admit about 90% of the maximum intensity at full window width. The detector was located 33 cm from the source with a receiving aperture of 7 × 7 mm. The 2θ scans were from 0.6° below the $K\alpha_1$ peak to 0.6° above the $K\alpha_2$ peak with a scan rate of 1.0°/min. Stationary 10-sec background counts were taken at the start and end of each scan and copper foil attenuators were automatically inserted to maintain the count rate for a given reflection below 10^4 counts/sec.

Table III. Calculated Positions for Cyclopentadienide and Benzyl Hydrogen Atoms[a]

Atom	x	y	z	Atom	x	y	z
H_{12}	0.2925	0.4140	0.3179	H_{b15}	0.1367	0.6637	0.5103
H_{13}	0.4378	0.2988	0.2935	H_{b16}	0.0561	0.5401	0.4462
H_{14}	0.4172	0.1882	0.3974	H_{b20}	−0.0743	0.0772	0.3305
H_{15}	0.2522	0.2263	0.4807	H'_{b20}	0.0323	0.0676	0.4128
H_{22}	−0.0010	0.0822	0.1805	H_{b22}	0.0853	−0.0658	0.4706
H_{23}	0.2075	0.0994	0.1409	H_{b23}	0.0334	−0.2064	0.4759
H_{24}	0.3713	0.0976	0.2657	H_{b24}	−0.0966	−0.2673	0.3653
H_{25}	0.2631	0.0739	0.3930	H_{b25}	−0.1867	−0.1901	0.2503
H_{32}	−0.1020	0.2771	0.1495	H_{b26}	−0.1357	−0.0484	0.2420
H_{33}	0.0472	0.2000	0.0772	H_{b30}	−0.1148	0.3794	0.2171
H_{34}	0.2535	0.2652	0.1018	H'_{b30}	0.0003	0.4280	0.2725
H_{35}	0.2296	0.4026	0.1908	H_{b32}	−0.0738	0.4501	0.0613
H_{b10}	0.1306[b]	0.3583	0.4942	H_{b33}	−0.1413	0.5707	−0.0077
H'_{b10}	0.0839	0.4021	0.4042	H_{b34}	−0.2172	0.6748	0.0644
H_{b12}	0.3842	0.4282	0.5283	H_{b35}	−0.2007	0.6681	0.2079
H_{b13}	0.4640	0.5527	0.5885	H_{b36}	−0.1197	0.5573	0.2813
H_{b14}	0.3408	0.6691	0.5809				

[a] Calculated positions. Trigonal (cyclopentadienide and benzene) or tetrahedral (methylene) geometries are assumed for the carbon atoms. A C–H bond length of 1.0 Å and an isotropic thermal parameter of 6.0 $Å^2$ were assumed. [b] The subscripts on the methylene hydrogen atoms specify first the ring number and then the atom number.

Throughout the experiment, the intensities of the three standard reflections, 400, 040, and 004, were measured every 75 reflections as a check on the stability of the crystal and the instrument. The 7413 reflections collected included almost two complete forms of intensity data ($\pm h, \pm k, +l$) out to $2\theta = 40°$. The crystal was lost at this point.

Data reduction and processing were accomplished as previously described.[28] The parameter p, introduced in the expression for $\sigma(F^2)$ to avoid overweighting strong reflections, was set to 0.04. Intensities were corrected for Lorentz and polarization effects and converted to F^2. The F^2 values of the standards showed maximum losses in intensity of only 6, 3, and 5%, respectively, for the three standards mentioned above. Our decay correction program, CHORT,[29] was used to correct the F^2 values for this minimal anisotropic decay. As a check, a comparison of standard F^2's taken at the beginning and end of data collection always agreed within 1% after the decay correction.

The calculated absorption coefficient, μ, is 85.60 cm^{-1}. The maximum and minimum thicknesses, t, for the crystal gave a range of μt from 1.45 to 4.04. An absorption correction was applied using a gaussian numerical integration program.[29] The transmission factors ranged from 0.18 to 0.31. After this correction the data were averaged to give the 2964 independent reflections with $F^2 > 3\sigma(F^2)$ which were used in the final refinement.

Solution and Refinement of the Structure

The structure was solved by the application of heavy-atom techniques. Full-matrix, least-squares refinements on F were used in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting factor, w, is $4F_o{}^2/\sigma(F_o{}^2)$. The atomic scattering factors for neutral U, Cl, and C were taken from the values tabulated by Cromer and Mann[30] and those for neutral hydrogen from Stewart, Davidson, and Simpson.[31a] The calculations included both $\Delta f'$ and $\Delta f''$ corrections for anomalous dispersion effects of the uranium and chlorine atoms.[31b]

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Table IV. Root-Mean-Square Amplitudes of Vibration of All Nonhydrogen Atoms along Principal Axes, Å × 10^3

Atom	Axis 1	Axis 2	Axis 3	Atom	Axis 1	Axis 2	Axis 3
U	164.2 (5)	208.9 (5)	240.4 (5)	C_{b12}	209 (16)	268 (15)	362 (15)
Cl	201 (3)	227 (3)	300 (3)	C_{b13}	225 (15)	260 (14)	372 (15)
C_{11}	204 (14)	248 (14)	277 (14)	C_{b14}	248 (15)	290 (16)	371 (17)
C_{12}	173 (15)	282 (15)	321 (13)	C_{b15}	215 (15)	284 (15)	373 (16)
C_{13}	180 (18)	247 (17)	506 (20)	C_{b16}	211 (15)	301 (14)	320 (15)
C_{14}	198 (16)	255 (16)	512 (23)	C_{b20}	201 (15)	232 (15)	424 (15)
C_{15}	207 (16)	282 (16)	396 (17)	C_{b21}	156 (17)	209 (14)	372 (15)
C_{21}	153 (14)	216 (14)	261 (13)	C_{b22}	244 (16)	276 (15)	345 (15)
C_{22}	151 (16)	240 (15)	352 (14)	C_{b23}	216 (16)	274 (16)	393 (17)
C_{23}	121 (21)	213 (18)	520 (19)	C_{b24}	201 (17)	278 (16)	396 (17)
C_{24}	176 (17)	212 (18)	498 (23)	C_{b25}	244 (16)	335 (18)	384 (16)
C_{25}	165 (16)	250 (16)	405 (17)	C_{b26}	236 (15)	271 (15)	362 (15)
C_{31}	176 (18)	289 (17)	418 (18)	C_{b30}	247 (22)	325 (23)	985 (38)
C_{32}	238 (18)	341 (18)	427 (21)	C_{b31}	177 (17)	318 (17)	453 (17)
C_{33}	210 (16)	240 (16)	412 (18)	C_{b32}	199 (17)	357 (18)	384 (17)
C_{34}	222 (16)	296 (14)	364 (17)	C_{b33}	265 (18)	349 (17)	429 (21)
C_{35}	159 (18)	249 (16)	457 (17)	C_{b34}	250 (19)	297 (20)	531 (26)
C_{b10}	221 (16)	286 (15)	423 (16)	C_{b35}	239 (19)	304 (19)	461 (24)
C_{b11}	181 (15)	256 (14)	333 (14)	C_{b36}	207 (18)	336 (17)	399 (17)

Table V. Bond Lengths and Angles for the Uranium Inner Coordination Sphere

Ring 1		Ring 2		Ring 3	
Atoms	Distance, Å	Atoms	Distance, Å	Atoms	Distance, Å
U-C_{11}	2.805 (9)	U-C_{21}	2.800 (7)	U-C_{31}	2.714 (10)
U-C_{12}	2.744 (8)	U-C_{22}	2.743 (8)	U-C_{32}	2.783 (13)
U-C_{13}	2.691 (10)	U-C_{23}	2.679 (9)	U-C_{33}	2.756 (11)
U-C_{14}	2.681 (13)	U-C_{24}	2.696 (11)	U-C_{34}	2.715 (11)
U-C_{15}	2.751 (10)	U-C_{25}	2.736 (9)	U-C_{35}	2.708 (10)
Mean U-C	2.734 (22)[a]	Mean U-C	2.731 (21)	Mean U-C	2.735 (15)

Group	Distance, Å	Group	Angle, deg
U-1[b]	2.472 (5)	Cl-U-1	99.9
U-2	2.470 (5)	Cl-U-2	101.2
U-3	2.473 (5)	Cl-U-3	98.8
U-Cl	2.627 (2)	1-U-2	117.2
U to 1-2-3 plane	0.428 (3)	1-U-3	118.1
		2-U-3	115.9

Ring 1		Ring 2		Ring 3	
Group mean	Angle, deg	Group mean	Angle, deg	Group mean	Angle, deg
C_i-U-C_{i+1}	29.09 (15)[c]	C_i-U-C_{i+1}	29.06 (36)	C_i-U-C_{i+1}	29.13 (65)

[a] Standard deviations for the mean values reported in this and subsequent tables were estimated from the variance using the equations $\sigma^2 = (\Sigma_{i=1}{}^n(x_i - \bar{x})^2)/n$ and $\sigma_{\bar{x}} = (1/(n-1)^{1/2})\sigma$, where σ is the standard deviation of an individual observation and $\sigma_{\bar{x}}$ is the standard deviation of the mean. [b] Center of ring 1 designated as 1, etc. [c] Atoms *i* and *i* + 1 are adjacent in the cyclopentadienide rings.

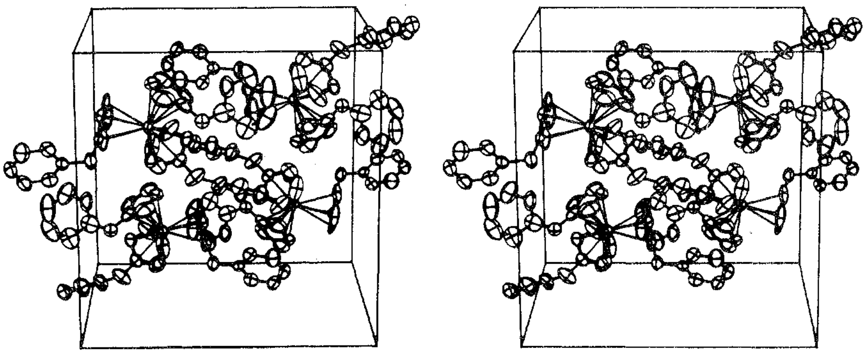

Figure 1. A stereoscopic packing diagram of $U(C_5H_4CH_2C_6H_5)_3Cl$ viewed normal to the *yz* plane. The entire unit cell is shown. The horizontal axis is *a* and the vertical is *c*. The origin of the cell is the lower left rear corner.

The positions of the uranium and chlorine atoms were determined from a three-dimensional Patterson map. Isotropic least-squares refinement of these two heavy-atom positions followed by a difference Fourier synthesis on *F* located nine carbon atoms of the three cyclopentadienide anions. Three additional least-squares cycles and another difference Fourier located all remaining carbon atoms. The hydrogen atom positions were calculated by assuming appropriate tetrahedral (for methylene carbon atoms) or planar (for the cyclopentadienide and benzene rings) geometry and C-H bond lengths of 1.0 Å. In the final anisotropic refinement, the hydrogen atom contributions to the structure factors were calculated from these fixed positions and the temperature factors for all hydrogens were set to 6.0 $Å^2$. The final agreement factors $R_1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$ and R_2 (weighted *R* factor) = $\{[\Sigma w(|F_o| - |F_c|)^2]/\Sigma wF_o{}^2\}^{1/2}$ were 3.13 and 3.47%, respectively. The final error in an observation of unit weight is 0.929. The final difference Fourier showed no peaks greater than 0.6 e/$Å^3$ which were not due to residual peaks around the uranium atom.[32]

The positional and anisotropic thermal parameters from the final least-squares cycle and their associated standard deviations are listed

Table VI. Bond Lengths and Angles for the Cyclopentadienide Anions and the Benzyl Groups

Unit 1		Unit 2		Unit 3	
Bond	Length, Å	Bond	Length, Å	Bond	Length, Å
C_{11}-C_{12}	1.379 (14)	C_{21}-C_{22}	1.367 (12)	C_{31}-C_{32}	1.320 (16)
C_{12}-C_{13}	1.368 (15)	C_{22}-C_{23}	1.377 (15)	C_{32}-C_{33}	1.355 (19)
C_{13}-C_{14}	1.357 (21)	C_{23}-C_{24}	1.312 (19)	C_{33}-C_{34}	1.346 (16)
C_{14}-C_{15}	1.387 (21)	C_{24}-C_{25}	1.421 (20)	C_{34}-C_{35}	1.466 (16)
C_{15}-C_{11}	1.383 (14)	C_{25}-C_{21}	1.380 (13)	C_{35}-C_{31}	1.391 (17)
C_{11}-C_{b10}	1.484 (13)	C_{21}-C_{b20}	1.514 (13)	C_{31}-C_{b30}	1.519 (20)
C_{b10}-C_{b11}	1.514 (13)	C_{b20}-C_{b21}	1.521 (12)	C_{b30}-C_{b31}	1.377 (18)
C_{b11}-C_{b12}	1.403 (13)	C_{b21}-C_{b22}	1.365 (15)	C_{b31}-C_{b32}	1.378 (17)
C_{b12}-C_{b13}	1.370 (13)	C_{b22}-C_{b23}	1.379 (14)	C_{b32}-C_{b33}	1.339 (16)
C_{b13}-C_{b14}	1.327 (15)	C_{b23}-C_{b24}	1.326 (16)	C_{b33}-C_{b34}	1.321 (22)
C_{b14}-C_{b15}	1.364 (15)	C_{b24}-C_{b25}	1.351 (17)	C_{b34}-C_{b35}	1.341 (24)
C_{b15}-C_{b16}	1.373 (15)	C_{b25}-C_{b26}	1.380 (15)	C_{b35}-C_{b36}	1.292 (20)
C_{b16}-C_{b11}	1.347 (13)	C_{b26}-C_{b21}	1.383 (15)	C_{b36}-C_{b31}	1.431 (17)
Mean C-C[a]	1.375 (5)	Mean C-C	1.371 (17)	Mean C-C	1.376 (25)
Mean C-C[b]	1.364 (10)	Mean C-C	1.364 (9)	Mean C-C	1.350 (20)

Unit 1		Unit 2		Unit 3	
Group	Angle, deg	Group	Angle, deg	Group	Angle, deg
C_{15}-C_{11}-C_{12}	107.5 (10)	C_{25}-C_{21}-C_{22}	108.0 (9)	C_{35}-C_{31}-C_{32}	113.8 (14)
C_{11}-C_{12}-C_{13}	110.8 (11)	C_{21}-C_{22}-C_{23}	105.8 (11)	C_{31}-C_{32}-C_{33}	104.7 (14)
C_{12}-C_{13}-C_{14}	104.4 (12)	C_{22}-C_{23}-C_{24}	113.1 (14)	C_{32}-C_{33}-C_{34}	113.8 (12)
C_{13}-C_{14}-C_{15}	112.4 (12)	C_{23}-C_{24}-C_{25}	105.0 (11)	C_{33}-C_{34}-C_{35}	104.6 (10)
C_{14}-C_{15}-C_{11}	104.8 (12)	C_{24}-C_{25}-C_{21}	108.1 (11)	C_{34}-C_{35}-C_{31}	103.0 (10)
C_{15}-C_{11}-C_{b10}	125.2 (12)	C_{25}-C_{21}-C_{b20}	125.7 (10)	C_{35}-C_{31}-C_{b30}	134.7 (20)
C_{12}-C_{11}-C_{b10}	127.2 (11)	C_{22}-C_{21}-C_{b20}	126.2 (10)	C_{32}-C_{31}-C_{b30}	110.9 (22)
C_{11}-C_{b10}-C_{b11}	114.8 (9)	C_{21}-C_{b20}-C_{b21}	113.7 (7)	C_{31}-C_{b30}-C_{b31}	126.2 (15)
C_{b16}-C_{b11}-C_{b10}	122.7 (11)	C_{b26}-C_{b21}-C_{b20}	120.8 (11)	C_{b36}-C_{b31}-C_{b30}	126.2 (16)
C_{b12}-C_{b11}-C_{b10}	120.9 (10)	C_{b22}-C_{b21}-C_{b20}	121.4 (12)	C_{b32}-C_{b31}-C_{b30}	120.4 (15)
C_{b16}-C_{b11}-C_{b12}	116.4 (9)	C_{b26}-C_{b21}-C_{b22}	117.8 (9)	C_{b36}-C_{b31}-C_{b32}	113.4 (11)
C_{b11}-C_{b12}-C_{b13}	121.8 (10)	C_{b21}-C_{b22}-C_{b23}	120.7 (11)	C_{b31}-C_{b32}-C_{b33}	124.2 (14)
C_{b12}-C_{b13}-C_{b14}	119.6 (11)	C_{b22}-C_{b23}-C_{b24}	120.3 (11)	C_{b32}-C_{b33}-C_{b34}	118.0 (18)
C_{b13}-C_{b14}-C_{b15}	120.3 (11)	C_{b23}-C_{b24}-C_{b25}	121.3 (11)	C_{b33}-C_{b34}-C_{b35}	121.4 (19)
C_{b14}-C_{b15}-C_{b16}	120.3 (10)	C_{b24}-C_{b25}-C_{b26}	119.2 (12)	C_{b34}-C_{b35}-C_{b36}	121.6 (18)
C_{b15}-C_{b16}-C_{b11}	121.5 (10)	C_{b25}-C_{b26}-C_{b21}	120.7 (11)	C_{b35}-C_{b36}-C_{b31}	121.1 (16)

[a] Cyclopentadienide ring. [b] Benzene ring.

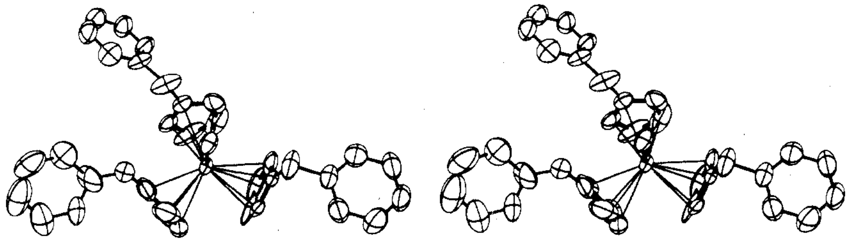

Figure 2. A stereoscopic diagram of $U(C_5H_4CH_2C_6H_5)_3Cl$ viewed approximately parallel to the uranium-chlorine bond. Thermal ellipsoids are drawn at the 40% probability contour scale. An isotropic temperature factor of 5.0 e/Å^3 has been assigned to methylene carbon atom, C_{b30} (located in lower left corner), since its anisotropic temperature factors are unusually large.

in Table II. The calculated hydrogen positions are given in Table III and the root-mean-square amplitudes of vibration of all nonhydrogen atoms are given in Table IV.

Description of the Structure and Discussion

The crystal structure consists of four discrete molecules of $U(C_5H_4CH_2C_6H_5)_3Cl$ per unit cell. A stereoscopic view of the unit cell is shown in Figure 1. There are no unusually short intermolecular nonbonded distances (less than 4.1 Å). In particular, there is no evidence of stacking of the phenyl rings. This surprising result counters the reason for preparing this derivative and is apparently due to the fan configuration of these rings imposed by the coordination geometry.

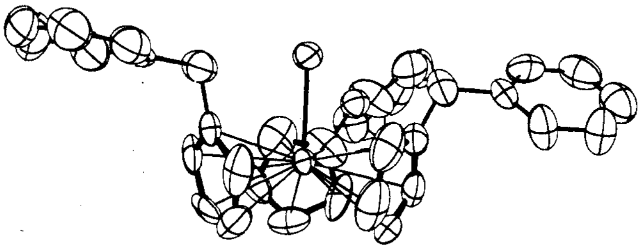

Figure 3. The $U(C_5H_4CH_2C_6H_5)_3Cl$ molecule viewed perpendicular to the uranium-chlorine bond. Thermal ellipsoids are drawn at the 40% probability contour scale. Isotropic methylene carbon, C_{b30}, is located to the right of the chlorine atom.

A stereoscopic drawing of the molecule viewed approximately parallel to the uranium-chlorine bond is shown in Figure 2. A perspective drawing of the molecule viewed

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(32) A listing of structure factors will appear following these pages in the microfilm edition of this journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1329.

perpendicular to the uranium-chlorine bond is shown in Figure 3. The chlorine and the five-membered rings of the three benzylcyclopentadienyl moieties are arranged in an approximate tetrahedron about the uranium atom. The extent of deviation of the structure from a regular tetrahedron is shown by the following angles about the uranium atom to the chlorine atom and to the centers of each of the three cyclopentadienide anions (designated as 1, 2, and 3 in Table V). The average Cl-U-center of ring angle of 100.0° agrees well with the corresponding angle of 101° reported for $U(C_5H_5)_3Cl$[17] but differs slightly from the value of 106.6° reported for $U(C_9H_7)_3Cl$.[18] The average center of ring-U-center of ring angle of 117.1° also agrees well with the corresponding value of 116.7° for $U(C_5H_5)_3Cl$[17] but differs slightly from the value of 112.3° for $U(C_9H_7)_3Cl$.[18] The average distance from the uranium atom to the center of each cyclopentadienide anion is 2.472 Å, which is in good agreement with the corresponding distance of 2.50 Å for $U(C_9H_7)_3Cl$.[18] If one assumes tetrahedral geometry about the uranium atom and an average uranium to center-of-ring distance of 2.472 Å, then the uranium atom should be located 0.824 Å above the plane defined by the centers of the three cyclopentadienide rings. Another measure of the trigonal distortion from a tetrahedral geometry is that this distance is 0.428 Å.

The most important result of the structure is that the uranium atom is bonded symmetrically to the carbon atoms of the three cyclopentadienide anions (Table V). The average uranium-carbon distance for all three rings is 2.733 (1) Å. This is in good agreement with the average distances of 2.78 Å reported for $U(C_9H_7)_3Cl$[18] and 2.74 Å for $U(C_5H_5)_3Cl$.[17] The average C-U-C angle for all three rings (Table V) is 29.1 (2)°. The uranium-chlorine bond distance of 2.627 (2) Å differs slightly from reported values of 2.593 (3) Å for $U(C_9H_7)_3Cl$[18] and 2.559 (16) Å for $U(C_5H_5)_3Cl$.[17] The thermal motion of the heavy atoms is nearly isotropic.

The bond lengths and angles for the cyclopentadienide anions and benzyl groups are summarized in Table VI. The three cyclopentadienide anions are planar and have average bond lengths of 1.375 (5), 1.371 (17), and 1.376 (25) Å, respectively. The average C-C bond length of 1.374 (2) Å in the present structure differs significantly from the bond length of 1.43 Å reported for $U(C_9H_7)_3Cl$.[18] The longer bond distances in $U(C_9H_7)_3Cl$ can be partially ascribed to the omission of hydrogen atom contributions in the structure factor calculations. A weighted least-squares plane (Table VII) through each of the three cyclopentadienide anions has all atoms within 0.02 Å of the plane with standard deviations of about 0.01 Å. The planar rings have the regular interior pentagonal angle of 108.0°. The planarity of the cyclopentadienide anions and their mean bond lengths and angles demonstrate the aromatic nature of these 6π-electron anion rings. The carbon atoms of each of the cyclopentadienide anions exhibit relatively large anisotropic thermal motion and show a preferential oscillation about their respective (pseudo) fivefold symmetry axes. The mean rms amplitudes of vibration along the major axes are 0.402 (48), 0.407 (48), and 0.416 (15) Å for the three cyclopentadienide anions, respectively. These approximately represent the average thermal motion along the circumferences of the cyclopentadienide rings. The three phenyl rings are planar and have average bond lengths (Table VI) of 1.364 (10), 1.364 (9), and 1.350 (20) Å, respectively. A weighted least-squares plane (Table VII) through each of the three phenyl rings has all atoms within 0.03 Å of the plane with standard deviations of about 0.01 Å. However, the interior angles about the phenyl carbon atoms bonded to the methylene carbons are significantly less than 120°, resulting in the benzene rings being drawn out at those carbon atoms.

Table VII. Weighted Least-Squares Planes

Cyclopentadienide Anion

Ring 1		Ring 2		Ring 3	
Atom	Distance[a]	Atom	Distance[a]	Atom	Distance[a]
C_{11}	0.006 (9)	C_{21}	0.011 (7)	C_{31}	0.000 (11)
C_{12}	−0.003 (9)	C_{22}	−0.015 (8)	C_{32}	0.008 (13)
C_{13}	−0.008 (12)	C_{23}	0.010 (9)	C_{33}	−0.009 (10)
C_{14}	0.018 (13)	C_{24}	0.002 (11)	C_{34}	0.011 (11)
C_{15}	−0.012 (10)	C_{25}	−0.011 (9)	C_{35}	−0.006 (11)

Parameters from Equation of Plane[b]

Ring 1		Ring 2		Ring 3	
A	6.75	*A*	1.30	*A*	1.48
B	6.61	*B*	−16.06	*B*	−8.56
C	9.20	*C*	−2.18	*C*	13.12
D	7.65	*D*	−1.67	*D*	−0.591

Benzene

Ring 1		Ring 2		Ring 3	
Atom	Distance[a]	Atom	Distance[a]	Atom	Distance[a]
C_{b11}	−0.014 (10)	C_{b21}	−0.007 (9)	C_{b31}	−0.002 (14)
C_{b12}	0.007 (12)	C_{b22}	0.009 (10)	C_{b32}	−0.013 (13)
C_{b13}	0.009 (13)	C_{b23}	−0.006 (11)	C_{b33}	0.026 (15)
C_{b14}	−0.012 (12)	C_{b24}	0.004 (12)	C_{b34}	−0.016 (15)
C_{b15}	−0.002 (12)	C_{b25}	−0.006 (13)	C_{b35}	−0.002 (15)
C_{b16}	0.016 (11)	C_{b26}	0.009 (11)	C_{b36}	0.009 (12)

Parameters from Equation of Plane[b]

Ring 1		Ring 2		Ring 3	
A	5.06	*A*	6.26	*A*	10.12
B	4.02	*B*	2.34	*B*	6.47
C	−15.13	*C*	6.24	*C*	−0.656
D	−4.35	*D*	2.27	*D*	2.18

[a] Distances (in angstroms) of individual atoms from weighted least-squares plane. [b] Equation for least-squares plane in monoclinic coordinates: $Ax + By + Cz - D = 0$.

The closest analog to $U(C_5H_4CH_2C_6H_5)_3Cl$ is $U(C_5H_5)_3Cl$. Since the individual carbon atom positions of the structure of $U(C_5H_5)_3Cl$[17] were not refined, comparisons can only be made for average values. The bond angles agree well but there are significant differences in individual bond lengths. Comparison with $U(C_9H_7)_3Cl$ is less direct because of the difference in electronic structure of the indenyl anion. In $U(C_9H_7)_3Cl$ the three carbon atoms of the indenyl anion which are in the five-membered ring but not in the six-membered ring were found to have shorter U-C bond lengths than the remaining two carbon atoms of the five-membered ring.[18] Molecular orbital calculations indicate that the negative charge of the indenyl anion primarily resides on the three isolated carbon atoms. This apparently imposes the trihapto character of the bonding observed in the structure of $U(C_9H_7)_3Cl$. If the difference in ionic radius of 0.10 Å for U(III) and U(IV)[33] is applied to the U-C distance in $U(C_6H_6)(AlCl_4)_3$ of 2.91 Å[14] to estimate a U(IV) distance, the U-C bond lengths for U(IV) π-carbocyclic ligands of charge 0, 1−, and 2− are 2.81, 2.73, and 2.65 Å, respectively. This satisfies a linear relationship: U-C distance = 2.81 + 0.0815*q*, where *q* is the ligand charge.

In summary, this structure provides the first proof of the

(33) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).

symmetrical pentahapto bonding in cyclopentadienyl complexes of the actinides. Presumably the lanthanide complexes also show this geometry. The complicated bridging structure found for $Sm(C_5H_5)_3$ would appear to be anomalous, but the severe experimental difficulties associated with that structure analysis leaves the issue open.

Registry No. $U(C_5H_4CH_2C_6H_5)_3Cl$, 37325-10-3.

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Crystal and Molecular Structure of Tetrakis(triphenylphosphine)di-μ-carbonyl-dirhodium(0)-Bis(dichloromethane) Solvate

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The crystal and molecular structure of tetrakis(triphenylphosphine)di-μ-carbonyl-dirhodium(0)-bis(dichloromethane) solvate, $[Rh(PPh_3)_2CO]_2 \cdot 2CH_2Cl_2$, has been obtained from counter X-ray data. The complex crystallizes in the monoclinic space group $C2/c$ with four dimeric formula units in a cell of dimensions $a = 23.213$ (19), $b = 13.171$ (6), $c = 24.423$ (12) Å, and $\beta = 65.45$ (1)°. The structure was refined by full-matrix least-squares methods to a final value of $R = 0.067$ for 5682 independent reflections having $F^2 > 3\sigma(F^2)$. The complex is dimeric, with the two rhodium(0) atoms linked by two carbonyl bridges; there is a twofold rotation axis passing through the center of the dimer. The Rh–Rh separation of 2.630 (1) Å is indicative of the presence of a metal–metal bond, and the geometry at the metals is very different from other five-coordinate structures. There may be an interaction between the carbonyl groups and the dichloromethane molecules.

Introduction

Complexes having the molecular formulation $[(Ph_3P)_2(S)Rh(CO)]_2$, where S is dichloromethane or ethanol, were first prepared by Wilkinson and coworkers[1] by concentrating a benzene solution of the parent dimer $[(Ph_3P)_2Rh(CO)_2]_2$ under a stream of nitrogen or argon in the presence of dichloromethane or ethanol, which results in the displacement of 2 mol of carbon monoxide per dimer. In contrast to this behavior, these workers found that treatment of a solution of the parent dimer with molecular hydrogen resulted in the reversible formation of the hydrido precursor according to the equilibrium expression

$$[(Ph_3P)_2Rh(CO)_2]_2 \underset{2CO}{\overset{H_2}{\rightleftarrows}} 2RhH(CO)_2(PPh_3)_2 \qquad (1)$$

The solvated complexes are reversibly converted to the parent dimer in the presence of carbon monoxide (eq 2), irreversibly

$$[(Ph_3P)_2(S)Rh(CO)]_2 \underset{2N_2}{\overset{CO}{\rightleftarrows}} [(Ph_3P)_2Rh(CO)_2]_2 + 2S \qquad (2)$$

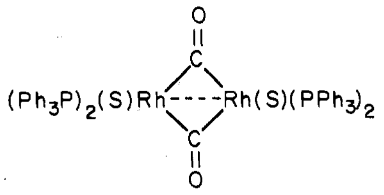
absorb hydrogen in the presence of a large excess of triphenylphosphine to re-form the hydrido starting complex $RhH(CO)(PPh_3)_3$ (eq 3), and readily undergo bridge cleavage

$$[(Ph_3P)_2(S)Rh(CO)]_2 \begin{cases} \xrightarrow{H_2 \,+\, 2PPh_3} 2RhH(CO)(PPh_3)_3 + 2S \\ \xrightarrow{I_2} 2(Ph_3P)_2(CO)RhI + 2S \end{cases} \qquad (3)$$

in the presence of iodine (eq 3).

The solid-state and solution infrared spectra of the parent dimer indicate the presence of *both* terminal and bridging carbonyl groups, whereas the solid-state infrared spectra of the solvated complexes show only bridging carbonyl bands. However, the solution infrared spectrum of the dichloromethane derivative shows the presence of both terminal and bridging carbonyl bands, the appearance of which was attributed to tautomeric isomerization of the complex in solution. This behavior is analogous to that observed for $Co_2(CO)_8$ in solution.[2]

Since the solid-state infrared spectra of the solvated complexes show bands attributable only to bridging carbonyl groups and since it is impossible to precipitate the complexes in the absence of dichloromethane or ethanol, Wilkinson and coworkers[1] suggested that the complexes should be formulated as dimers (I), but in the absence of crystallographic and magnetic data they were unable to present any compelling evidence for the presence of a rhodium–rhodium bond or for an interaction between the solvent molecules and the metal. In order to determine both the coordination geometry about each rhodium(0) atom and the role of the solvent molecules, we have undertaken a three-dimensional structural investigation of the dichloromethane complex.[3]



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(1) D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. A*, 2660 (1968).

(2) K. Noack, *Spectrochim. Acta*, 19, 1925 (1963); G. Bor, *ibid.*, 2065 (1963).

(3) A preliminary account of this structure has already appeared: C. B. Damman, P. Singh, and D. J. Hodgson, *J. Chem. Soc., Chem. Commun.*, 586 (1972).