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Synthesis and Crystal Structure of $UCp_3(C_3H_3N_2)$. A New Mode of Pyrazolate Bonding

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The title compound has been prepared by the reaction of tricyclopentadienyluranium chloride (UCp_3Cl) and sodium pyrazolate ($NaC_3H_3N_2$) in tetrahydrofuran (THF). The compound has been characterized by its infrared, visible–near-IR, ^1H NMR, and mass spectra and by single-crystal X-ray diffraction. The molecular structure consists of discrete $UCp_3(C_3H_3N_2)$ molecules in which the uranium(IV) ion is coordinated by three η^5-Cp rings in a nearly trigonal array similar to that of other lanthanide and actinide MCp_3X structures. However, unlike these other structures, an 11-coordinate geometry is achieved by having both the adjacent nitrogen atoms of the pyrazolate ring coordinate to the metal ion such that the local twofold axis of the pyrazolate ring and the local threefold axis of the UCp_3 fragment coincide. This is the first example of this type of endo-bidentate η^2 coordination for the pyrazolate anion. Red-brown crystals from toluene conform to space group $P2_1/a$ (an alternate setting of $P2_1/c$) with $a = 14.295$ (1) Å, $b = 8.383$ (1) Å, $c = 14.282$ (1) Å, $\beta = 112.80$ (1)°, and four molecules per unit cell. For the 3631 independent reflections collected by counter methods with $F^2 > 3\sigma(F^2)$, the final weighted and unweighted R factors are both 3.14%. The U–N distances are 2.40 (1) and 2.36 (1) Å. The average U–C distance of 2.76 Å is consistent with that predicted for an 11-coordinate uranium(IV) cyclopentadienyl complex. The 90-MHz proton resonances of the Cp rings occur at −9.51 (35 °C), −11.59 (−10 °C), −14.22 (−50 °C), and −15.84 (−75 °C) ppm. Susceptibility studies from 5 to 80 K show a temperature-independent paramagnetism from 7.5 to 37.1 K; above this temperature $\mu_{eff} = 2.67\ \mu_B$.

Introduction

As part of our effort to create and examine complexes which constitute structural and magnetic probes of the mode of bonding in organoactinide and -lanthanide compounds,[1,2] we have sought the synthesis and characterization of particular dimeric organouranium compounds. The pyrazolate anion has been used extensively throughout transition-metal chemistry,[3] where its coordination is almost always exo-bidentate, i.e., an η^2 bridging ligand. Stucky and Fieselman recently reported that the reaction of $TiCp_2Cl$ with sodium pyrazolate yields a dimeric compound of formula $[TiCp_2(pyrazolate)]_2$.[4] And, while the large class of MCp_3X compounds (M = lanthanide or actinide) are all formally 10-coordinate, Fischer and coworkers have reported 11-coordinate $UCp_3(NCS)(CH_3CN)$.[5] Thus we anticipated that results similar to those with $TiCp_2Cl$ might be obtained with UCp_3Cl. Instead, we report the first example of an endo-bidentate (η^2 nonbridging) pyrazolate anion in formally 11-coordinate $UCp_3(C_3H_3N_2)$.

Experimental Section

All reactions were carried out under an inert atmosphere of argon on a Schlenk or vacuum line. Transfer and some handling were facilitated by a Vacuum Atmospheres HE-93-A glovebox with recirculating moisture and an oxygen-free argon atmosphere. Elemental analyses were performed by the Analytical Laboratory, University of California, Berkeley, CA. Infrared spectra were recorded on a Perkin-Elmer Model 597 spectrophotometer, mass spectra were obtained on an AEI-MS12 mass spectrometer, electronic spectra were recorded on a Cary 14 spectrophotometer, and ^1H NMR spectra were obtained with a JEOL Model FX90Q spectrometer. Crystalline samples for X-ray diffraction were mounted in glass capillaries under a He atmosphere in a horizontal-format inert-atmosphere glovebox equipped with a binocular microscope.

Materials. Toluene and tetrahydrofuran (THF) were distilled from potassium benzophenone ketyl. Pyrazole was obtained from Aldrich (98%) and recrystallized from toluene at −15 °C before use. Sodium pyrazolate was prepared from NaH and pyrazole in THF.[6]

$UCp_3(C_3H_3N_2)$. To a clear brown solution of 2.00 g of UCp_3Cl (4.27 mmol) dissolved in 100 mL THF was added 0.38 g of $Na(C_3H_3N_2)$ (4.22 mmol) in 10 mL of THF. A fine precipitate was visible after the solution was stirred for a few hours at room temperature. The mixture was filtered through diatomaceous earth and the THF removed from the filtrate under vacuum. A saturated toluene solution was cooled to −15 °C whereupon large crystals formed. Anal. Calcd for $UC_{18}H_{18}N_2$: C, 43.20; H, 3.60; N, 5.60. Found: C, 43.55; H, 3.63; N, 5.64.

Table I. Molar Susceptibilities

T, K	$10^3 \times \chi_m^{cor}$, cm^3/mol	T, K	$10^3 \times \chi_m^{cor}$, cm^3/mol	T, K	$10^3 \times \chi_m^{cor}$, cm^3/mol
7.5	12.92	27.2	12.23	56.7	10.94
10.7	12.80	37.1	13.14	77.3	8.57
18.3	12.62	50.0	11.55		

Infrared spectrum (Nujol mull) (relative intensity): 1469 (w), 1440 (w), 1409 (w), 1343 (w), 1280 (s), 1070 (s), 1022 (m), 998 (s), 970 (m), 776 (s), 616 (m) cm^{-1}.

Mass spectrum (70 eV) (relative abundance): 500(21.66), 435(86.52), 370(18.73), 343(13.23), 317(28.76), 68(100).

Electronic spectrum (toluene solution): 1640, 1600, 1520, 1370, 1325, 1290, 1260, 1230, 1160, 1110, 1080, 980, 892, 790, 760, 738, 690, 662, 587, 548 nm.

Variable-temperature ^1H NMR (in toluene-d_8) (δ vs. Me_4Si) at 35 °C: −9.51 (s, Cp), 10.68 (s, pyrazolate), 8.75 (s, pyrazolate). The respective peaks at other temperatures are as follows: at −10 °C −11.59, 11.31, 9.18; at −50 °C −14.22, 12.06, 9.69; at −75 °C −15.84, 12.53, 10.03.

Magnetic susceptibility measurements were made with a PAR Model 155 vibrating-sample magnetometer used with a homogeneous field produced by a Varian Associates 12-in. electromagnet capable of a maximum field strength of 12.5 kG. A 173-mg sample was weighed and transferred to a diamagnetic, calibrated sample holder machined from Kel-F rod. A variable-temperature liquid-helium dewar produced sample temperatures in the range 5–80 K which were measured by a calibrated GaAs diode approximately 12 mm above the sample. The magnetometer was calibrated with $HgCo(CNS)_4$. The resulting susceptibilities were corrected for underlying diamagnetism and yield a temperature-independent paramagnetism from 7.5 to 37.1 K, above which μ_{eff} calculated from the slope of $1/\chi$ vs. T is equal to 2.67 μ_B (Table I).

X-ray Diffraction Data Collection and Structure Solution and Refinement. Suitable crystals for diffraction were obtained by cooling an unsaturated toluene solution of $UCp_3(C_3H_3N_2)$ to −75 °C overnight. Several crystals were mounted in 0.2-mm glass capillaries under He, and the capillaries were sealed with grease and later sealed in a flame. A crystal was mounted on a CAD-4 automatic diffractometer with graphite monochromator and molybdenum X-ray tube. The lattice

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Table II. Positional and Thermal Parameters ($\times 10^4$)[a]

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U(1)	0.23092 (2)	0.22442 (3)	0.24961 (2)	42.42 (18)	75.5 (4)	35.79 (17)	4.9 (3)	15.33 (13)	4.2 (3)
C(1)	0.3752 (8)	0.3632 (14)	0.4215 (8)	63 (8)	196 (23)	67 (8)	−18 (10)	16 (6)	−49 (11)
C(2)	0.3091 (9)	0.2799 (13)	0.4551 (7)	101 (9)	149 (18)	37 (6)	−8 (11)	25 (5)	−16 (10)
C(3)	0.2171 (9)	0.3602 (15)	0.4201 (9)	88 (9)	207 (23)	78 (9)	−26 (12)	52 (8)	−52 (12)
C(4)	0.2250 (10)	0.4882 (13)	0.3624 (9)	90 (10)	148 (21)	75 (9)	24 (11)	27 (7)	−32 (11)
C(5)	0.3206 (11)	0.4924 (13)	0.3634 (9)	117 (12)	138 (21)	77 (10)	−34 (12)	42 (8)	−12 (11)
C(6)	0.1581 (10)	0.2577 (14)	0.0425 (7)	110 (11)	190 (26)	49 (7)	−2 (12)	19 (6)	9 (11)
C(7)	0.1061 (9)	0.3735 (18)	0.0726 (9)	70 (9)	305 (33)	73 (9)	51 (14)	11 (7)	69 (14)
C(8)	0.1782 (12)	0.4912 (14)	0.1243 (10)	127 (13)	144 (22)	83 (10)	46 (13)	41 (9)	44 (12)
C(9)	0.2702 (10)	0.4428 (18)	0.1242 (10)	78 (10)	274 (31)	85 (10)	−27 (14)	26 (8)	78 (15)
C(10)	0.2568 (10)	0.3004 (18)	0.0723 (9)	107 (11)	266 (29)	60 (8)	16 (14)	47 (7)	21 (13)
C(11)	0.0486 (8)	0.1293 (13)	0.2550 (9)	56 (7)	200 (22)	86 (9)	−15 (10)	42 (7)	9 (11)
C(12)	0.0467 (8)	0.0751 (15)	0.1609 (9)	66 (9)	225 (25)	75 (9)	−44 (11)	8 (7)	22 (17)
C(13)	0.1168 (10)	−0.0476 (15)	0.1786 (11)	100 (11)	165 (24)	115 (13)	−57 (12)	66 (10)	−36 (14)
C(14)	0.1627 (9)	−0.0720 (12)	0.2801 (12)	73 (9)	100 (19)	144 (14)	−24 (9)	34 (9)	33 (13)
C(15)	0.1203 (9)	0.0357 (14)	0.3291 (9)	91 (10)	176 (22)	83 (9)	−37 (11)	36 (8)	27 (12)
N(1)	0.3722 (6)	0.0455 (9)	0.3204 (6)	62 (6)	140 (15)	58 (6)	18 (7)	19 (5)	−13 (7)
N(2)	0.3472 (6)	0.0497 (10)	0.2213 (6)	69 (6)	175 (16)	52 (6)	21 (7)	20 (5)	−25 (8)
C(16)	0.4015 (10)	−0.0660 (16)	0.1986 (11)	85 (10)	265 (29)	110 (12)	7 (13)	49 (9)	−72 (15)
C(17)	0.4575 (9)	−0.14681 (13)	0.2826 (11)	82 (10)	121 (19)	140 (13)	23 (10)	35 (10)	−20 (14)
C(18)	0.4369 (9)	−0.0777 (14)	0.3576 (10)	95 (10)	185 (24)	88 (10)	45 (12)	14 (8)	34 (12)

atom	x	y	z	atom	x	y	z
H(1)	0.4439	0.3370	0.4353	H(10)	0.3078	0.2422	0.0596
H(2)	0.3245	0.1853	0.4949	H(11)	0.0090	0.2131	0.2657
H(3)	0.1589	0.3325	0.4334	H(12)	0.0044	0.1149	0.0960
H(4)	0.1718	0.5611	0.3276	H(13)	0.1308	−0.1043	0.1276
H(5)	0.3456	0.5697	0.3303	H(14)	0.2143	−0.1483	0.3128
H(6)	0.1289	0.1629	0.0067	H(15)	0.1378	0.0425	0.4002
H(7)	0.0359	0.3735	0.0608	H(16)	0.4003	−0.0861	0.1327
H(8)	0.1656	0.5863	0.1536	H(17)	0.5017	−0.2340	0.2882
H(9)	0.3326	0.4982	0.1547	H(18)	0.4641	−0.1102	0.4269

[a] B_{iso} equals 8.0 Å^2 for all H atoms.

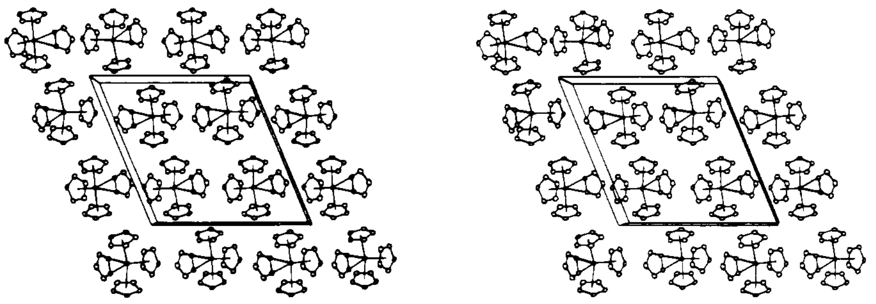

Figure 1. Stereoscopic packing diagram for $UCp_3(C_3H_3N_2)$. The view is down the *b* axis. Thermal ellipsoids are drawn to the 50% probability level.

constants were determined from a least-squares refinement on 25 automatically centered reflections with 2θ values between 27 and 38°. Data reduction and processing were carried out as described elsewhere.[7] The intensities were corrected for Lorentz and polarization effects and converted to values of F^2. Crystal faces were identified with the help of the diffractometer, and the dimensions of the nine faces found were measured at 7× magnification under a binocular microscope. Absorption corrections were then made with use of an analytical algorithm.[8] Azimuthal scans of six reflections revealed an intensity variation of roughly ±10%. Minor adjustments to the observed dimensions of the crystal were made to minimize the variation after the absorption correction was made ($\mu = 97.50$ cm^{-1}). The best fit of observed and calculated dimensions left a maximum variation of ±4% after the correction was applied. The actual data were then subjected to an absorption correction which ranged from 2.76 to 3.84. No crystal decay was observed in the three reflections monitored throughout data collection. The data were averaged to yield the 3631 independent reflections with $F^2 > 3\sigma(F^2)$ used in the final refinement.

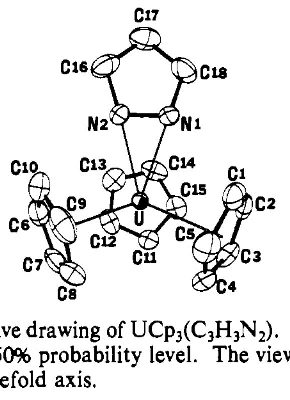

Figure 2. Perspective drawing of $UCp_3(C_3H_3N_2)$. Thermal ellipsoids are drawn at the 50% probability level. The view is perpendicular to the pseudo-threefold axis.

The calculated density agrees well with that observed for $Z = 4$ (2.11 and 2.25 g cm^{-3}, respectively). The initial Patterson map confirmed the space group $P2_1/a$.[9] The structure was then solved with use of heavy-atom methods.[10-13] In the final refinement the

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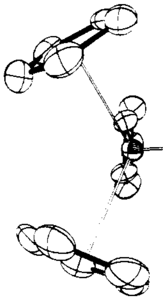

Figure 3. Perspective drawing of $UCp_3(C_3H_3N_2)$ down the pseudo-threefold axis. Thermal ellipsoids are drawn at the 50% level.

Table III. Selected Bond Distances (Å)

U–C(1)	2.777 (10)	U–C(9)	2.766 (10)	U–N(1)	2.402 (7)
U–C(2)	2.746 (8)	U–C(10)	2.772 (10)	U–N(2)	2.364 (7)
U–C(3)	2.764 (9)	U–C(11)	2.755 (9)	C(16)–N(2)	1.358 (13)
U–C(4)	2.756 (10)	U–C(12)	2.742 (10)	C(16)–C(17)	1.340 (16)
U–C(5)	2.778 (11)	U–C(13)	2.758 (11)	C(17)–C(18)	1.347 (16)
U–C(6)	2.743 (10)	U–C(14)	2.765 (10)	C(18)–N(1)	1.350 (12)
U–C(7)	2.764 (10)	U–C(15)	2.772 (10)	N(1)–N(2)	1.318 (10)
U–C(8)	2.780 (10)	av U–C	2.762 (12)		

temperature factors of all nonhydrogen atoms were treated anisotropically, and hydrogen atoms were fixed in calculated positions with a C–H distance of 0.95 Å[14] and an isotropic temperature factor of 8.0 Å^2. The model converged to give both weighted and unweighted R factors of 3.14%. On the final cycle all parameters shifted by less than 0.1σ. The variation of residuals with both $(\sin\theta)/\lambda$ and F_o showed no abnormalities. In the final difference Fourier, the only peaks of greater than 1.0 e Å^{-3} were within 1.4 Å of the uranium, and the most negative electron density at a grid point was −0.95 e Å^{-3}. Positional and thermal parameters are listed in Table II.

Description of the Structure

The crystal structure consists of discrete mononuclear units at general positions in the unit cell (Figure 1). A perspective drawing of the complex is shown in Figure 2. The molecular structure consists of a uranium ion coordinated by three η^5-coordinated cyclopentadienyl rings and by the two nitrogens of the pyrazolate ion. If the coordination polyhedron is considered to be formed by the centers of the Cp rings and the midpoint of the N–N bond, the coordination about the uranium can be considered roughly C_{3v} in symmetry, with the Cp rings at the base and the N–N midpoint at the apex of a flattened tetrahedron (Figure 3). The angles for this polyhedron are [(Cp centroid)–U–(N–N)] 106.3, 108.4, and 97.1° for rings 1–3, respectively. The angles between centroids are 114.2, 115.0, and 113.8° (1-U-2, 1-U-3, 2-U-3).

The pyrazolate ring exhibits local C_{2v} symmetry as before.[4] The pyrazolate ring and the Cp rings are planar with average deviations from their least-squares planes of 0.0075, 0.0055, 0.0044, and 0.0134 Å (Cp 1, 2, and 3 and pyrazolate).[15] The angle between the U–N–N plane and the pyrazolate plane is 10.4°. The N–U–N angle is 32.19°. Cp 3 and the pyrazolate are nearly parallel, the angle between their least-squares planes being 5.7°. The Cp C–C distances average 1.38 (2) Å, and the internal angles average 108.0 (1.0)°. The Cp's are symmetrically bound to the uranium with an average U–C distance of 2.76 (1) Å. The U–N distances are 2.40 (1) and 2.36 (1) Å. The closest intramolecular nonbonded contact is 2.91 Å between N(2) and C(10), and the closest intermolecular contact is 3.53 Å between C(16) and C(6). Pertinent bond distances are listed in Table III.

Table IV. Bond Angles (Deg) and Distances (Å) for Representative Uranium Cp Complexes

formula	Cp–U–Cp	Cp–U-X	av U–C(Cp)	ref
$U(BzCp)_3Cl$	117, 118, 116	100, 101, 99	2.73	19
$UCp_3[2\text{-}CH_3\text{-}C(CH_2)_2]$	119, 115, 118	102, 100, 98	2.74	20
$UCp_3(n\text{-}Bu)$	118, 116, 116	98, 102, 101	2.74	21
$UCp_3(C_3H_3N_2)$	114, 115, 114	106, 108, 97	2.76	this work
$UCp_3(NCS)(CH_3CN)$	121, 119, 119	92, 95, 90 86, 89, 88	2.76	5

Discussion

The endo-bidentate coordination of the pyrazolate ion in this structure was unexpected; the failure to adopt a bridging geometry is best attributed to the highly ionic character of the U–N bond. In numerous pyrazolate complexes of the d-block transition metals, the pyrazolate bridges two metal ions. This is the appropriate geometry for directional covalent bonding involving the nitrogen lone-pair electrons, and substantial orbital overlap seems to be implied by the observation of magnetic interaction mediated by such bridging pyrazolates.[16,17] In the present compound, the ionic character of the U–N bond dominates, with the coordination being a nondirectional association of the N–N bond (the more negative side of the pyrazolate ring) with the uranium cation.

The geometry of the large class of compounds of the type MCp_3X, where X is a monodentate Lewis base, anion, or η^1 bridging Cp ring, is best described as a flattened tetrahedron[18] in which the Cp rings are shifted toward the sterically less bulky X ligand, decreasing the X–M–Cp (centroid) angles and increasing the Cp–M–Cp angles. This is also observed here, in that the Cp–U–Cp angles are nearly identical and greater than 109°, while the Cp–U–(N–N) angles are all less than 109°.

The placement of the pyrazolate ring divides the Cp rings into two classes. Cp 1 and Cp 2 are nonparallel with the pyrazolate (the angles are 62.0 and 73.2°), while Cp 3 is nearly parallel to the pyrazolate. In addition, the angle from the Cp 3 centroid to the midpoint of the N–N bond is much less than for the other two Cp rings (vide supra).

The average U–C distance of 2.76 Å is somewhat longer than those typically found in the 10-coordinate, UCp_3X-type structures and is a reflection of the greater effective ionic radius of the uranium[1] in a formally 11-coordinate complex. The compound $UCp_3(NCS)(CH_3CN)$[5] is also formally 11-coordinate and conforms to a trigonal-bipyramidal geometry with the Cp rings occupying the equatorial sites. Table IV contains angles and distances for a comparison of these and other representative uranium Cp complexes. The compounds $U(BzCp)_3Cl$,[19] UCp_3(2-Me-allyl),[20] and $UCp_3(C_4H_9)$[21] all ex-

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(10) Full-matrix least-squares refinement on F was used in which the function minimized was $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors and the weighting factor, w, is $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for neutral U, C, and N were taken from the tables of Cromer and Mann,[11] and those for neutral H were taken from Stewart, Davidson, and Simpson.[12] Corrections for anomalous dispersion using both $\Delta f'$ and $\Delta f''$ were included for all atoms except H.[13]

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hibit the flattened tetrahedral geometry described above. However, in UCp$_3$(NCS)(CH$_3$CN) the Cp–U–Cp angles are close to 120° and the Cp–U–N angles are close to 90°. This clearly represents a geometry different from the flattened tetrahedron characterizing the MCp$_3$X compounds, including the present one.

While the angles and geometries of the thiocyanato and pyrazolate complexes are distinctly different, there are marked similarities in their bond lengths, which are in turn consistent with the ionic radius calculated for an 11-coordinate uranium(IV) complex. The average U–C distances (2.76 Å) for both compounds and U–N distances (2.40 and 2.36 Å for the pyrazolate vs. 2.40 Å for the thiocyanate) agree well. The reason for the 0.04 Å difference in the U–N distances of the pyrazolate is unclear; the closest intramolecular contact [between N(2) and C(10)] must be expected to make U–N(2) the longer bond, but the opposite is true.

The structure of Cu(PhN=NPh)(CNCMe$_3$)$_2$[22] reveals a roughly analogous, endo-bidentate, η^2 coordination of an N$_2$ moiety. Structural evidence for a covalent σ-bond formation which affects the π-bond structure of the ligand includes a lengthening of the N–N bond vs. uncoordinated azobenzene (from an average of 1.20 Å to 1.38 Å). However, the N–N bond in the pyrazolate anion should be less susceptible to such an effect because of its incorporation in an aromatic π system. In any case, in [TiCp$_2$(pyrazolate)]$_2$ the N–N distance [1.312 (6) Å] is quite similar to that observed here [1.318 (10) Å].

In summary, we report the synthesis and first structure analysis of a compound with an endo-bidentate pyrazolate anion. The coordination geometry and the distance in this compound are consistent with a highly ionic description of the bonding.

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Registry No. UCp$_3$(C$_3$H$_3$N$_2$), 76613-61-1; UCp$_3$Cl, 1284-81-7.

Supplementary Material Available: A listing of observed and calculated structure factors and Table V, least-squares plane parameters (17 pages). Ordering information is given on any current masthead page.

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Studies of Ruthenium(II) Porphyrins Containing Tertiary Diphosphine Ligands, Including the Crystal Structure of (5,10,15,20-Tetraphenylporphinato)bis(bis(diphenylphosphino)methane)ruthenium(II)-Dichloromethane

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The ruthenium(II) porphyrins Ru(porp)($\widehat{\mathrm{PP}}$)$_2$, containing tertiary diphosphine ligands, have been prepared in high yields from Ru(porp)(CO)(C$_2$H$_5$OH) [porp = dianion of octaethylporphyrin (OEP) or tetraphenylporphyrin (TPP)] and the $\widehat{\mathrm{PP}}$ phosphines [Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1, 2) and Ph$_2$P(CH$_2$)$_2$N(C$_2$H$_5$)(CH$_2$)$_2$PPh$_2$]. The crystal structure of Ru(TPP)(Ph$_2$PCH$_2$PPh$_2$)$_2$ shows six-coordinate ruthenium situated in the porphyrin plane and coordinated to two axial monodentate phosphine ligands, which each have a free dangling phosphorus atom. The analogous bis(1,2-bis(diphenylphosphino)ethane) complex almost certainly has the same structure and is the first reported case of a compound containing this common diphosphine in a monodentate fashion. The ^{31}P NMR spectra of the Ru(porp)[Ph$_2$P(CH$_2$)$_n$PPh$_2$]$_2$ compounds indicate further structures in solution, including species with a chelated diphosphine. An isolated Ru(OEP)[Ph$_2$P(CH$_2$)$_4$PPh$_2$] complex is likely a polymer incorporating diphosphine bridges.

Introduction

During investigations of ruthenium porphyrins containing tertiary phosphines[1-3] we observed highly efficient catalytic decarbonylation of aldehydes by a system involving Ru(TPP)(PPh$_3$)$_2$[4] (TPP = the dianion of 5,10,15,20-tetraphenylporphyrin). As the mechanism of decarbonylation is usually thought to involve initial oxidative addition of the aldehyde to the catalyst complex,[5] we became interested in studying the potential of ruthenium porphyrins to become greater than six-coordinate. To date, only six-coordinate species of ruthenium(II) porphyrins have been reported, for example, in the X-ray structures of Ru(TPP)(py)$_2$[6] (py = pyridine), Ru(TPP)(CO)(py),[7] and Ru(TPP)(CO)(C$_2$H$_5$OH).[8] However, kinetic data have suggested that ruthenium(II) porphyrin complexes containing potentially bidentate ligands (e.g., pyrazoles) may form seven-coordinate species such as I during intramolecular ligand-exchange processes.[9,10]

We set out to prepare a complex with a stereochemistry similar to that of I (L′ = CO, vacant site, or another $\widehat{\mathrm{LL}}$

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