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Synthesis, Characterization, and Crystal and Molecular Structure of Tricyclopentadienylgallium(III)[1]

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The new compound Ga(C_5H_5)$_3$ has been prepared and fully characterized by elemental analyses, cryoscopic molecular weight measurements, IR and ^{1}H NMR data, Lewis acid–base studies, and an X-ray structural study. The new tricyclopentadienyl derivative is a colorless, volatile, pentane-soluble, crystalline solid, which decomposes very slowly at room temperature and more rapidly at 45 °C to form a yellow, pentane insoluble solid. An X-ray structural study of Ga(C_5H_5)$_3$ demonstrates that the compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions a = 10.904 (8) Å, b = 8.928 (6) Å, c = 13.533 (8) Å, β = 92.19 (5)°, and d_{calcd} = 1.34 g cm^{-3} for Z = 4. Full-matrix least-squares refinement led to a final R value of 0.057 for 371 observed reflections. The crystal consists of discrete isolated moelcules of Ga(C_5H_5)$_3$, separated by normal van der Waals distances. There are no abnormally short intermolecular contacts. All cyclopentadienyl rings exhibit η^1 coordination to gallium with Ga–C(av) distance of 2.05 [3] Å. The three α-carbon atoms of the cyclopentadienyl rings and gallium are coplanar to within ±0.001 Å, and Ga(C_5H_5)$_3$ exhibits the properties of a weak Lewis acid. The strong bases NMe$_3$ and THF react with Ga(C_5H_5)$_3$ to form four-coordinate complexes, but the weaker base, diethyl ether, can be readily removed.

Introduction

The cyclopentadienyl ligand has played an important role in the development of transition-metal organometallic chemistry. In contrast to the extensive range of synthetic and theoretical studies of cyclopentadienyl complexes of transition metal and even f-block elements, relatively little is known about the nature of cyclopentadienyl main-group compounds. Even though progress has been made in synthesizing a variety of cyclopentadienyl derivatives of groups 1, 2, and 4, the compounds of the group 3 elements have received very little attention. The indium compound In(C_5H_5)$_3$ is the only typical +3 oxidation state homoleptic cyclopentadienyl group 3 derivative for which the details of its synthesis,[3] properties,[3] and structure[4] have been described. The X-ray structural study[4] reveals the compound as a polymeric solid with one bridging and two η^1-cyclopentadienyl σ-bonded rings. The synthesis[5] of B(C_5H_5)$_3$ has been reported but the reaction involves an unusual ratio of reactants, a large excess of BF$_3$·O(C_5H_5)$_2$ over the amount of the cyclopentadienyl Grignard reagent. However, when the typical stoichiometry, 3 mol of Grignard reagent/mol of BF$_3$·O(C_2H_5)$_3$, was used, (C_5H_5)BF$_2$ was reported to be the product. In contrast, the syntheses and properties of tris(cyclopentadienyl)aluminum and -gallium have not been described in the standard synthetic chemical literature. However, the aluminum compound Al(C_5H_5)$_3$ has been reported in a patent[6] as a gray material with a melting point of 50–60 °C. It is also surprising that only two cyclopentadienylhalogen derivatives of aluminum, gallium, or indium of the type M(C_5H_5)$_{3-x}$X$_x$ (x = 2, 1), (C_5H_5)$_2$InI,[7] and (C_5H_5)InI$_2$[7] have been described. However, the cyclopentadienyl alkyl derivatives such as (C_5H_5)AlMe$_2$,[8,9] (C_5H_5)AlEt$_2$,[8,9] (C_5H_5)GaMe$_2$.[9-11] (C_5H_5)GaEt$_2$,[9-11] and (C_5H_5)InMe$_2$[12] have been the subject of a variety of spectroscopic studies and (C_5H_5)AlMe$_2$[13] and (C_5H_5)GaMe$_2$[14] have been investigated by X-ray crystallographic techniques. These X-ray structural studies indicate that crystals of both (C_5H_5)AlMe$_2$ and (C_5H_5)GaMe$_2$ are composed of infinite chains with the cyclopentadienyl groups serving as the bridging ligand between MMe$_2$ units.

In this paper we report the synthesis of Ga(C_5H_5)$_3$. This compound has been fully characterized by elemental analyses, molecular weight data, spectroscopic data, Lewis acid–base studies, and an X-ray structural study.

Experimental Section

General Data. All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or a purified argon atmosphere. Gallium(III) chloride was purified by sublimation at 70–80 °C immediately prior to use. Lithium cyclopentadienide was purchased from Alfa Inorganics and used as received. The solvents and other reagents were purified by conventional means and vacuum distilled immediately prior to use. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol and Kel-F mulls between CsI plates were recorded by means of a Perkin-Elmer Model 683 spectrometer. Absorption intensities are reported with abbreviations w (weak), m (medium), s (strong), vs (very strong), and sh (shoulder). The ^{1}H NMR spectra were recorded at 90 MHz by using a Varian Model EM-390 spectrometer. Chemical shifts are

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Table I. Crystal Data for $Ga(C_5H_5)_3$

compd	$GaC_{15}H_{15}$
mol wt	264.99
space group	$P2_1/n$
cell constants	
a, Å	10.904 (8)
b, Å	8.928 (6)
c, Å	13.533 (8)
β, deg	92.19 (5)
cell vol, Å^3	1316.5
molecules/unit cell (*Z*)	4
ρ(calcd), g cm^{-3}	1.34
μ(calcd), cm^{-1}	21.74
radiatn	Mo Kα
max cryst dimens, mm	0.15 × 0.10 × 0.10
scan width, deg	0.8 + 0.2 tan θ
std reflctns	200, 020, 002
decay of stds	< 3%
reflctns measd	2844
2θ range	1-20
obsd reflctns	371
no. of parameters varied	38
GOF	0.95
R	0.057
R_w	0.063

reported in δ units (ppm) and are referenced to $SiMe_4$ as δ 0.00 and benzene as δ 7.13. All NMR tubes were sealed under vacuum. The molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver.[15]

Synthesis of $Ga(C_5H_5)_3$. In a typical reaction, 4.80 g (27.3 mmol) of $GaCl_3$ was sublimed at 70 °C into a 100-mL two-necked flask at −196 °C. Halocarbon grease was used in all joints. In the drybox the flask containing the $GaCl_3$ was attached by means of a 90° bent-tube adapter to a 500-mL flask which was charged with 6.76 g (94.0 mmol) of LiC_5H_5 and a magnetic stirrer. Then, 250 mL of Et_2O was vacuum distilled onto the LiC_5H_5 and 50 mL onto the $GaCl_3$. The two Et_2O–reagent mixtures were slowly warmed to room temperature without external heating. Then, the 500-mL reaction flask was cooled to 0 °C, and the $GaCl_3$ ether solution was added slowly to the LiC_5H_5 over a 30-min period. The reaction mixture was stirred overnight, while the temperature was permitted to increase to room temperature. The 90° bent-tube adapter and small flask were then replaced with a sintered glass frit attached to a clean 500-mL flask. The solution was filtered, and finally the Et_2O was removed by vacuum distillation. Then, the original reaction flask and filter were replaced with a clean frit and 100-mL flask. Finally, 70-mL pentane was vacuum distilled onto the crude product and it was extracted five times to yield 4.61 g (17.4 mmol, 63.7% yield) of colorless, pentane-soluble $Ga(C_5H_5)_3$. The product can also be purified by very careful vacuum sublimation at 40–42 °C. During this process, care must be taken to ensure that the temperature remains below 45 °C because $Ga(C_5H_5)_3$ readily decomposes at this temperature. Any heating above room temperature of the reaction mixture or product at any stage of the process leads to significantly reduced yields. $Ga(C_5H_5)_3$: mp, decomposes without melting at 45 °C; ^1H NMR (benzene) δ 5.92 (s), (THF-d_8) (adduct) 5.82 (s), (C_6H_{12}) 5.92 (s); IR (Nujol mull, cm^{-1}) 3900 (w), 3470 (w, br), 3085 (m), 3070 (m, sh), 1800 (w, br), 1635 (m, br), 1495 (w, sh), 1404 (m), 1308 (vw), 1260 (vw), 1242 (vw), 1103 (m), 1072 (m), 1040 (w), 985 (m, sh), 968 (vs), 840 (vs, br), 745 (vs, br), 635 (s, br), 545 (vw), 380 (vs), (Kel-F mull) (4000–2500 cm^{-1} only) 3915 (w), 3900 (w), 3117 (s, sh), 3085 (s), 3070 (s, sh), 3010 (w), 2960 (w, sh), 2920 (w, br), 2850 (w, sh). Cryoscopic molecular weight: formula weight $Ga(C_5H_5)_3$ 249.9, obsd mol wt 260. Solubility: soluble benzene, *n*-pentane, cyclohexane; CH_3CN reacts to form an unknown yellow viscous material; CH_2Cl_2 reacts very slowly; THF and NMe_3 form adducts. ^1H NMR adducts (CH_2Cl_2): $Ga(C_5H_5)_3$·THF δ 6.00 (s), 3.86 (m), 1.97 (m); $Ga(C_5H_5)_3$·NMe_3 δ 6.04 (s), 2.27 (s). Anal. Calcd: C, 67.98; H, 5.71. Found: C, 67.69; H, 5.75. Crystalline $Ga(C_5H_5)_3$ slowly decomposes at room temperature to form a pentane-insoluble, yellow solid.

Table II. Final Fractional Coordinates for $Ga(C_5H_5)_3$

atom	*x/a*	*y/b*	*z/c*	*U*(eqv), Å^2
Ga	−0.0519 (3)	−0.1412 (4)	0.7456 (2)	0.083
Cp(1)	0.040 (2)	0.001 (2)	0.839 (1)	0.107
Cp(2)	−0.007 (2)	0.150 (2)	0.794 (1)	0.102
Cp(3)	0.077 (2)	0.183 (2)	0.729 (1)	0.111
Cp(4)	0.184 (2)	0.090 (2)	0.729 (1)	0.120
Cp(5)	0.161 (2)	−0.024 (2)	0.802 (1)	0.109
Cp(6)	−0.043 (2)	−0.115 (2)	0.593 (1)	0.108
Cp(7)	−0.178 (2)	−0.124 (2)	0.570 (1)	0.109
Cp(8)	−0.208 (2)	−0.268 (2)	0.547 (1)	0.121
Cp(9)	−0.102 (2)	−0.351 (2)	0.552 (1)	0.100
Cp(10)	0.003 (2)	−0.277 (2)	0.579 (1)	0.118
Cp(11)	−0.152 (2)	−0.309 (2)	0.8015 (9)	0.083
Cp(12)	−0.230 (2)	−0.215 (2)	0.8690 (9)	0.095
Cp(13)	−0.170 (2)	−0.230 (2)	0.9613 (9)	0.103
Cp(14)	−0.064 (2)	−0.319 (2)	0.9577 (9)	0.092
Cp(15)	−0.049 (2)	−0.373 (2)	0.8641 (9)	0.097

Crystallographic Studies. The crystal used for the X-ray structural study was obtained by slow sublimation of a sample of $Ga(C_5H_5)_3$ in a sealed tube heated at 42 °C and cooled by room air. The crystal was sealed under N_2 in a thin-walled glass capillary. The crystal was mounted, and data were collected on a Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. This method has been previously described.[16] Data were corrected for Lorentz and polarization effects but not for absorption effects. A summary of the data collection parameters and final lattice parameters as determined from a least-squares refinement of $(\sin \theta/\lambda)^2$ values for 25 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table I.

Solution and Refinement of the Structure. Calculations were carried out with the SHELX system of computer programs.[17] Neutral atom scattering factors for Ga were taken from Cromer and Waber.[18] Scattering factors stored within the SHELX program were used for the other atoms. The scattering factor for Ga was corrected for both the real and imaginary components of an anomalous dispersion using the table of Cromer and Liberman.[19] The gallium atom was located on a Patterson map, and a difference Fourier map phased on the gallium position afforded the coordinates of the carbon atoms. Because of the paucity of reflection data, the cyclopentadienyl rings were treated as rigid groups. Each carbon atom was given an isotropic temperature factor, and the six parameters of each group (three positional and three rotational variables) were used in the refinement. The gallium atom was also refined with an isotropic temperature factor. Further refinement led to final values of $R = 0.057$ and $R_w = 0.063$.

A final difference Fourier showed no feature greater than 0.6 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)^2$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the position parameters of atoms other than hydrogen are given in Table II.

Results and Discussion

The compound $Ga(C_5H_5)_3$ is only the second example of a fully characterized homoleptic cyclopentadienyl group 3 derivative with the metal in its typical +3 oxidation state. The indium derivative $In(C_5H_5)_3$ was first.[3] The characterization data of $Ga(C_5H_5)_3$ include elemental analyses, molecular weight measurements, ^1H NMR and IR spectroscopic data, an evaluation of its Lewis acidity, and an X-ray structural study. The experimental procedure for the synthesis of $Ga(C_5H_5)_3$ uses typical reagents, $GaCl_3$ and a slight stoichiometric excess of LiC_5H_5 in diethyl ether, but the conditions for the preparative reaction and for the

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Table III. Bond Lengths (Å) and Bond Angles (deg) for $Ga(C_5H_5)_3$

		Bond Distances			
Ga-Cp(1)	2.03 (2)	Cp(9)-Cp(10)	1.36	Cp(4)-Cp(5)	1.44
Ga-Cp(11)	2.02 (2)	Cp(11)-Cp(15)	1.49	Cp(6)-Cp(10)	1.54
Cp(1)-Cp(5)	1.44	Cp(13)-Cp(14)	1.40	Cp(8)-Cp(9)	1.37
Cp(3)-Cp(4)	1.43	Ga-Cp(6)	2.09 (2)	Cp(11)-Cp(12)	1.52
Cp(6)-Cp(7)	1.49	Cp(1)-Cp(2)	1.54	Cp(12)-Cp(13)	1.39
Cp(7)-Cp(8)	1.36	Cp(2)-Cp(3)	1.32	Cp(14)-Cp(15)	1.37
		Bond Angles			
Cp(1)-Ga-Cp(6)	120.4 (6)	Cp(6)-Cp(10)-Cp(9)	102.0	Cp(1)-Cp(5)-Cp(4)	108.0
Cp(6)-Ga-Cp(11)	120.0 (5)	Ga-Cp(11)-Cp(15)	95.3 (5)	Ga-Cp(6)-Cp(10)	92.4 (5)
Ga-Cp(1)-Cp(5)	97.1 (5)	Cp(11)-Cp(12)-Cp(13)	103.3	Cp(6)-Cp(7)-Cp(8)	109.1
Cp(1)-Cp(2)-Cp(3)	102.6	Cp(13)-Cp(14)-Cp(15)	111.2	Cp(8)-Cp(9)-Cp(10)	116.9
Cp(3)-Cp(4)-Cp(5)	104.2	Cp(1)-Ga-Cp(11)	119.6 (5)	Ga-Cp(11)-Cp(12)	97.8 (5)
Ga-Cp(6)-Cp(7)	96.7 (5)	Ga-Cp(1)-Cp(2)	98.3 (5)	Cp(12)-Cp(11)-Cp(15)	107.1
Cp(7)-Cp(6)-Cp(10)	104.3	Cp(2)-Cp(1)-Cp(5)	107.1	Cp(12)-Cp(13)-Cp(14)	112.3
Cp(7)-Cp(8)-Cp(9)	107.5	Cp(2)-Cp(3)-Cp(4)	117.1	Cp(11)-Cp(15)-Cp(14)	105.8

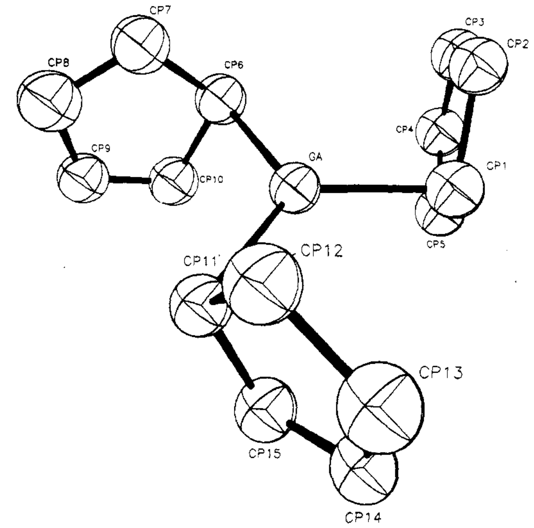

Figure 1. Labeling of atoms in $Ga(C_5H_5)_3$ (ORTEP-II diagram).

purification of the product must be carefully controlled in order to achieve high and reproducible yields. The temperature must be maintained at or below room temperature for all stages of the process. Solid gallium(III) chloride should not be added to the LiC_5H_5–diethyl ether reactant mixture because solvation of $GaCl_3$ is sufficiently exothermic to raise the temperature of the system. Similarly, refluxing the ether reaction mixture leads to greatly reduced yields of product. All of these observations must be related to the observed ease of thermal decomposition of $Ga(C_5H_5)_3$. The compound decomposes slowly but irreversibly at room temperature and more rapidly at temperatures as low as 45 °C as well as photolytically. Upon decomposition the material changes from colorless to yellow. The yellow decomposition product is insoluble in pentane. Consequently, pure $Ga(C_5H_5)_3$ can be recovered from partially decomposed material by extraction with pentane. The $Ga(C_5H_5)_3$ can also be separated from the yellow decomposition product by vacuum sublimation at 40–42 °C, but the temperature must be controlled very carefully in order to minimize further decomposition.

The X-ray structural study demonstrates that the crystal consists of discrete isolated molecules of $Ga(C_5H_5)_3$, separated by normal van der Waals distances. There are no abnormally short intermolecular contacts. Selected interatomic distances and angles are presented in Table III. Figure 1 shows the scheme used in labeling the atoms, while Figure 2 provides a stereoview of the molecule. The cyclopentadienyl rings are exhibiting η^1 coordination to gallium as shown by the C–C bond length patterns within each cyclopentadienyl ring. Thus, the cyclopentadienyl rings of $Ga(C_5H_5)_3$ can be classified as an "allyl" type as opposed to "vinyl". The three α-carbon atoms, Cp(1), Cp(6), and Cp(11) of the three cyclopentadienyl rings and gallium are coplanar to within 0.001 Å. This is shown quite clearly in the stereoview (Figure 2). This configuration with a trigonal-planar group 3 atom represents a departure from the polymeric arrangements found in all other structurally characterized group 3 derivatives, $(C_5H_5)GaMe_2$,[14] $(C_5H_5)AlMe_2$,[13] and $In(C_5H_5)_3$.[4] In these compounds, the cyclopentadienyl ring forms a bridge between $GaMe_2$, $AlMe_2$, or $In(C_5H_5)_2$ units.

The gallium–carbon(Cp) distances are Ga–Cp(1) = 2.03 (2) Å, Ga–Cp(6) = 2.09 (2) Å, and Ga–Cp(11) = 2.02 (2) Å; the average Ga–C distance is 2.05 [3] Å. These distances are slightly longer than normal Ga–C(alkyl) σ bond lengths but similar to that observed for $KGa(CH_2SiMe_3)_3H$,[20] 2.003

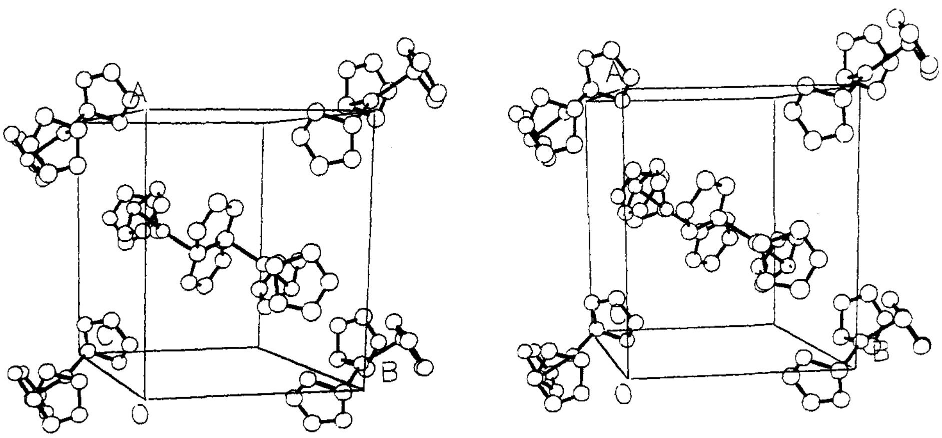

Figure 2. Stereoview of $Ga(C_5H_5)_3$.

(9) to 2.048 (9) Å.

The molecular weight measurements and spectroscopic properties of $Ga(C_5H_5)_3$ suggest that the compound exists in hydrocarbon solvents as the monomeric species with η^1-C_5H_5 coordination. The infrared spectrum has several bands above 3000 cm^{-1}, and it is typical of that expected for $Ga(\eta^1\text{-}C_5H_5)_3$. The ^1H NMR spectrum exhibits only one line at ambient temperature, a property which is consistent with the expected fluxional nature of the molecule. No attempt has been made to study the effects of temperature on the ^1H NMR spectrum. It is noteworthy that the molecule exhibits the typical Lewis acidic behavior expected for a three-coordinate organogallium compound but only the stronger Lewis bases are able to form adducts with little or no dissociation pressure of base at room temperature. The bases NMe_3 and THF form 1:1 adducts at room temperature, whereas diethyl ether can be readily removed from $Ga(\eta^1\text{-}C_5H_5)_3$. These adducts have been characterized by only their ^1H NMR spectra, but it is of interest that the chemical shift of the C_5H_5 resonance (a single, sharp line) is surprisingly insensitive to coordination by the Lewis base.

The chloro derivatives $Ga(C_5H_5)_2Cl$ and $Ga(C_5H_5)Cl_2$ have also been prepared from stoichiometric quantities of $Ga(C_5H_5)_3$ and $GaCl_3$ by standard ligand redistribution reactions. These compounds have been characterized, but they have a variety of properties which are unusual for organogallium halide derivatives. Consequently, these compounds will be the subject of a future communication.

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Supplementary Material Available: Table IV-S showing calculated structure factor amplitudes (3 pages). Order information is given on any current masthead page.

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Protonation of Dicyclopentadiene Complexes of Ruthenium(0), Osmium(0), Rhodium(I), and Iridium(I). Single-Crystal X-ray Study of $[Os(2,3,5\text{-}\eta\text{-}C_{10}H_{13})(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]PF_6$, a Complex Containing an Os–H–C Interaction

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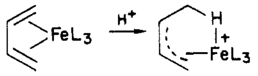
Treatment of the arene *endo*-dicyclopentadiene complexes of zerovalent ruthenium and osmium $M(\eta\text{-arene})(\eta^4\text{-}C_{10}H_{12})$ (M = Ru, arene = C_6Me_6; M = Os, arene = $C_6H_3Me_3$-1,3,5) with HPF_6 gives monoprotonated salts $[M(C_{10}H_{13})(\eta\text{-arene})]PF_6$. Similar salts are obtained by treatment of the complexes $Rh(\eta\text{-}C_5R_5)(\eta^4\text{-}C_{10}H_{12})$ (R = H, Me) and $Ir(\eta\text{-}C_5Me_5)(\eta^4\text{-}C_{10}H_{12})$ with HPF_6. The salt $[Os(C_{10}H_{13})(\eta\text{-}C_6H_3Me_3)]PF_6$ crystallizes in two modifications, 2a and 2b. The former belongs to space group $P2_1/n$, with $a = 11.584$ (2) Å, $b = 12.235$ (2) Å, $c = 13.990$ (2) Å, $\beta = 88.40$ (2)°, and $Z = 4$, and the latter to space group $P2_1$, with $a = 12.484$ (2) Å, $b = 10.124$ (2) Å, $c = 7.611$ (1) Å, $\beta = 95.54$ (2)°, and $Z = 2$. The structures of both forms have been solved by heavy-atom methods and refined by least-squares analysis to $R = 0.042$ and $R_w = 0.055$ for 2150 unique reflections ($I > 3\sigma$) (**2a**) and to $R = 0.041$ and $R_w = 0.041$ for 3065 unique reflections ($I > 3\sigma$) (**2b**), the derived metrical data for **2a** being more precise and reliable than those for **2b**. The cation consists of a (η^6-mesitylene)osmium(II) unit attached to dicyclopentadiene by a σ-bond to one of the norbornene carbon atoms [Os–C(5) = 2.19 (2) Å] and by an η^2-olefin bond to the cyclopentene fragment [Os–C(1) = 2.20 (2) Å; Os–C(2) = 2.25 (2) Å]. Although not located directly, the added proton probably bridges the osmium atom and the second norbornene carbon atom C(6) by a two-electron–three-center interaction [Os–C(6) = 2.30 (2) Å]. This is supported by an examination of the bonding geometry about C(6), by R factor analysis, and by ^1H and ^{13}C NMR spectroscopic studies on all the protonated dicyclopentadiene complexes. Assuming the bridging hydrogen atom to be tetrahedrally disposed at 0.95 Å from C(6) (undoubtedly an underestimate), the calculated Os–H distance is 1.81 Å in **2a** [1.90 Å in **2b**] and the C–H–Os angle is 110° in **2a** (104° in **2b**).

Introduction

It has become clear from recent work that protonation of 1,3-diene complexes of many transition elements, especially of the first row, gives cations containing a two-electron–three-center M–H–C interaction. For example, addition of acids to various acyclic and cyclic conjugated diene complexes of the type $FeL_3(\eta^4\text{-}1,3\text{-diene})$ (L = tertiary phosphine or phosphite) gives monoprotonated η^3-allylic species in which the added proton bridges the metal and a terminal diene carbon atom (eq 1).[1] This feature



(1)

has been conclusively demonstrated by single-crystal X-ray and neutron diffraction studies of the η^3-cyclooctenyl derivative $[Fe\{P(OMe)_3\}_3(\eta^3\text{-}C_8H_{13})]BF_4$ formed from the 1,3-cyclooctadiene complex $Fe\{P(OMe)_3\}_3(\eta^4\text{-}1,3\text{-}C_8H_{12})$.[2,3]

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(1) Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 6905.