found for the reactions of Pt_2 with Ph_2SiH_2 or $MePhSiH_2$. This might be attributed to the difference in the reactivity of $HR^1R^2Si^•$ radicals. The stability of $HR^1R^2Si^•$ radicals decreases in a sequence of $HPh_2Si^• > HMePhSi^• > HEt_2Si^•$. Clearly, $HEt_2Si^•$ radicals have the largest reactivity toward recombination with HPt_2 in cage.

As can be seen in Figure 3, a gradual rise in the absorption at 350 nm during irradiation reveals the occurrence of secondary photoprocesses. Prolonged irradiation (5 min and longer) causes the disappearance of the absorbance at 301 nm and the shift of the main absorption band from 370 to 350 nm. Owing to high reactivity of $HR^1R^2Si^•$ radicals, their reactions with Pt_2 or unreacted $R^1R^2SiH_2$ or solvent or other unidentified silicon-containing photolytic products are probable,[11,14] either singly or collectively.

It appears that the photochemical reactions of Pt_2 with disubstituted silanes in CH_3CN under argon are quite complicated. The proton-coupled ^{31}P NMR spectra of the reaction mixture of Pt_2 and Et_2SiH_2 after photolysis exhibit the chemical shifts $\delta = -10.1, -9.3$, and -8.5 ppm with $J(P-H) = 577, 573$, and 584 Hz, respectively.[15] The magnitudes of these ^{31}P chemical shifts and P–H coupling constants are in accord with the structures of salts or derivatives of phosphorous acid or pyrophosphorous acid in which there are hydrogen atoms attached directly to phosphorus atoms.[16] This signifies that the disassembly of the binuclear platinum diphosphite complexes occurs during photolysis. Attack of $HR^1R^2Si^•$ radicals on P–Pt and O–H bonds of $Pt_2(P_2O_5H_2)_4^{4-}$ cannot be excluded.

Experimental Section

Materials. K_2PtCl_4, H_3PO_3, and Bu_4NCl were purchased from Aldrich Chemical Co. Bu_4NCl was purified by recrystallization from benzene and petroleum ether. Deionized water was degassed with argon in advance. Acetonitrile of analytical reagent grade was dried and distilled over P_2O_5 under argon directly prior to use. Disubstituted silanes were dried over 4-Å molecular sieves and distilled under argon (at reduced pressures for Ph_2SiH_2 and $MePhSiH_2$). A UV lamp (UVP Inc., UVGL-25, 4 W) was used as a radiation source of narrow-band light centered on 366 nm. A second UV lamp (UVP Inc., UVS-11) was modified by the replacement of the 254-nm filter with a Pyrex glass filter for use as a radiation source for $\lambda > 300$ nm UV light.

Synthesis of $(Bu_4N)_4Pt_2(P_2O_5H_2)_4$. Gray's method[1] was followed. The purity of Pt_2 was checked by ^{31}P NMR. ^{31}P NMR: δ 68.3, $J(^{31}P-^{195}Pt) = 2975$ Hz. No other peaks were observed in the ^{31}P NMR spectrum. This complex has an extinction coefficient of 3.37×10^4 M^{-1} cm^{-1}.

Reactions of Pt_2 with Disubstituted Silanes under 366-nm Radiation. All the reactions, except those for preparation of samples for measurements of ^{31}P NMR, were carried out in acetonitrile under argon in a 1-cm quartz cell (for UV measurements). Pt_2 was degassed under vacuum and purged with argon prior to use. The concentrations of Pt_2 were $(2.80 \pm 0.80) \times 10^{-5}$ mol/L. The mole ratio of Pt_2 to silane was 1:300 in all experiments. The reaction mixture was irradiated with UV light of $\lambda = 366$ nm at 23 ± 2 °C immediately after preparation. The reaction was followed by UV measurements at different irradiation times.

The samples used for measurements of ^{31}P NMR spectra were prepared by irradiating a reaction mixture in which the concentration of Pt_2 was 3.30×10^{-3} mol/L and the mole ratio of Pt_2 to Et_2SiH_2 was 1:300. The radiation source of 366 nm was a 500-W Hanovia medium-pressure mercury lamp enclosed in a water-cooled Pyrex glass well, combined with an interference filter PSR35-3078 from the Ealing Co. All procedures were carried out under argon. The progress of the reaction was traced by UV measurements for the samples taken at different irradiation times. The UV irradiation was stopped when the position of the absorbance above 300 nm moved to 350 nm. The solvent and unreacted silane were removed under vacuum at room temperature to increase the concentration for ^{31}P NMR measurements.

Instrumentation. Ultraviolet absorption spectra were measured in CH_3CN on a HP-8450 UV/vis spectrophotometer. The 121.4-MHz ^{31}P NMR spectra were obtained on a Varian VXR 300-MHz NMR spectrometer, relative to external 85% H_3PO_4, with CD_3CN used as solvent.

Acknowledgment. This work was supported by grants from the IBM Corp. and the Department of Energy (DE-FG06-84ER45123). Their financial assistance is greatly appreciated.

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[14] Armitage, D. A.; Riviere, P.; Riviere-Baudet, M.; Satge, J.; Davies, A. G.; Smith, P. J. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 2; pp 91–92, 1–203, 399–627.

[15] There are three other main chemical shifts $\delta = 58.68, 58.84$, and 51.1 ppm with $J(^{195}Pt-^{31}P) = 3096, 3059$, and 3260 Hz and $J(P-H) = 6.4$, 5.5, and 0 Hz, respectively. The structures of the compounds that these ^{31}P chemical shifts and coupling constants represent are not yet clear. Attack of HR^1R^2Si radicals on the P–O bonds of $P_2O_5H_2^{2-}$ cannot be excluded.

[16] Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. *^{31}P Nuclear Magnetic Resonance*; Topics in Phosphorus Chemistry 5; Interscience: New York, 1967; pp 47, 290–291.

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Crystal Structure and Pyrolysis of $[(Os(NH_3)_5)_2(\eta^2:\eta^2-\mu-C_6H_6)]^{4+}$: Evidence for the Formation of a Stable $\eta^2:\eta^6-\mu$-Arene Complex

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Received April 25, 1989

In the course of investigating η^2-bound arene complexes of pentaammineosmium(II),[1] we have consistently observed the formation of trace amounts of a species in which the arene appears to act as a bridging ligand. Recently we reported that $[Os(NH_3)_5(\eta^2-C_6H_6)](OTf)_2$ ($OTf = CF_3SO_3^-$) (**1**), when allowed to stand in an inert solvent for 24 h, condenses to form the binuclear species $[(Os(NH_3)_5)_2(\eta^2:\eta^2-\mu-C_6H_6))](OTf)_4$ (**2**) and free benzene in high yield.[2] ^1H and ^{13}C NMR data indicate three inequivalent positions in the ring, and chemical shift data suggest that the metal centers engage separate double bonds. This bonding arrangement would result in a single *localized* olefin site that is expected to show enhanced reactivity relative to the free ligand. However, whereas single-metal coordination has been shown to activate an arene toward hydrogenation[3] or further coordination,[4] double-metal coordination appears to limit further reactivity: attempts to add a third pentaammineosmium(II) moiety were unsuccessful, as were our attempts to hydrogenate[3] or epoxidize[5] the complex. We attributed the failure of **2** to undergo these reactions to steric rather than electronic effects, reasoning that steric constraints require the metal centers to lie on opposite faces of the arene plane. To settle the question of geometry, we have determined the crystal structure for **2**.

Experimental Section

Compounds **1** and **2** were prepared according to procedures previously reported.[2] Crystals of **2** were grown from the vapor diffusion of ether into an acetone solution. A single crystal (approximately 0.4 mm^3) was sealed in a glass capillary tube along with a drop of mother liquor. The data set was acquired by using the $\theta-2\theta$ scan technique on a Syntex $P(2)_1$ diffractometer with graphite-monochromated Mo Kα radiation (Table I). The osmium positions were located for the space group $C2/c$ by Patterson techniques and the remaining atoms by difference Fourier synthesis. No attempt was made to locate or refine hydrogen atoms. Final full-matrix least-squares refinement was calculated with anisotropic temperature factors based on 5015 unique reflections over the range $6° < 2\theta < 55°$ with the condition $|F_0|^2 > 3\sigma|F_0|^2$. Over an irradiation period of 190 h, the intensity of standard reflections showed a decay of 4%. Both linear decay and empirical absorption corrections were applied. The observed and calculated structure factors and temperature factors are available as supplementary material.

The pyrolyses of **1** and **2** were carried out under vacuum (pressure > 1 μm) in a glass vessel immersed in an oil heat bath at temperatures ranging from 85 to 150 °C over periods of hours to days. The maximum yield of 4 (about 30%) was obtained by heating **2** for 16 h at 90 °C.

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[1] Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725.

[2] Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883.

[3] Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7906.

[4] Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7555.

[5] The reaction of **1** with 1 equiv of *m*-chloroperbenzoic acid resulted in the slow oxidation of metal centers.

Table I. Crystallographic Data for $[(Os(NH_3)_5)_2(C_6H_6)](CF_3SO_3)_4 \cdot 2(CH_3)_2CO$

asym unit	$C_{16}H_{48}Os_2S_4F_{12}O_1N_{10} \cdot 2C_3H_6O$	*Z*	8
		temp, °C	20
fw	1457	μ, cm^{-1}	58.2
space group	*C*2/*c*	no. of unique reflcns	5015
a, Å	29.98 (1)		
b, Å	11.857 (2)	scan range, deg	$6 > 2\theta > 55$
c, Å	25.90 (1)	$R(F_o)$	0.064
β, deg	93.26 (3)	$R_w(F_o)$	0.077
V, Å^3	9190.5	ρ_{calc}, g/cm^3	1.94

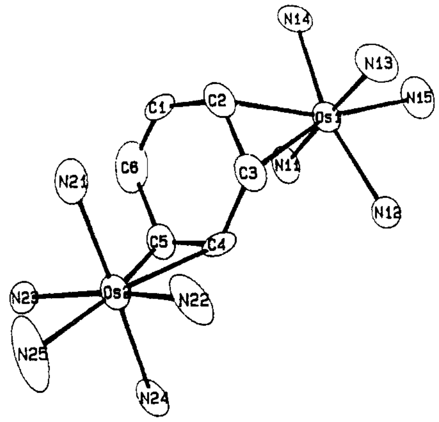
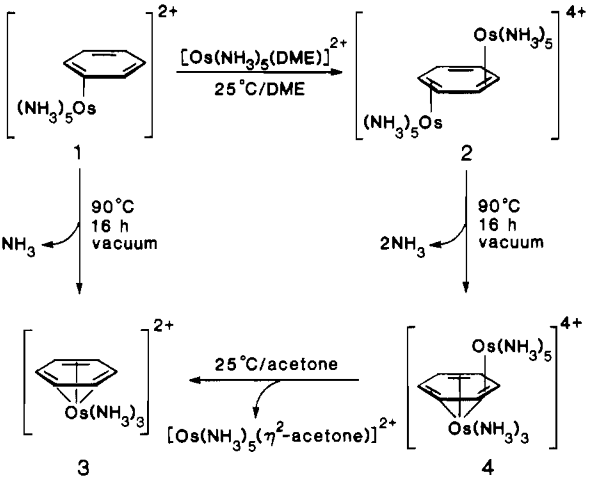


Figure 1. Thermal ellipsoid plot (50% ellipsoids) for the $[(Os(NH_3)_5)_2(C_6H_6)]^{4+}$ cation (of **2**) showing the atom-labeling scheme.

Scheme I. Chemistry Associated with the Complex $[\{Os(NH_3)_5\}\{Os(NH_3)_3\}(C_6H_6)]^{4+}$ [a]



[a] DME = 1,2-dimethoxyethane; $CF_3SO_3^-$ anions not shown.

Greater temperatures or reaction times resulted in the decomposition of **4**, and repeated attempts to purify **4**, either by recrystallization or chromatography, have failed, owing to the inherent instability of this material in solution.

Results

The molecular structure for the cation of **2** is shown in Figure 1. As hypothesized, the osmiums lie on opposite faces of the arene in a 1,2:3,4-η^2 configuration. An average dihedral angle of 110° is observed between the metal–ligand bond plane and that of the ring. The coordinated C–C bond lengths average 1.46 Å, which is within the range of that found for transition-metal-coordinated olefins.[6] The benzene ring remains approximately planar (rms deviation = 0.017 Å), but the uncoordinated fragment displays a C(1)–C(6) bond length of 1.32 (2) Å, a value which is close to that of an isolated double bond (1.34 Å) and considerably shorter than that for free benzene (1.40 Å).[7] The average Os–N distance of 2.14 Å is typical for pentaammineosmium(II) complexes;[8] any trans effect imparted by the benzene is negligible. In addition to the cation, the crystal structure reveals two acetone molecules and four triflate anions per asymmetric unit, several of which show disorder.

Table II. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*,[a] Å^2
Os1	0.20004 (3)	0.05991 (6)	0.15008 (3)	2.96 (1)
Os2	0.15388 (3)	−0.09170 (6)	−0.03317 (2)	2.96 (1)
S1	0.1800 (2)	0.2851 (5)	0.3037 (2)	4.7 (1)
S2	0.3305 (2)	0.3015 (5)	0.1879 (2)	5.8 (2)
S3	0.3154 (2)	0.0717 (5)	0.4148 (2)	5.4 (1)
S4	−0.0150 (3)	0.1275 (9)	0.4407 (3)	9.3 (3)
F11	0.0982 (6)	0.345 (2)	0.3135 (6)	10.8 (5)
F12	0.1392 (8)	0.471 (2)	0.2820 (8)	13.9 (7)
F13	0.1169 (6)	0.336 (1)	0.2346 (6)	9.2 (5)
F21	0.4011 (7)	0.195 (3)	0.1690 (9)	25 (1)
F22	0.4007 (9)	0.361 (3)	0.166 (1)	17.8 (9)*
F23	0.4065 (9)	0.286 (2)	0.234 (1)	16.9 (9)*
F31	0.3521 (7)	0.146 (2)	0.3346 (6)	13.1 (6)
F32	0.3661 (6)	−0.030 (2)	0.3528 (7)	14.5 (6)
F33	0.3047 (8)	0.012 (2)	0.3212 (9)	14.4 (7)*
F41	0.0065 (9)	0.289 (2)	0.382 (1)	16.1 (8)*
F42	−0.037 (1)	−0.181 (3)	−0.151 (1)	19 (1)*
F43	−0.059 (1)	−0.304 (3)	−0.095 (1)	24 (1)*
O11	0.1664 (5)	0.172 (1)	0.2997 (5)	5.3 (4)
O12	0.2125 (6)	0.321 (1)	0.2683 (5)	7.0 (4)
O13	0.1900 (6)	0.328 (1)	0.3559 (5)	6.2 (4)
O21	0.3133 (7)	0.213 (2)	0.215 (1)	11.7 (7)
O22	0.3156 (7)	0.291 (2)	0.1354 (7)	9.2 (6)
O23	0.3241 (8)	0.407 (2)	0.2120 (8)	10.6 (7)
O31	0.2989 (7)	−0.042 (1)	0.4261 (7)	8.7 (5)
O32	0.3534 (7)	0.117 (2)	0.4411 (7)	12.0 (7)
O33	0.2818 (5)	0.155 (1)	0.4093 (7)	7.6 (5)
O41	0.0237 (7)	0.066 (2)	0.425 (1)	14.9 (7)
O42	−0.0535 (6)	0.055 (2)	0.4418 (9)	10.7 (7)
O43	0.504 (1)	0.307 (3)	0.515 (1)	18 (1)*
O101	0.1088 (7)	0.394 (2)	0.4424 (7)	13.0 (7)
O201	0.0879 (7)	0.136 (2)	0.6472 (7)	9.0 (6)
N11	0.2644 (5)	0.047 (1)	0.1168 (5)	3.8 (4)
N12	0.1976 (6)	−0.116 (1)	0.1640 (5)	4.0 (4)
N13	0.1376 (6)	0.072 (1)	0.1866 (6)	4.5 (4)
N14	0.2113 (6)	0.236 (1)	0.1575 (6)	4.8 (4)
N15	0.2373 (5)	0.055 (1)	0.2250 (6)	3.9 (4)
N21	0.1160 (6)	0.064 (1)	−0.0339 (6)	4.7 (4)
N22	0.1039 (5)	−0.164 (1)	0.0127 (6)	4.3 (4)
N23	0.1913 (6)	−0.030 (1)	−0.0964 (5)	3.6 (4)
N24	0.1910 (5)	−0.244 (1)	−0.0355 (5)	3.8 (4)
N25	0.1087 (6)	−0.147 (2)	−0.0946 (6)	6.2 (5)
C11	0.1311 (9)	0.362 (2)	0.283 (1)	7.3 (7)
C12	0.383 (2)	0.249 (4)	0.189 (2)	16 (2)*
C13	0.841 (1)	0.462 (3)	0.852 (1)	10.7 (9)
C14	0.540 (1)	0.741 (4)	0.114 (2)	14 (1)*
C101	0.0978 (9)	0.490 (2)	0.455 (1)	8.3 (8)
C102	0.057 (1)	0.493 (3)	0.481 (2)	15 (1)
C103	0.127 (1)	0.586 (3)	0.460 (1)	13 (1)
C1	0.1924 (7)	0.169 (1)	0.0399 (7)	3.6 (5)
C2	0.1655 (6)	0.126 (2)	0.0797 (7)	3.5 (4)
C3	0.1596 (6)	0.002 (2)	0.0811 (7)	3.4 (4)
C4	0.1849 (6)	−0.070 (1)	0.0444 (7)	2.5 (4)
C5	0.2119 (7)	−0.019 (2)	0.0071 (7)	3.7 (5)
C6	0.2144 (7)	0.111 (2)	0.0061 (8)	4.8 (5)
C201	0.045 (1)	−0.170 (3)	0.145 (1)	12 (1)
C202	0.026 (1)	−0.246 (3)	0.110 (2)	21 (1)
C203	0.020 (2)	−0.120 (4)	0.183 (2)	17 (2)*

[a] Starred values denote atoms refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

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(6) *Comprehensive Organometallic Chemistry*; Vol III, eds. Wilkinson, G., Stone, F. G. A., Abel, E. W., Pergamon: London, 1982; Vol. III.

(7) *International Tables for X-ray Crystallography*, Kynoch Press: Birmingham, England, 1975; Vols. III and IV.

(8) Harman, W. D. Ph.D. Dissertation, Stanford University, 1987.

Table III. Selected Bond Distances (Å) and Angles (deg) in $[(Os(NH_3)_5)_2(C_6H_6)](CF_3SO_3)_4{\cdot}2(CH_3)_2CO$

Bond Distances			
Os1–N11	2.16 (1)[a]	Os1–C3	2.21 (1)
Os1–N12	2.12 (1)	C1–C2	1.44 (2)
Os1–N13	2.15 (1)	C2–C3	1.49 (2)
Os1–N14	2.12 (1)	C3–C4	1.51 (2)
Os1–N15	2.18 (1)	C4–C5	1.43 (2)
Os1C2	2.19 (1)	C5–C6	1.54 (2)
Bond Angles			
N11–Os1–C2	94.8 (4)	C2–C3–C4	118 (1)
N11–Os1–C3	96.7 (4)	C3–C4–C5	121 (1)
N12–Os1–C3	78.8 (4)	C4–C5–C6	118 (1)
N14–Os1–C2	77.6 (5)	C5–C6–C1	119 (1)
C1–C2–C3	116 (1)	C6–C1–C2	128 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

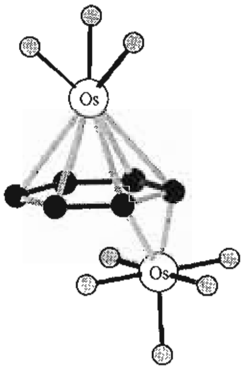

Figure 2. Proposed structure for the cation of **4**: $[\{Os(NH_3)_5\}\{Os(NH_3)_3\}(C_6H_6)]^{4+}$.

When a freshly prepared sample of the η^2-benzene salt (**1**) was heated (90 °C) under vacuum for 16 h, ammonia was liberated and the isolated solid (**3**) gave an ^{1}H NMR spectrum consistent with that reported by Hung et al.[9] for the cation $[Os(NH_3)_3(\eta^6\text{-}C_6H_6)]^{2+}$ (Scheme I). In an attempt to generate a binuclear μ-η^6:η^6 benzene analogue, a sample of **2** was heated under similar conditions. The ^{1}H NMR of the pyrolysis mixture[10] revealed the formation of a new binuclear species (**4**), which accounted for roughly 30% of the total osmium.[11]

The cation of **4** contains only a single pentaammineosmium(II) metal center.[12] Three arene peaks appear at positions similar and upfield to those observed for **1**[13] and an ammine signal is found at 4.72 (b, 9 H) ppm, corresponding to a second osmium center. Over a period of 24 h, **4** decomposes in acetone-d_6 to yield exactly 1 equiv each of the complexes $[Os(NH_3)_5(\eta^2\text{-acetone})]^{2+}$ and $[Os(NH_3)_3(\eta^6\text{-benzene})]^{2+}$ (Scheme I). Compound **4** can also be generated in acetone solution by reducing $[Os(NH_3)_4(OTf)_2](OTf)$, a known precursor to triammineosmium(II) arene complexes,[14] in the presence of 1 equiv of **1**.[15] After **4** was precipitated from $(CH_3)_2CO$, an NMR spectrum of this material in $(CD_3)_2CO$ indicated far less than a stoichiometric amount of either free of ligated $(CH_3)_2CO$, an observation suggesting that **4** does not contain coordinated solvent. Taken together, the above experiments indicate that **4** is a salt of the species $[\{Os(NH_3)_5\}\{Os(NH_3)_3\}(\mu\text{-}\eta^2{:}\eta^6\text{-benzene})]^{4+}$ as depicted in Figure 2.

When a sample of **4** is cooled to −85 °C, the triammine resonance (4.72 ppm) splits into two peaks at 5.0 (b, 6 H) and 4.4 (b, 3 H) ppm, which indicates a rapid rotation ($k \gg 500$ s^{-1}) of the triammineosmium fragment about the η^6 bond axis at room temperature. Spin saturation exchange,[16] revealed by homonuclear decoupling of the arene resonances in **4**, identifies a second fluxional process ($k \cong 1$ s^{-1} at 20 °C) in which the pentaammine metal center migrates around the ring. This represents a significant increase in the barrier to tautomerization relative to the mononuclear pentaammine analogue (for **1**: $k = 1 \times 10^4$ s^{-1}).[1]

Heating the binuclear salt **2** at 90 °C for longer periods of time or elevating the temperature above 100 °C produces only the mononuclear triammine complex (**3**) and an unidentified paramagnetic material, detected by cyclic voltammetry ($E_{1/2} = -0.84$ V), which is presumed to be an Os(III) species.

Discussion

To date, only one other structure has been reported featuring the unusual η^2:η^2 bonding mode for arenes:[17] the complex $[(Re(C_5H_5)(CO)_2)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_6)]$ shows a metal–arene morphology which is virtually identical with that of the cation of **2**. As for the present case, the Re complex is formed by condensation of the mononuclear analogue and is stable for extended periods in solution, in contrast to a related class of materials, also characterized by bridging η^2-bound arenes. The latter, which are chiefly comprised of Ag$^+$ or Cu$^+$ adducts, readily dissociate in solution and feature weak and asymmetric metal–arene bonds.[18] Neithamer et al.[19] recently reported a binuclear Ta complex of benzene in which bulky t-Bu$_3$SiO$^-$ ligands apparently give rise to a trans-1,2:4,5-η^2 arrangement. Due to significant disorder of the arene, however, a bis(η^3-allyl) interpretation could not be ruled out.

The "triple-decker" sandwich complex $[(CpV)_2(\eta^6{:}\eta^6\text{-}\mu\text{-}C_6H_6)]$ has been structurally characterized.[20] In addition, the complexes $[Cp_2Rh_2(C_8H_8)]^{2+}$ and $[Cp^*{}_2Co_2(C_8H_8)]^{2+}$ have been found to contain an olefinic fragment of the briding cyclooctatetraene ligand that is shared by the two metal centers.[21] To our knowledge, the η^2:η^6 bonding arrangement we suggest for the cation of **4** is unprecedented for an arene. An alternative η^2:η^4 bonding arrangement has been considered, in which solvent loosely occupies the sixth position of the triammine metal center, but it seems unlikely considering the equivalence of the triammine ^{1}H NMR resonances at room temperature and the lack of an exchanged or ligated solvent resonance in the NMR of **4** as prepared in solution.

Acknowledgment. We gratefully acknowledge Richard E. Marsh and Britt Hedman for their helpful suggestions. Support of this work by National Science Foundation Grants CHE85-11658 and CHE84-14329 (400-MHz NMR) and National Institutes of Health Grant GM13638-23 is also gratefully acknowledged.

Supplementary Material Available: Tables of thermal parameters, rms amplitudes of anisotropic displacement, complete bond distances and angles, and least-squares planes and an ORTEP drawing of the unit cell (18 pages); a table of observed and calculated structure factors (55 pages). Ordering information is given on any current masthead page.

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(9) Hung, Y.; Kung, W.; Taube, H. *Inorg. Chem.* **1981**, *20*, 457. ^{1}H NMR (acetone-d_6): δ 6.17 (s, 6 H), 4.70 (b, 9 H).

(10) ^{1}H NMR for **4** (acetone-d_6): δ 6.71 (b, 2 H), 5.71 (b, 2 H), 5.45 (b, 3 H), 4.77 (b, 9 H), 4.57 (b, 2 H), 3.68 (b, 12 H).

(11) As determined by ^{1}H NMR and electrochemical data.

(12) Cis and trans ammine resonances appear at 3.68 (12 H) and 5.45 (3 H) ppm, respectively.

(13) ^{1}H NMR of **1** recorded at −87 °C in acetone-d_6: δ 7.25 (b, 2 H), 6.55 (b, 2 H), 5.22 (b, 2 H).

(14) Li, Z. W.; Harman, W. D.; Taube, H. Manuscript in preparation.

(15) A solution of $[Os(NH_3)_4(OTf)_2](OTf)$ (100 mg) and **1** (100 mg) was stirred with Zn/Hg amalgam for 1 h. An NMR spectrum of the isolated reaction mixture showed that >50% of the Os(II) was in the form of **4**. The preparation of $[Os(NH_3)_4(OTf)_2](OTf)$ and its reactivity will be reported separately: Li, Z. W.; Harman, W. D.; Lay, P. A.; Taube, H. Manuscript in preparation.

(16) Sandström, J. *Dynamic NMR Spectroscopy*, 2nd ed.; Academic Press: London, 1982.

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