(Arene)osmium Trihydride Complexes: Synthesis and Studies of Proton–Proton Exchange Coupling

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The synthesis of cationic osmium trihydride complexes of the form $[(\eta\text{-}C_6H_6)Os(L)H_3]^+$ is reported (L = PCy_3, PPh_3, MPTB). The cations are readily prepared by protonation of the corresponding neutral dihydrides. Efficient synthetic methods have been developed for the preparation of the dihalide precursors. The cationic trihydride complexes are fluxional at room temperature, giving a single resonance for the hydridic protons, but low-temperature $^1H\{^{31}P\}$ NMR spectra exhibit well-resolved AB_2 or A_2B spin systems with large, temperature-dependent values of J_{A-B} = 70–370 Hz. These large couplings are attributed to the operation of quantum mechanical exchange coupling between the hydrogen nuclei in these complexes.

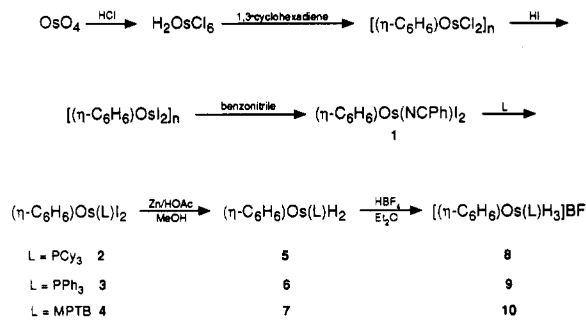
Introduction

We have recently proposed the existence of a quantum mechanical exchange coupling between the hydrogen nuclei in certain transition-metal polyhydride complexes.[1–3] Such couplings are commonly encountered for electrons as demonstrated by the ESR spectra of certain biradicals.[4] The only direct precedent for such interactions between heavy particles is provided by studies of ^3He at cryogenic temperatures.[5] In several cases, molecular polyhydrides have now been shown to demonstrate substantial exchange couplings between hydrogen nuclei in fluid solution at high temperatures (150–300 K). The magnitude of these couplings is quite variable, depending on the metal and the nature of the coligands. The occurrence of exchange coupling between protons can in principle lead to observed proton–proton couplings that are considerably larger than magnetic couplings arising from the normal Fermi contact mechanism. In practice, couplings of up to 1565 Hz have been observed in an iridium complex, with the magnitude of the observed coupling shown to be a sensitive function of the ancillary ligands and of the temperature of observation.[2]

A model quantitatively describing this coupling has been previously reported.[2,3] In brief, the observed coupling is found to depend on the distance between the adjacent hydrides and on the vibrational potential that the hydride ligands experience. In our earlier work on cationic iridium complexes of the form $[(\eta\text{-}C_5H_5)Ir(L)H_3]^+$ (L = various phosphine and phosphite ligands), it was clearly established that the magnitude of the exchange coupling observed is highly dependent on the nature of the ligand L. The smallest couplings are observed with the most basic ligands (trialkylphosphines). Larger couplings are seen when L = PPh_3, and extremely large couplings occur for phosphite ligands.

While there is no evidence for exchange coupling in closely related *neutral* iridium(V) complexes exemplified by $(\eta\text{-}C_5Me_5)Ir(SnPh_3)H_3$,[6] the neutral ruthenium(IV) complex $(\eta\text{-}C_5H_5)Ru(PPh_3)H_3$ exhibits a very large exchange coupling of 900 Hz.[7] Related ruthenium complexes of the form $(\eta\text{-}C_5Me_5)Ru(PR_3)H_3$ also exhibit large couplings,[8] which have been attributed to exchange coupling.[7] In contrast to these observations of large couplings in ruthenium complexes, a closely related osmium(IV) derivative $(\eta\text{-}C_5Me_5)Os(CO)H_3$ has been reported to have J_{A-B} = 8.9 Hz.[9] This low value of the coupling implies that there is no exchange coupling manifest in this complex and seems to indicate that the factors affecting the magnitude of the exchange coupling are apparently greatly affected by changing the metal from ruthenium to osmium.

Scheme I. Synthesis of Osmium Trihydride Complexes



In order to explore the effects of variations in the metal–ligand set and charge on the magnitude of the observed exchange coupling, we have now studied cationic osmium and ruthenium complexes of the form $[(\eta^6\text{-}arene)M(L)H_3]^+$. In this paper, we present the development of efficient synthetic methodology for the osmium hydride complexes. Large exchange couplings are indeed observed

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Table I. ^1H NMR Data and Analyses for 2–8

	δ, ppm[a]	assignment	% C, found (calcd)	% H, found (calcd)
2	6.0 s	C_6H_6	35.27 (35.92)	4.90 (4.91)
	1.2–2.8 m	$P(c\text{-}C_6H_{11})$		
3	5.62 s	C_6H_6	37.06 (36.75)	2.87 (2.70)
	7.38 m, 7.64 m	$P(C_6H_5)$		
4	5.85 s	C_6H_6	19.94 (19.71)	2.37 (2.26)
	4.33 d, J_{H-P} = 5.2 Hz	$P(OCH_2)_3CCH_3$		
	1.53 s	$P(OCH_2)_3CCH_3$		
5	5.30 s	C_6H_6	50.05 (52.34)	6.73 (7.50)
	1.2–2.3 m	$P(c\text{-}C_6H_{11})$		
	–9.94 d, J_{H-P} = 41.5 Hz	OsH_2		
6	6.14 s	C_6H_6	51.75 (54.12)	3.68 (4.35)
	7.17 m, 7.24 m	$P(C_6H_5)_3$		
	–11.7 d, J_{H-P} = 44 Hz	OsH_2		
7	5.50 s	C_6H_6	30.61 (31.57)	4.13 (4.10)
	4.22 d, J_{H-P} = 5.6 Hz	$P(OCH_2)_3CCH_3$		
	0.75 s	$P(OCH_2)_3CCH_3$		
	–11.35 d, J_{H-P} = 47 Hz	OsH_2		
8	6.25 s	C_6H_6	42.91 (45.14)	6.29 (6.63)
	1.6–2.8 m	$P(c\text{-}C_6H_{11})$		
	–12.62 d, J_{H-P} = 16 Hz	OsH_3		
9	4.75 s	C_6H_6	44.49 (46.46)	3.79 (3.90)
	7.75 m, 7.0 m	$P(C_6H_5)$		
	–11.8 d, J_{H-P} = 15 Hz	OsH_3		
10	5.24 s	C_6H_6	26.40 (26.10)	3.61 (3.60)
	3.97 d, J_{H-P} = 6 Hz	$P(OCH_2)_3CCH_3$		
	0.54 s	$P(OCH_2)_3CCH_3$		
	–13.4 d, J_{H-P} = 15 Hz	OsH_3		

[a] Spectra of 2–7 are in $CDCl_3$; 8–10 are in $CDFCl_2$.

in the osmium complexes. Comparisons to the ruthenium analogues focused on the known complex $[(\eta\text{-}C_6Me_6)Ru(PMe_3)H_3]^+$.

Results

Synthesis. The osmium trihydride complexes were prepared by the route outlined in Scheme I. The first step in the preparation is the reaction of OsO_4 with concentrated HCl.[10] The red, hygroscopic residue obtained by removing the water from this reaction mixture was directly dissolved in ethanol and reacted with 1,3-cyclohexadiene.[11] The isolation of the arene dichloride complex $[(\eta\text{-}C_6H_6)OsCl_2]_n$ was conveniently carried out by using slight modifications of the published procedure.[11] (See Discussion section.) Metathesis to the corresponding diiodide complex is readily effected by aqueous HI. The limited solubility of the halide complexes presents some difficulties in further derivatization. Prolonged heating to reflux of a suspension of $[(\eta\text{-}C_6H_6)OsI_2]_n$ in CH_2Cl_2 with benzonitrile in the presence of basic alumina affords an orange solution from which $(\eta\text{-}C_6H_6)Os(NCPh)I_2$ can be isolated in 70% yield. The benzonitrile ligand in complex 1 is readily displaced by phosphine and phosphite ligands to afford complexes 2–4. The diiodide complexes were readily reduced in good yield to the dihydride complexes 5–7 by using the zinc/acetic acid/methanol methodology of Graham and Moss.[12] Protonation of the neutral dihydrides was effected with $HBF_4{\cdot}Et_2O$ in methylene chloride to afford the cationic trihydrides 8–10 as colorless microcrystalline solids upon addition of Et_2O. The cationic complexes are insoluble in ether but are freely soluble in methylene chloride and freon solvents, which were employed for NMR studies. Some decomposition was noted upon prolonged exposure to chlorinated solvents at ambient temperature, but complexes 8–10 are indefinitely stable at the temperatures employed for the NMR studies. Analytical and NMR data for 2–10 are tabulated in Table I.

Table II. Temperature and Ligand Dependence of J_{A-B}[a]

	L	153 K	157 K	163 K	168 K	173 K
8	PCy_3[b]			70	78	89
9	$P(Ph)_3$[c]	219	245	282	326	374
10	MPTB	186	203	246	311	368

[a] Spectra were recorded in $CDFCl_2$ at 500 MHz. Couplings are in Hz. [b] A coupling of 98 Hz was recorded at 178 K. [c] A coupling of 200 Hz was recorded at 148 K.

A ruthenium analogue, $[(\eta\text{-}C_6Me_6)Ru(PMe_3)H_3]BF_4$, was prepared by the published procedure.[13]

^1H NMR Observations. In addition to a resonance due to the bound benzene and appropriate ligand resonances, compounds 8–10 exhibit a single hydride resonance (doublet, J_{P-H} = 15–16 Hz) in the ^1H NMR spectrum at ambient temperature. Upon lowering the sample temperature, broadening of the hydride resonances occurs, leading ultimately to a decoalescence at very low temperatures (ca. 173 K) into complex patterns of well-resolved resonances consistent with an A_2BX (8) or AB_2X (9, 10) spin system (X = ^{31}P). With phosphorus decoupling, the spectra are simplified to A_2B or AB_2 spin systems, respectively. The coupling constants J_{A-B} were calculated for these spectra by computer simulation. The coupling constants obtained by this procedure are highly dependent on the observation temperature, but the chemical shifts of the hydride protons show very little dependence on the temperature. The data obtained for 8–10 are tabulated in Table II.

Discussion

Synthesis. Our synthetic objective is to develop a convenient, high-yield preparation of Os(II) complexes of the form $(\eta\text{-}C_6H_6)Os(L)X_2$. The preparation of complexes of the empirical formula $(\eta\text{-}C_6H_6)OsX_2$ (X = Cl,[14] I[15]) has been reported. The state of aggregation of these materials has not been clearly established, although a dimeric structure for the iodide complex has been proposed.[16] A recent report by Taube and co-workers indicated some difficulty in obtaining useful yields from the original procedures.[11] We have adopted the procedure of Taube and co-workers for the preparation of $[(\eta\text{-}C_6H_6)OsCl_2]_n$, which employs the reaction of 1,3-cyclohexadiene with $H_2OsCl_6{\cdot}nH_2O$ in aqueous ethanol. The hydrated acid can be generated by treatment of $(NH_4)_2OsCl_6$ with an acidic ion-exchange resin. We find that a useful modification which leads to greater yields is to use directly the hydrated acid formed in the reaction between OsO_4 and HCl, which is obtained as a red, hygroscopic solid upon removal of water. Reaction of this material with 1,3-cyclohexadiene by the method of Taube[11] affords $[(\eta\text{-}C_6H_6)OsCl_2]_n$ as a yellow solid, insoluble in aqueous ethanol. The yellow solid dissolves in water (likely to form a completely aquated cationic species, as previously demonstrated by conduc-

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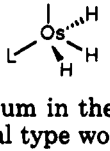
tivity measurements[11]), and treatment of the aqueous solution with hydroiodic acid affords an orange precipitate of $[(\eta\text{-}C_6H_6)OsI_2]_n$. This material was dried at 110 °C. The yield (based on OsO_4) is 97%.

A report by Werner and co-workers[16] indicated that $(\eta\text{-}C_6H_6)Os(PR_3)I_2$ (R = Me, Ph, ^iPr) could be obtained by a straightforward reaction of the appropriate phosphine ligand with $[(\eta\text{-}C_6H_6)OsI_2]_n$. We have found that this reaction indeed works very well for L = PPh_3 but fails for PCy_3 and MPTB (1-methyl-4-phospha-3,6,8-trioxabicyclo[2.2.2]octane). Seeking a generally useful starting material for this chemistry, we have investigated the reaction of the diiodide complex with nitriles. We have found that the benzonitrile complex $(\eta\text{-}C_6H_6)Os(NCPh)I_2$ (**1**) is a versatile and convenient precursor for phosphine and phosphite complexes. Reaction of **1** in CH_2Cl_2 with the appropriate ligand affords complexes **2–4** in 70–80% yield.

In our previous work on iridium complexes, it was found that conversion of $(\eta\text{-}C_5H_5)Ir(L)I_2$ complexes to the corresonding dihydrides could be carried out with borohydride and aluminum hydride reagents, but superior yields were obtained[3] with zinc metal and acetic acid in methanol by using the procedure of Moss and Graham.[12] We have made similar observations in the osmium arene system. Reduction of the diiodide complexes is conveniently carried out with zinc metal, to afford the corresponding dihydrides **5–7** in 80–90% yield. The dihydride complexes are thermally stable, but we have found that they are somewhat reactive with chlorinated solvents. Reaction with chloroform at room temperature rapidly affords the corresponding hydridochloride complexes. The same reaction occurs slowly with CH_2Cl_2.

The dihydride complexes are readily protonated by $HBF_4{\cdot}Et_2O$ to afford the corresponding trihydrido cations **8–10**. This reaction is most conveniently carried out in CH_2Cl_2 at −40 °C, from which the cations are obtained as colorless precipitates by the addition of Et_2O.

^1H NMR Studies of the Trihydride Cations. In our previous studies of the cationic iridium complexes of the form $[(\eta\text{-}C_5H_5)Ir(L)H_3]^+$, it was established that the molecules undergo a rapid thermally activated rearrangement process that renders the hydride ligands equivalent on the NMR time scale at ambient temperature. The complexes also display exchange coupling between the hydride ligands, the magnitude of which is a sensitive function of the observation temperature and the nature of the ligand L. The structure of a representative complex (L = PMe_3) was established by neutron diffraction.[2] The structure is best described as a distorted capped square pyramid, with the cyclopentadienyl ligand capping. The closest H–H distance between the hydride ligands is 1.68 Å. Although we have no structural data on the osmium complexes studied here, it is reasonable to assume that they will be broadly similar to the iridium complexes. A representation of this proposed structure is shown:



The ^1H NMR spectrum in the hydride region anticipated for this structural type would consist of two resonances in the intensity ratio 2:1. The room-temperature ^1H NMR spectra of the trihydride cations **8–10** exhibit a single doublet resonance in the hydride region (J_{H-P} = 15–16 Hz). This observation is consistent with the operation of a thermally activated site exchange process, which proceeds at a rate sufficient to lead to a single hydride resonance. Consistent with this, lowering the sample temperature leads to broadening of the resonances. At very low temperatures (ca. 200 K), decoalescence occurs and complex patterns corresponding to an AB_2X or A_2BX spin system (X = ^{31}P) are observed, which become quite well resolved at 180 K and below. With ^{31}P decoupling, the spectra are simplified to the expected eight line pattern for an AB_2 or A_2B spin system. These results are exemplified by the ^1H NMR spectrum of $[(\eta\text{-}C_6H_6)Os(PPh_3)H_3]BF_4$ (**9**) at 163 K, shown in Figure 1. The AB_2 spin system is defined by three parameters, δ_A, δ_B, and J_{A-B}, which are readily extracted from the observed line positions and intensities by computer simulation. In the absence of phosphorus decoupling, the couplings J_{A-P} and J_{B-P} must also be determined. Simulation of the spectrum shown in Figure 1 leads to the value of J_{A-B} = 282 Hz. This large coupling was found to vary dramatically with changes in the temperature, but the chemical shifts show only a very slight dependence on the observation temperature. Similar results were obtained for compounds **8** and **10**. The data obtained are tabulated in Table II.

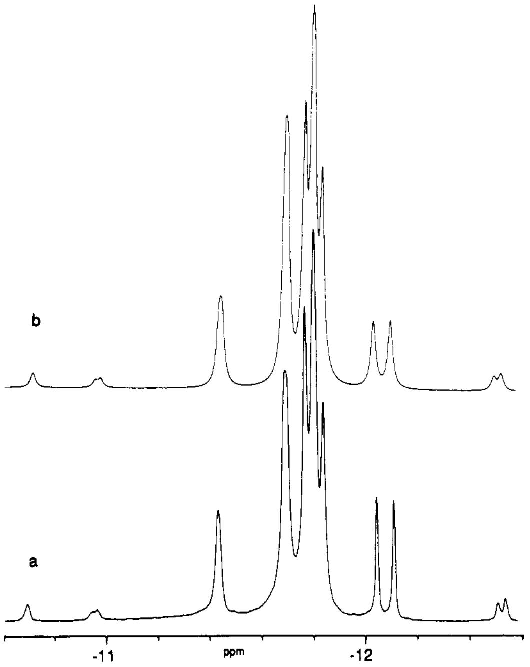


Figure 1. (a) Partial ^1H NMR spectrum (hydride region) of $[(\eta\text{-}C_6H_6)Os(PPh_3)H_3]BF_4$ (**9**) at 163 K. (b) Computer simulated spectrum. Parameters employed in the calculation are δ_A = −11.45 ppm; δ_B = −11.94 ppm; J_{A-B} = 282 Hz; J_{A-P} = ±6 Hz; J_{B-P} = ∓25.5 Hz; line width = 8 Hz; k (rate constant for site exchange) = 2 s^{-1}.

These large, temperature-dependent couplings are similar to those that we have previously reported in the analogous cationic trihydridoiridium complexes. In the case of the iridium complexes, we have interpreted these observations in terms of exchange coupling between the hydrogen nuclei.[2] A quantitative model was developed by using the model of Landesman for exchange coupling in solid ^3He.[2,3] In this model, which assumes a hard sphere potential, J is given by eq 1, where m is the proton mass,

$$J \cong -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/2}\frac{\hbar}{m}\left(\frac{a}{\delta^3}\right)\exp-\left\{\frac{3}{4}\,\frac{a^2+\lambda^2}{\delta^2}\right\} \qquad (1)$$

a is the internuclear distance, δ is the amplitude of the vibrational motion, and λ is the range of the interaction potential between the two protons. Although this model greatly oversimplifies the real situation, particularly in the assumption of a purely harmonic oscillator, we have found that we were able to model quite accurately the temperature dependence of the exchange couplings in several iridium complexes.[3] Qualitatively, it is clear that the magnitude of the exchange coupling rapidly diminishes as the distance between the protons, *a*, is increased. The exchange coupling is also greatly diminished by decreasing the value of δ. This is reasonable, since a fairly flat potential surface and large amplitude motion of the protons is required for significant exchange coupling to occur. In the case of iridium complexes of the form $[(\eta\text{-}C_5H_5)Ir(L)H_3]BF_4$, we have previously reported that the values of the exchange coupling observed are critically dependent on the nature of the ligand. At 176 K, the value for L = PCy_3 is 61 Hz, for L = PPh_3, a value of 260 Hz was obtained, and for the caged phosphite ligand MPTB, a coupling of 972 Hz was observed. These large variations in the magnitude of the coupling are primarily due to an increase in δ with the less effective donor ligands.[3] This implies that lowering of the electron density at the metal center leads to increased motion of the hydride ligands.

In the current study, we can compare the values of the exchange coupling noted above for the iridium complexes to those observed for the osmium complexes with the same phosphorus ligands. Our expectation was that, for analogous compounds, the (arene)osmium system would give larger exchange couplings than the (cyclopentadienyl)iridium complexes, since the arene ligand is a less effective donor than the cyclopentadienyl ligand. For complex **8** (L = PCy_3), a coupling of 89 Hz was observed at 173 K. This is about 50% greater than that observed in the iridium analogues in keeping with our expectations. For complex **9** (L = PPh_3), a coupling of 374 Hz was observed at 173 K. Again, this is approximately 50% greater than that observed in the iridium analogues. The caged phosphite complex **10** gave a coupling of only 368 Hz at this temperature. This is a surprising result, since the iridium analogue has a coupling nearly 3 times as large at this temperature.

In the iridium trihydride complexes, the observed exchange coupling is inversely proportional to the ligand basicity, as defined by Tolman.[17] There is no apparent contribution to the exchange coupling phenomenon from steric factors. These conclusions are based on our previous study of 10 iridium trihydride complexes.[2] The osmium complexes with L = PCy_3 and PPh_3 seem to follow a similar trend, with generally larger couplings at comparable temperatures. The caged phosphite complex (**10**) is a striking exception to this generalization. While a coupling of ca. 1400 Hz was anticipated, the observed coupling is only 368 Hz.

An informative comparison can also be made between these cationic osmium complexes and the aforementioned *neutral* osmium analogue, $(\eta\text{-}C_5Me_5)Os(CO)H_3$, where *no* exchange coupling is observed.[9] The introduction of a positive charge has a dramatic effect on the observation of exchange coupling. While we can offer no firm explanation for this observation at this time, it is consistent with the trend mentioned above where decreased electron density at the metal center led to larger couplings, primarily through increases in the motion of the hydride ligands. Recalling that the neutral ruthenium complexes of the form $(\eta\text{-}C_5H_5)Ru(PR_3)H_3$ exhibit very large exchange coupling, it would seem likely that cationic ruthenium complexes analogous to **8**–**10** will have extremely large exchange coupling.

In order to investigate this possibility, we have examined the ^1H NMR spectrum in the hydride region of the known[13] complex $[(\eta\text{-}C_6Me_6)Ru(PMe_3)H_3]^+$. Unfortunately, even at 150 K, only a single resonance was observed in the hydride region of the ^1H NMR spectrum. While this observation suggests that the barrier to thermally activated exchange is very low (≤ 6 kcal mol^{-1}), an extremely large exchange coupling is known to produce spectra of deceptive simplicity.[7] In order to examine this possibility, we have taken advantage of the fact that exchange coupling is quenched by deuterium substitution. The ruthenium complex was enriched with deuterium in the hydride position by treatment with D_2 gas. The proton NMR spectrum of $[(\eta\text{-}C_6Me_6)Ru(PMe_3)HD_2]^+$ exhibits only a single resonance in the hydride region at temperatures as low as 150 K. Thus, we are not able to assess the magnitude of any exchange coupling that might be manifest in this compound, since the barrier to thermally activated site exchange is extremely low and chemical shift inequivalence could not be established at temperatures accessible to solution NMR spectroscopy.

We are continuing the study of these and related polyhydride complexes in the hope of further increasing our understanding of the novel phenomenon of exchange coupling.

Experimental Section

General Considerations. All reactions were carried out by standard Schlenk, drybox, or vacuum line techniques. An inert atmosphere was provided by argon or nitrogen that was passed through a heated column of Cu catalyst (BASF R3-11) to remove oxygen and subsequently through P_2O_5. All solvents were dried and distilled from Na/K benzophenone or activated 4-Å molecular sieves. Elemental analyses were performed by Galbraith Analytical Laboratory. ^1H NMR spectra were recorded on Bruker WM-250 and WM-500 spectrometers. $CDFCl_2$ was prepared by the method of Siegel and Anet.[18]

Preparation of $[(\eta\text{-}C_6H_6)OsI_2]_n$. OsO_4 (1 g) was converted to $H_2OsCl_6\cdot nH_2O$ by treatment with concentrated HCl by the method of Dwyer and Hogarth.[10] The water was removed from the reaction mixture, and the red, hygroscopic residue was used without further purification in the reaction with 1,3-cyclohexadiene, which was carried out by the method of Taube.[11] The yellow precipitate resulting from this procedure was dissolved in water and added to a stirred suspension of acidified Dowex 50X2-400 cation-exchange resin. After suitable washing, the osmium complex was released from the resin by the addition of 1 M HCl, to give a yellow solution that was taken to dryness on the rotary evaporator, affording a yellow powder. After dissolution in water (ca. 50 mL), treatment with HI (0.5 mL) affords an orange precipitate of $[(\eta\text{-}C_6H_6)OsI_2]$, which was collected by filtration and oven dried at 110 °C. The overall yield (from OsO_4) was 1.99 g (97%).

Synthesis of $(\eta\text{-}C_6H_6)Os(NCPh)I_2$ (1). Benzonitrile (1 mL), basic alumina (2 g), and 500 mg of $[(\eta\text{-}C_6H_6)OsI_2]_n$ were combined in CH_2Cl_2 and heated to reflux for 2 days. The resulting orange solution was filtered, reduced in volume, and layered with heptane to afford $(\eta\text{-}C_6H_6)Os(NCPh)I_2$ as orange crystals (474 mg, 70% yield). ^1H NMR ($CDCl_3$, 250 MHz) δ 7.67–7.47 (m, 5 H, C_6H_5); 6.08 (s, 6 H, C_6H_6).

Synthesis of Diiodide Complexes. The procedure for **2** is given here. Compounds **3** and **4** were similarly prepared. To a solution of **1** (520 mg, 0.83 mmol) in 15 mL of CH_2Cl_2 was added PCy_3 (254 mg, 0.92 mmol). After stirring at room temperature for 18 h, the solution was filtered, reduced in volume by half, and layered with Et_2O. Compound **2** was obtained as red crystals, which were collected by filtration (485 mg, 0.60 mmol, 73%). Compounds **3** and **4** were obtained in 71% and 78% yield, respectively. Characterization data are in Table I.

Synthesis of Dihydride Complexes. Typically, 50–100 mg of the diiodide complex was suspended in 10 mL of methanol. After degassing, 100–200 mg of Zn dust and acetic acid (0.5 mL)

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were added, and the mixture was stirred until the orange color was discharged and replaced by a pale yellow color. For compounds **5** and **6**, this required ca. 3 h of stirring at room temperature, but the preparation of **7** required 3 h of heating to reflux. A saturated NaCl solution was added to the reaction mixture. Extraction with toluene (**5**, **6**) or CH_2Cl_2 (**7**), filtration, and drying of the organic layer followed by removal of solvent gave the dihydride complexes as colorless solids. Yield: **5** (88%), **6** (80%), **7** (84%). See Table I.

Synthesis of Trihydride Cations. A typical preparation is as follows: A 100-mg quantity of **5** was dissolved in 5 mL of CH_2Cl_2 and cooled to −40 °C. One equivalent of $HBF_4{\cdot}Et_2O$ was added, and the trihydrido cation was precipitated with the addition of 10 mL of Et_2O. The solid was allowed to settle, and the supernatant was removed. The precipitate was washed with 2 × 10 mL of Et_2O and dried in vacuo at room temperature to afford 45 mg of **8** (39%). A similar procedure gave **9** (89%) and **10** (69%). See Table I.

^{1}H NMR Studies. A 10–15-mg quantity of the trihydride was loaded into an NMR tube in the inert atmosphere drybox. The sample was degassed under vacuum and $CDFCl_2$ was condensed in. The samples were freeze/pump/thaw/degassed and sealed under dynamic vacuum. During the thaw portion of the cycle, the samples were warmed only to −78 °C and were kept at that temperature until use.

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Metallacarborane Complexes as Guests for Cyclodextrins. Molecular Structure of the Inclusion Complex $Cs[\textit{closo}\text{-}3,3,3\text{-}(CO)_3\text{-}3,1,2\text{-}ReC_2B_9H_{11}{\cdot}\alpha\text{-}CD]{\cdot}8H_2O$

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Inclusion complexes of the metallacarboranes $Cs[\textit{closo}\text{-}3,3,3\text{-}(CO)_3\text{-}3,1,2,\text{-}MC_2B_9H_{11}]$ (M = Mn, Re) with α- and β-cyclodextrin have been prepared in aqueous solution to yield $Cs[\textit{closo}\text{-}3,3,3\text{-}(CO)_3\text{-}3,1,2\text{-}MC_2B_9H_{11}{\cdot}\alpha\text{-}CD]$ [M = Mn (**1a**), M = Re (**2a**)] and $Cs[\textit{closo}\text{-}3,3,3\text{-}(CO)_3\text{-}3,1,2\text{-}MC_2B_9H_{11}{\cdot}\beta\text{-}CD]$ [M = Mn (**1b**), M = Re (**2b**)]. The binding constants of these inclusion complexes have been determined by NMR studies. Very strong binding was observed in aqueous solution with β-cyclodextrin as host, and the binding constants obtained for **1b** and **2b** were 1080 (±150) and 942 (±73) M^{-1}, respectively, in D_2O/DMSO-d_6 (50:50 volume ratios). The single-crystal X-ray diffraction study of **2a**$\cdot 8H_2O$ is reported. Crystal data for **2a**$\cdot 8H_2O$: $C_{41}H_{71}B_9CsReO_{33} + 8H_2O$, orthorhombic, $P2_12_12_1$, $a = 13.705$ (1) Å, $b = 20.280$ (2) Å, $c = 23.384$ (2) Å, $V = 6499$ Å^3, $Z = 4$, D(calcd) = 1.689 g cm^{-3}, $T = 188$ K, $\lambda = 0.709\,26$ Å, crystal size 0.4 × 0.3 × 0.1 mm, $\mu = 25.29$ cm^{-1}. Of the 6432 unique reflections measured, in the range $\theta < 28°$, 3960 were considered observed ($I > 3\sigma(I)$). The final R factor was $R = 0.075$, $R_w = 0.085$.

The study of inclusion complexes of cyclodextrins with both organic[1] and organometallic[2] guest molecules has stimulated interest due to their possible application in catalysis[3] and as enzyme models.[4] A number of inclusion complexes have been prepared with organometallic compounds as guests;[5] adduct formation results from insertion of a hydrophobic moeity such as a cyclopentadienyl, arene, or diene ligand on the metal into the cyclodextrin cavity.[6] In most cases the structures of these ligands do not allow for optimal host–guest interaction within the cyclodextrin

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