was not possible to characterize this species.

No reaction between **2** and diphenylacetylene or dimethyl acetylenedicarboxylate was observed.

Discussion

The results described here indicate that the Pt_2S core in these binuclear Pt(I) complexes is remarkably stable. The metal-metal bond is unreactive toward insertion of small molecules like carbon monoxide and isocyanides. Substitution reactions proceed readily at positions 3 and 4. This is perhaps not surprising since in all cases investigated substitution at these positions alleviates steric interaction between these two proximate positions. Substitution at the 1 and 2 positions has not been achieved. In this context, it should be noted that substitution of $M_2(CNCH_3)_6^{2+}$ (M = Pd, Pt) by triphenylphosphine occurs exclusively at the positions trans to the metal-metal bond.[20]

The coupling constants for these platinum complexes are organized in Table I for ready comparison. The comparable coupling constants are remarkably similar in the different compounds. Notice also that methylation at sulfur causes a uniform effect, i.e., all coupling constants diminish in absolute magnitude except for $J(3,5)$ and $J(1,3)$ which increase. Since $^1J(P,Pt)$ can be expected to be positive,[21] the signs of $^2J(P,Pt)$ can be confidently assigned. For a nearly linear Pt-Pt-P unit, $^2J(P,Pt)$ (that is $J(1,6)$ and $J(2,5)$) has the same sign as $^1J(P,Pt)$ and can be assumed to be positive. However, with the Pt-Pt-P angle near 90°, $^2J(P,Pt)$ is smaller in absolute magnitude and its sign is negative; that is, $J(3,6)$ has the opposite sign from $J(3,5)$, the direct Pt-P coupling, whose sign may be confidently taken as positive. Similarly, in $(Ph_2MeP)_2Pt_2(dpm)_2^{2+}$, the linear $^2J(P,Pt)$ is large and positive (+750 Hz) while the bent $^2J(P,Pt)$ is smaller in magnitude and negative (−120 Hz). This relationship may have utility in other structural work. The other coupling constants have similar magnitudes to those determined for related compounds.[4,7,19]

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-7924575) for support, Matthey Bishop for a loan of precious metal salts, and Dr. B. E. Mann for helpful discussions. Purchase of the NMR spectrometer by the UCD NMR Facility was made possible by an NSF instrumentation grant (CHE-7904832) to the Department of Chemistry.

Registry No. 2, 27664-43-3; **6**, 77462-34-1; **7**, 77462-33-0; **8**, iodide salt, 77462-32-9; **9**, hexafluorophosphate salt, 77462-31-8; $(Ph_3P)_2PtS_2CS$, 65354-15-6; *cis*-$(PPh_3)_2PtI_2$, 35085-00-8; $Pt(PPh_3)_3$, 13517-35-6; CS_2, 75-15-0; I_2, 7553-56-2; *trans*-$(Ph_3P)_2PtI_2$, 35085-01-9.

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Arene Transition-Metal Chemistry. 6. Hydride Reduction of η^6-Arene Iridium(I) Complexes[1]

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Received September 9, 1980

Arene complexes of the type $[Ir(\eta^6\text{-}C_6R_6)(\eta^4\text{-c-1,5-}C_8H_{12})^+](BF_4^-)$ (R = H or CH_3) react rapidly with $LiB(C_2H_5)_3H$ to produce the cyclohexadienyl complexes $[Ir(\eta^5\text{-}C_6R_6H)(\eta^4\text{-c-1,5-}C_8H_{12})]$ (R = H or CH_3). Reduction of $[Ir(\eta^6\text{-}C_6D_6)(\eta^4\text{-c-1,5-}C_8H_{12})^+](BF_4^-)$ verified that the added hydrogen appears in the exo position of the cyclohexadienyl ring. The site of hydride attack is discussed in terms of related reactions reported in the literature.

Introduction

It has long been recognized that arenes coordinated to transition metals are activated with respect to nucleophilic attack.[3] The importance of this reaction in organic synthesis has recently been reviewed.[4,5] In connection with our interest in the chemistry of coordinated arenes[1,2] and the general problem of nucleophilic attack on coordinated hydrocarbons,[6,7] we undertook a study of the reaction of $LiB(C_2H_5)_3H$ with $[Ir(\eta^6\text{-}C_6R_6)(\eta^4\text{-c-1,5-}C_8H_{12})^+](BF_4^-)$ complexes (R = H, D, or CH_3).

Experimental Section

General Information. Synthetic procedures and solvent purification methods have been described in a previous paper.[1] $[Ir(\eta^6\text{-}C_6R_6)(\eta^4\text{-COD})^+](BF_4^-)$ complexes (COD = 1,5-cyclooctadiene), R = H or CH_3) were prepared according to the literature procedures.[1,2] $LiB(C_2H_5)_3H$ (1.0 M) in tetrahydrofuran was purchased from Aldrich Chemical Co., Milwaukee, WI.

Infrared spectra were recorded as Nujol or halocarbon oil mulls between NaCl or KBr windows on a Perkin-Elmer 597 spectrometer; peaks are reported in cm^{-1}. The following abbreviations are used in reporting infrared data: w = weak, m = moderate, v = very.

Proton NMR spectra were recorded at 90 MHz on a Varian EM-390 spectrometer or at 180 MHz on a modified Bruker 42-kG multinuclear, pulse-FT NMR spectrometer equipped with Nicolet Technology Corp. software. Chemical shifts of all ^1H NMR spectra are reported with use of the δ scale; positive shifts are downfield from internal Me_4Si standard. The numbers and symbols in parentheses following the chemical shift value indicate the peak multiplicity (m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet, br =

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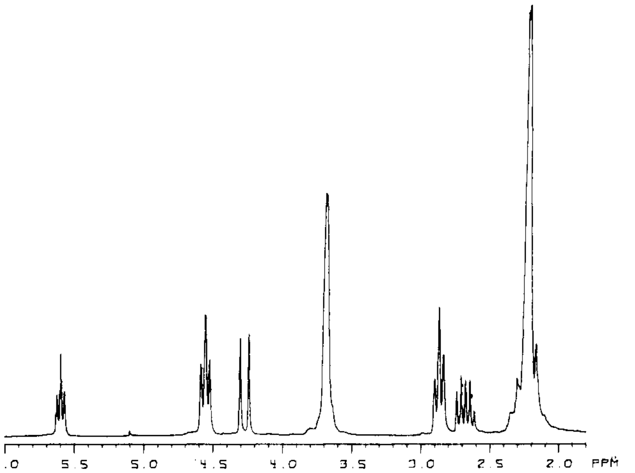


Figure 1. ^{1}H NMR spectrum of a sublimed sample of [Ir(η^5-C_6H_7)(η^4-c-1,5-C_8H_{12})] in C_6D_6 at 25 °C.

broad), coupling constants, integration, and peak assignment, respectively.

Microanalyses were performed by Mr. Vazken Tashinian at the University of California, Department of Chemistry Microanalytical Laboratory, Berkeley.

Preparation of [Ir(η^5-C_6H_7)(η^4-c-1,5-C_8H_{12})] (2a). [Ir(η^6-C_6H_6)(η^4-c-1,5-C_8H_{12})$^+$](BF_4^-) (**1a**) (0.25 g, 0.54 mmol) was slurried in 10 mL of tetrahydrofuran at 0 °C under N_2. The white mixture was treated with 0.50 mL of 1.0 M LiB(C_2H_5)$_3$H in tetrahydrofuran. The reaction immediately became homogeneous, and the pale yellow solution was stirred for 1 h at 0 °C. Volatile materials were then removed under vacuum. After thorough vacuum drying, the residue was extracted with freshly distilled pentane and filtered under nitrogen through a Schlenk frit. Concentration of the filtrate under vacuum and cooling to −78 °C afforded 60 mg (32%) of **2a** as tan crystals, mp 64–70 °C dec. Anal. Calcd for $IrC_{14}H_{19}$: C, 44.31; H, 5.05; N, 0.00. Found: C, 44.18; H, 5.05; N, 0.04. ^{1}H NMR (90 MHz, toluene-d_8, 35 °C): δ 5.55 (t of m, $J_{H(3),H(2)}$ = 5.1 Hz, $J_{H(3),H(1)}$ = 1.0 Hz, 1.0 H, H(3)), 4.49 (t of m, J = 5.5, 2.1 H, H(2) and H(4)), 4.14 (d, $J_{H(6,exo),H(6,endo)}$ = 10.5 Hz, 1.1 H, H(6,exo)), 3.57 (br, 4.2 H, COD vinyl H), 2.78 (m, J = ca. 6 Hz, H(1) and H(5)), 2.58 (m, H(6,endo)) (the latter two peaks integrate as 3.3 H, δ 2.16 (br, COD methylene H)). ^{1}H NMR (180 MHz, C_6D_6, 25 °C, sublimed sample): δ 5.60 (t of t, $J_{H(3),H(2)}$ = 5.1 Hz, $J_{H(3),H(1)}$ = 1.1 Hz, 1.0 H, H(3)), 4.55 (br t, J = ca. 5.8 Hz, 2.1 H, H(2) and H(4)), 4.27 (d, $J_{H(6,exo),H(6,endo)}$ = 11.3 Hz, 1.2 H, H(6,exo)), 3.68 (br, 4.8 H, COD vinyl H), 2.87 (br t, J = ca. 6 Hz, 2.2 H, H(1) and H(5)), 2.67 (d of t, $J_{H(6,endo),H(1)}$ = ca. 5.6 Hz, $J_{H(6,endo),H(6,exo)}$ = 11.3 Hz, 1.3 H, H(6,endo)), 2.21 (br m, 10.7 H, COD methylene H). IR (mull): ν(C–H(exo)) 2820 (m), 2788 (m).

Preparation of {Ir[1-5-η-6-*exo*-H-C_6D_6H](η^4-c-1,5-C_8H_{12})} (2b). White [Ir(η^6-C_6D_6)(η^4-c-1,5-C_8H_{12})$^+$](BF_4^-) was prepared in 65% yield from [Ir(η^4-c-1,5-C_8H_{12})HCl_2]$_2$, $AgBF_4$, and C_6D_6 in diethyl ether.[1] Anal. Calcd for $IrC_{14}H_{12}D_6BF_4$: C, 35.67; H, 3.85; N, 0.00. Found: C, 35.97; H, 3.92; N, 0.15. ^{1}H NMR (90 MHz, acetone-d_6, 35 °C): δ 6.95 (br, very weak, residual protiobenzene), 4.76 (br, COD vinyl H), 2.14 (br, COD methylene H). IR (mull): ν(C–D) 2334 (vw), 2308 (w), 2283 (vw).

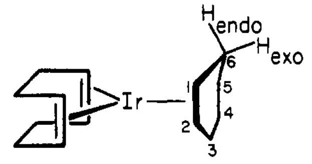
Treatment of [Ir(η^6-C_6D_6)(η^4-c-1,5-C_8H_{12})$^+$](BF_4^-) (0.20 g, 0.43 mmol) with a slight deficiency of LiB(C_2H_5)$_3$H in tetrahydrofuran at 0 °C gave a 48% yield of [Ir(η^5-C_6D_6H)(η^4-c-1,5-C_8H_{12})] as bronze plates from pentane. ^{1}H NMR (90 MHz, C_6D_6, 35 °C): δ 4.18 (br s, 0.99 H, H(6,exo)), 3.61 (br, 4.0 H, COD vinyl H), 2.19 (br, 8.0 H, COD methylene H). IR (mull): ν(C–H(exo)) 2820 (m), 2794 (m); ν(C–D) 2275 (vw), 2242 (w), 2208 (vvw), 2190 (vw).

Preparation of {Ir[1-5-η-6-*exo*-H-C_6(CH_3)$_6$H](η^4-c-1,5-C_8H_{12})} (2c). {Ir[η^6-C_6(CH_3)$_6$](η^4-c-1,5-C_8H_{12})$^+$}(BF_4^-) (**1c**) (0.10 g, 0.18 mmol) in 7 mL of freshly distilled tetrahydrofuran was treated with LiB(C_2H_5)$_3$H (0.20 mmol) at 0 °C under N_2. After the resulting homogeneous solution was stirred for 1.5 h, the volatile materials were removed under vacuum. Recrystallization of the crude product from pentane at −78 °C afforded 60 mg (72%) of **2c** as pale yellow crystals, mp 108–116 °C (darkened above ca. 84 °C). Anal. Calcd for $IrC_{20}H_{31}$: C, 51.81; H, 6.74; N, 0.00. Found: C, 51.88; H, 6.67; N, 0.02. ^{1}H NMR (90 MHz, C_6D_6, 35 °C): δ 4.08 (q, $J_{H(6,exo),CH_3(6)}$ = 7.5 Hz, 1.1 H, H(6,exo)), 2.92 (br, 4.0 H, COD vinyl H), 2.18 (br, 7.9 H, COD methylene H), 2.00 (s, 3.4 H, CH_3(3)), 1.62 (s, 6.0 H, CH_3(2) and CH_3(4)), 1.13 (s, CH_3(1) and CH_3(5)), 1.20 (downfield portion of a doublet, CH_3(6)) (the last two peaks integrate as 9.4 H; irradiation of the resonance at 4.08 ppm collapsed the doublet at ca. 1.2 ppm to a singlet superimposed on the resonance at 1.13 ppm).

Preparation of {[η^6-C_6(CH_3)$_6$](η^4-c-1,5-C_8H_{12})$^+$}(BF_4^-) from the Cyclohexadienyl Complex. {Ir[η^5-C_6(CH_3)$_6$H](η^4-c-1,5-C_8H_{12})} (30 mg, 0.07 mmol) was dissolved in 1 mL of CH_2Cl_2 under a nitrogen atmosphere. The pale yellow solution was treated with CH_2Cl_2 solution of C(C_6H_5)$_3{}^+BF_4^-$ (25 mg, 0.08 mmol, 1 mL). The yellow solution was stirred for 22 h at room temperature. Addition of 16 mL of diethyl ether gave a white solid. This crude product was recrystallized from dichloromethane–diethyl ether to yield 10 mg (28%) of **1c** identified by ^{1}H NMR.[2]

Results

[Ir(η^6-C_6H_6)(η^4-COD)$^+$](BF_4^-) (**1a**) reacted rapidly with LiB(C_2H_5)$_3$H to produce [Ir(η^5-C_6H_7)(η^4-COD)] (**2a**). The proton NMR spectrum of **2a** had a series of resonances typical of a coordinated cyclohexadienyl ligand:[8] three "triplets" were observed of relative intensity 1:2:2 as well as a doublet at 4.14 ppm and a multiplet at 2.58 ppm, each of relative intensity 1 (see Figure 1). The cyclooctadiene ligand showed the usual two broad resonances in a relative 4:8 ratio.



2a

The endo proton of **2a** was assigned to the multiplet at 2.58 ppm in the ^{1}H NMR spectrum since it was coupled to the ring protons (H(1) and H(5)); H(exo) was only coupled to H(endo) and was assigned to the doublet at 4.14 ppm. This would be expected on the basis of the difference in dihedral angles that these protons make with the ring hydrogens.[10] White and Maitlis have recently prepared some cyclohexadienyl complexes of Rh(III) and Ir(III);[11] their spectral assignments of H(endo) and H(exo) are consistent with those reported here. In a review of the properties of a series of cyclohexadienyl complexes of V, Cr, Mo, Mn, Re, Fe, Co, and Rh,[12] it was noted that in all cases the exo protons were upfield of the endo protons. Clearly comparisons among metals must be made with care.

The infrared spectrum of **2a** was distinguished by two low-energy C–H stretching modes at ca. 2820 and 2788 cm^{-1} which were assigned to the exo hydrogen of the methylene fragment in C_6H_7.[8,9,12] The recrystallized complex was tan or bronze and sublimed with decomposition at about 50 °C to give a very pale yellow complex which had the same ^{1}H NMR spectrum as the original material. Hence, the pure complex is considered to be pale yellow, and the bronze color is attributed to a small amount of a highly colored impurity. Indeed, **2a** was thermally labile in solution, yielding free benzene and a dark, uncharacterized material showing metal hydride resonances in the ^{1}H NMR spectrum.

Hydride reduction of [Ir(η^6-C_6D_6)(η^4-COD)$^+$](BF_4^-) (**1b**) afforded [Ir(η^5-C_6D_6H)(η^4-COD)] (**2b**) with the H exo to the metal. The complex had two C–H stretching modes at ca. 2820 and 2794 cm^{-1} and a broad singlet at 4.18 ppm in the

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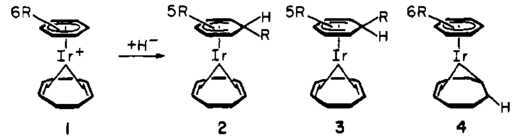
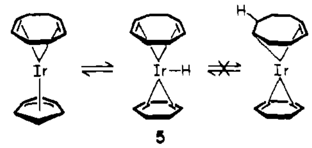
Scheme I



Scheme II



^{1}H NMR spectrum. The reaction of {Ir[η^6-C$_6$(CH$_3$)$_6$](η^4-COD)$^+$}(BF$_4^-$) (**1c**) with LiB(C$_2$H$_5$)$_3$H gave pale yellow {Ir[η^5-C$_6$(CH$_3$)$_6$H](η^4-COD)} (**2c**). The ^{1}H NMR spectrum of **2c** indicated four types of methyl environments in a 1:2:2:1 ratio; the two upfield methyl signals were almost superimposed, with the methyl of unit intensity split into a doublet. A quartet appeared at 4.08 ppm and was assigned to the exo H on the basis of the chemical shift. This complex did not show low-frequency C–H stretching modes in the infrared spectrum; however, these bands are not always observed.[6,10,11] Treatment of **2c** with triphenylmethyl tetrafluoroborate regenerated {Ir[η^6-C$_6$(CH$_3$)$_6$](η^4-COD)$^+$}(BF$_4^-$).

Discussion

Green, Davies, and Mingos have recently considered the general reaction of nucleophilic attack on coordinated hydrocarbons and, on the basis of molecular orbital considerations, have proposed guidelines that are successful in systematizing a wide body of chemistry.[7] The first two generalizations, the ones applicable to the present study, are as follows. (i) In a metal–polyene complex a nucleophile will attack preferentially at the polyene ligand having an even η number.[13] (ii) In a metal–polyene complex a nucleophile will attack preferentially at the polyene which is not cyclically conjugated (e.g., benzene is cyclically conjugated whereas cyclohexadienyl is not). Since both ligands in [Ir(η^6-arene)(η^4-COD)]$^+$ complexes have even η numbers, guideline ii would predict that **1** would react with hydride to give **4** (or a rearrangment product) in preference to **2** or **3** (see Scheme I) where the R radicals are, respectively, H in **1a**–**4a**, D in **1b**–**4b**, and CH$_3$ in **1c**–**4c**). Instead, the evidence presented above indicates that **2**, the product expected for direct nucleophilic attack at the arene ring, is formed.

This apparent departure from the guidelines can be rationalized in terms of the likely charge distribution in the [Ir(η^6-arene)(η^4-COD)]$^+$ complexes. While Pd(II) and Pt(II) 1,5-cyclooctadiene complexes commonly undergo nucleophilic attack at the diene to give enyl complexes such as **4**, Hazeldine has pointed out that analogous Ir(I) and Rh(I) complexes show little tendency to undergo this reaction.[14] For example, [Pd(η^4-c-1,5-C$_8$H$_{12}$)Cl$_2$] reacts with silver acetate to produce [Pd(5,6-η-2-acetoxycyclooct-5-en-1-yl)(μ-O$_2$CCH$_3$)]$_2$,[15] while [Rh(η^4-c-1,5-C$_8$H$_{12}$)Cl]$_2$ and potassium acetate give [Rh(η^4-COD)(μ-O$_2$CCH$_3$)]$_2$.[16] Ir(I) and Pt(II) behave analogously. This was rationalized in terms of the higher positive charge likely to be on the diene in the complexes of the divalent metals.[14] Also, in the Ir(I) arene complexes it would seem that the superior π acid and poorer σ-donor properties of 1,5-cyclooctadiene compared with an arene would result in a higher positive charge on the arene. Thus, nucleophilic attack would be expected to occur at the arene rather than at the olefin.

Although hydrogen transfer between metal and ligand can be a facile process in Co, Rh, and Ir chemistry,[17-21] the observation of exo hydride attack on the coordinated arene precludes the possibility of initial attack at cyclooctadiene or iridium followed by transfer to the arene since this reaction path would most likely yield an endo product (**3**).[22] While Müller observed hydride exchange between the metal and the C$_6$ ring in **5**, he did not observe any evidence for hydrogen transfer to the coordinated cyclooctadiene ligand (Scheme II).[20] This suggests that the stability of the [M(η^4-COD)]$^+$ moiety (M = Rh or Ir) may reduce the tendency of these sorts of compounds to undergo nucleophilic attack at the COD ligand. Further study of nucleophilic attack on a wide variety of platinum metal olefin complexes is warranted.

Acknowledgment. Important to this research was a loan of iridium chloride from Johnson Matthey, Inc., Malvern, PA. We gratefully acknowledge the National Science Foundation for support of this research and for a Departmental Equipment Grant to the Department of Chemistry, University of California, Berkeley, for purchase of a 180-MHz NMR spectrometer. In addition, we thank Professor J. R. Shapley for helpful discussions.

Registry No. **1a**, 74238-34-9; **1b**, 75751-36-9; **1c**, 74238-50-9; **2a**, 77462-29-4; **2b**, 77462-28-3; **2c**, 77462-27-2; LiB(C$_2$H$_5$)$_3$H, 22560-16-3.

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(22) Green has cited several examples of reversible nucleophilic addition reactions.[7] The possibility of initial hydride attack at cyclooctadiene followed by H$^-$ abstraction by free B(C$_2$H$_5$)$_3$ and subsequent readdition at the arene to give the *exo*-cyclohexadienyl complex cannot be excluded without further study. An endo = exo equilibrium can be excluded because the reaction of **1b** with hydride gave only **2b** and not a mixture of **2b** and **3b**.