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Protonation of dicyclopentadiene complexes of ruthenium(0), osmium(0), rhodium(I), and iridium(I). Single-crystal X-ray study of $[\text{Os}(2,3,5\text{-}\eta\text{-C}_{10}\text{H}_{13})(\eta\text{-C}_6\text{H}_3\text{Me}_3\text{-}1,3,5)]\text{PF}_6$, a comple...

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(9) to 2.048 (9) Å.

The molecular weight measurements and spectroscopic properties of $\text{Ga}(\text{C}_5\text{H}_5)_3$ suggest that the compound exists in hydrocarbon solvents as the monomeric species with $\eta^1\text{-C}_5\text{H}_5$ coordination. The infrared spectrum has several bands above 3000 cm^{-1} , and it is typical of that expected for $\text{Ga}(\eta^1\text{-C}_5\text{H}_5)_3$. 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 $\text{Ga}(\eta^1\text{-C}_5\text{H}_5)_3$. 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 $\text{Ga}(\text{C}_5\text{H}_5)_2\text{Cl}$ and $\text{Ga}(\text{C}_5\text{H}_5)\text{Cl}_2$ have also been prepared from stoichiometric quantities of $\text{Ga}(\text{C}_5\text{H}_5)_3$ 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 $[\text{Os}(\text{2,3,5-}\eta\text{-C}_{10}\text{H}_{13})(\eta\text{-C}_6\text{H}_3\text{Me}_3\text{-1,3,5})]\text{PF}_6$, a Complex Containing an Os-H-C Interaction

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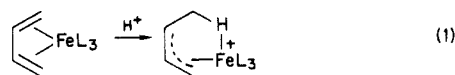
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Treatment of the arene *endo*-dicyclopentadiene complexes of zerovalent ruthenium and osmium $\text{M}(\eta\text{-arene})(\eta^4\text{-C}_{10}\text{H}_{12})$ ($\text{M} = \text{Ru}$, arene = C_6Me_6 ; $\text{M} = \text{Os}$, arene = $\text{C}_6\text{H}_3\text{Me}_3\text{-1,3,5}$) with HPF_6 gives monoprotonated salts $[\text{M}(\text{C}_{10}\text{H}_{13})(\eta\text{-arene})]\text{PF}_6$. Similar salts are obtained by treatment of the complexes $\text{Rh}(\eta\text{-C}_5\text{R}_5)(\eta^4\text{-C}_{10}\text{H}_{12})$ ($\text{R} = \text{H}$, Me) and $\text{Ir}(\eta\text{-C}_5\text{Me}_5)(\eta^4\text{-C}_{10}\text{H}_{12})$ with HPF_6 . The salt $[\text{Os}(\text{C}_{10}\text{H}_{13})(\eta\text{-C}_6\text{H}_3\text{Me}_3\text{-1,3,5})]\text{PF}_6$ 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 [$\text{Os-C}(5) = 2.19$ (2) Å] and by an η^2 -olefin bond to the cyclopentene fragment [$\text{Os-C}(1) = 2.20$ (2) Å; $\text{Os-C}(2) = 2.25$ (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 [$\text{Os-C}(6) = 2.30$ (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 $\text{FeL}_3(\eta^4\text{-1,3-diene})$ ($\text{L} = \text{tertiary phosphine or phosphite}$) 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

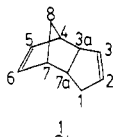


has been conclusively demonstrated by single-crystal X-ray and neutron diffraction studies of the η^3 -cyclooctenyl derivative $[\text{Fe}\{\text{P}(\text{OMe})_3\}_3(\eta^3\text{-C}_8\text{H}_{13})]\text{BF}_4$ formed from the 1,3-cyclooctadiene complex $\text{Fe}\{\text{P}(\text{OMe})_3\}_3(\eta^4\text{-1,3-C}_8\text{H}_{12})$.^{2,3}

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The bridging hydrogen atom occupies the sixth position of a distorted octahedron about iron and the C-H bond can be considered to donate two electrons to give the metal its 18-electron configuration. This type of interaction has been termed "agostic".⁴ The corresponding iron tricarbonyl cations probably are present in solutions of $Fe(CO)_3(\eta^4-1,3\text{-diene})$ complexes in strongly acidic media, though they cannot usually be isolated.⁵ This conclusion is strongly supported by the demonstration of a Mn-H-C interaction in the neutral $\eta^3\text{-cyclohexenyl}$ complex $Mn(CO)_3(\eta^3-C_6H_9)$ and in its 6-*endo*-methyl analogue $Mn(CO)_3(\eta^3-C_6H_8Me)$.⁶

Closely related to the (diene)iron tricarbonyls are complexes of the iron triad $M(\eta\text{-arene})(\eta\text{-diene})$ ($M = Fe, Ru, Os$) and of the cobalt triad $M(\eta-C_5R_5)(\eta\text{-diene})$ ($M = Co, Rh, Ir$; $R = H, Me$), in which the three strong π -acceptor CO groups have been replaced by a poorer π -acceptor/stronger σ -donor ligand $\eta^6\text{-arene}$ or $\eta^5\text{-cyclopentadienyl}$. Such compounds, which may contain either conjugated or unconjugated diolefins, react with noncoordinating acids to give isolable hydrido-diene salts,⁷⁻⁹ and it is of obvious interest to see whether these compounds also contain bridging M-H-C interactions. We describe here the preparation and protonation of (hexamethylbenzene)ruthenium(0) and (mesitylene)osmium(0) complexes of the nonconjugated diene *endo*-dicyclopentadiene (3a,4,7,7a-tetrahydro-4,7-methano-1H-indene, 1) and an X-ray



structural characterization of the protonated osmium complex 2. We have also studied the protonation of the corresponding $\eta\text{-C}_5\text{H}_5\text{Rh}$, $\eta\text{-C}_5\text{Me}_5\text{Rh}$, and $\eta\text{-C}_5\text{Me}_5\text{Ir}$ complexes of dicyclopentadiene.

Experimental Section

Proton NMR spectra were measured on Varian HA100, JEOL FX200, Bruker CXP200, and Bruker HFX270 instruments with $(CH_3)_4Si$ or CD_2Cl_2 as internal references. Carbon-13 NMR spectra were recorded at 15.04, 50.10, 50.29, and 67.89 MHz on JEOL FX60, JEOL FX200, Bruker CXP200, and Bruker HFX270 spectrometers, respectively. IR spectra were taken on Perkin-Elmer 457 and 683 grating instruments. All preparations were carried out with use of standard Schlenk tube, inert-atmosphere techniques.

Starting Materials. The complex $[RuCl_2(\eta\text{-C}_6\text{Me}_6)]_2$ was prepared by fusing the *p*-cymene complex $[RuCl_2(\eta\text{-C}_6\text{H}_4\text{-1-Me-4-CHMe}_2)]_2$ with an excess of hexamethylbenzene.¹⁰ The (mesitylene)osmium complex $[OsCl_2(\eta\text{-C}_6\text{H}_3\text{Me}_3\text{-1,3,5})]_2$ was made by heating OsO_4 with concentrated HCl, evaporating to dryness, and heating the product with 1,3,5-trimethyl-1,4-cyclohexadiene

in ethanol.^{11,12} The complex $[RhCl_2(\eta\text{-C}_5\text{Me}_5)]_2$ was prepared by heating ethanolic $RhCl_3 \cdot 3H_2O$ with pentamethylcyclopentadiene following the literature procedure¹³ and $[RhCl(C_2H_4)_2]_2$ was made by Cramer's method.¹⁴ The complex $[IrCl_2(\eta\text{-C}_5\text{Me}_5)]_2$ has been made in 9% yield from the reaction of hydrated $IrCl_3$ with hexamethyl(Dewar benzene) and in 85% yield from the reaction of hydrated $IrCl_3$ with 1-(1-chloroethyl)pentamethylcyclopentadiene.¹⁵ We obtained it in 22% yield by heating $(NH_4)_2IrCl_6$ with pentamethylcyclopentadiene in 2-propanol for 24 h, extracting the brown solid formed with dichloromethane, evaporating to small volume, and precipitating the orange crystalline product by addition of ether.

Preparations. ($\eta\text{-Cyclopentadienyl})(\eta^4\text{-dicyclopentadiene})\text{rhodium(I)}$, $Rh(C_5H_5)(C_{10}H_{12})$. A suspension of $[RhCl(C_2H_4)_2]_2$ (300 mg, 0.77 mmol) in degassed methanol (20 mL) was stirred with dicyclopentadiene (0.25 mL) for 16 h. The red-brown slurry turned yellow. The solution was removed by syringe and evaporated to dryness. The solid residue was washed with *n*-hexane to remove excess of dicyclopentadiene to leave yellow $[RhCl(C_{10}H_{12})]_2$.¹⁶ This was dissolved in THF (20 mL) and treated with $C_5H_5Na\text{-DME}$ (310 mg, 1.74 mmol). The mixture was stirred for 30 min to give a brown slurry and then evaporated to dryness under reduced pressure. The residue was extracted with two 10-mL portions of dichloromethane. The yellow extract was filtered and evaporated to dryness giving an oily yellow solid. This was purified by recrystallization from *n*-hexane at -78°C to give the yellow, microcrystalline product (370 mg, 80% based on $[RhCl(C_2H_4)_2]_2$): 1H NMR (C_6D_6 , 200 MHz) δ 4.82 (d, 5, C_5H_5 , $J_{RH} = 0.7$ Hz), 5.15, 4.54, 4.23, 3.64, 3.03, 2.67 (each m, 1), 2.3-1.7 (m, 6) (dicp). Anal. Calcd for $C_{15}H_{17}Rh$: C, 60.1; H, 5.7; mol wt, 300. Found: C, 60.2; H, 6.0; mol wt (mass spectrometry), 300.

($\eta^4\text{-Dicyclopentadiene})(\eta\text{-pentamethylcyclopentadienyl})\text{rhodium(I)}$, $Rh(C_5Me_5)(C_{10}H_{12})$.¹⁷ A mixture of $[RhCl_2(\eta\text{-C}_5\text{Me}_5)]_2$ (410 mg, 0.66 mmol), dicyclopentadiene (1.5 mL), anhydrous Na_2CO_3 (0.5 g), and ethanol (30 mL) was heated under reflux overnight. The resulting dark brown solution was evaporated to dryness under reduced pressure, and the residue was extracted with two 20 mL and one 10-mL portion of hexane. The extract was filtered, evaporated to ca. 5 mL, and cooled to -78°C to give orange needles. A second recrystallization from hexane gave the pure product (340 mg, 70%), which was identified by its 1H NMR spectrum: 1H NMR (C_6D_6 , 200 MHz) δ 1.58 (s, 15, C_5Me_5), 4.00 (m, 1), 3.76 (m, 1), 3.14 (m, 2), 2.80 (m, 2), 2.4-2.2 (br m, 3), 2.0-1.6 (br m, 3) (dicp).

($\eta^4\text{-Dicyclopentadiene})(\eta\text{-pentamethylcyclopentadienyl})\text{iridium(I)}$, $Ir(C_5Me_5)(C_{10}H_{12})$. A mixture of $[IrCl_2(\eta\text{-C}_5\text{Me}_5)]_2$ (300 mg, 0.38 mmol), dicyclopentadiene (0.5 mL), anhydrous Na_2CO_3 (0.3 g), and ethanol (25 mL) was heated under reflux for 2.5 h. The pale yellow solution was worked up as described for the rhodium compound to give the product as pale yellow needles (310 mg, 90%): 1H NMR (C_6D_6 , 200 MHz) δ 1.56 (s, 15, C_5Me_5), 3.55 (t, 1), 3.35 (m, 2), 3.15 (m, 3), 2.6-2.2 (br m, 5), 2.01 (m, 2) (dicp). Anal. Calcd for $C_{20}H_{27}Ir$: C, 52.3; H, 5.9; mol wt, 459. Found: C, 52.6; H, 6.1; mol wt (mass spectrometry), 459.

($\eta^4\text{-Dicyclopentadiene})(\eta\text{-hexamethylbenzene})\text{ruthenium(0)}$, $Ru(C_6Me_6)(C_{10}H_{12})$. A suspension of $[RuCl_2(\eta\text{-C}_6\text{Me}_6)]_2$ (200 mg, 0.3 mmol) in 2-propanol (20 mL) containing dicyclopentadiene (2 mL) was stirred and heated under reflux with anhydrous Na_2CO_3 (0.4 g) for 3 h. The yellow-brown solution was evaporated to dryness in vacuo, and the residue was extracted

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Table I. Decoupling Experiments on $[\text{Os}(\text{C}_{10}\text{H}_{13})(\eta\text{-C}_6\text{H}_3\text{Me}_3)]\text{PF}_6$ (2)

nucleus irradiated	result
H^3	$\text{H}^2 \rightarrow \text{d}$, $\text{H}^{3a} \rightarrow \text{dd}$
H^5	$\text{H}^4 \rightarrow \text{d}$, $\text{H}^{6a} \rightarrow \text{br d}$, $\text{H}^{6b} \rightarrow \text{d}$
H^2	$\text{H}^3 \rightarrow \text{d}$
H^{6a}	$\text{H}^{6b} \rightarrow \text{s}$, $\text{H}^5 \rightarrow \text{d}$

with *n*-hexane (40 mL). The filtered extract was concentrated in vacuo and cooled to -78°C . The resulting oily yellow solid was chromatographed on neutral alumina (activity 1), and the yellow band which eluted with 1:1 ether/*n*-hexane was collected. Evaporation to small volume and cooling to -78°C gave pale yellow microcrystals in ca. 30% yield: ^1H NMR (C_6D_6 , 100 MHz) δ 3.57–2.90 (m, 4), 2.65–2.17 (m, 8) (dicp), 1.75 (s, 18, C_6Me_6). Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{Ru}$: C, 66.8; H, 7.6. Found: C, 66.4; H, 8.0.

(η^4 -Dicyclopentadiene)(η -mesitylene)osmium(0), $\text{Os}(\text{C}_5\text{H}_3\text{Me}_3)(\text{C}_{10}\text{H}_{12})$. A suspension of $[\text{OsCl}_2(\eta\text{-C}_6\text{H}_3\text{Me}_3)]_2$ (540 mg, 0.71 mmol) in 2-propanol (20 mL) containing dicyclopentadiene (2.5 mL) was stirred and heated under reflux with anhydrous Na_2CO_3 (0.6 g) for 2.5 h. The dark solution was evaporated to dryness in vacuo, and the residue was extracted with two 20-mL portions and one 10-mL portion of *n*-hexane. Filtration and evaporation of the extracts gave a dark oil. This was taken up in petrol (60–80 $^\circ\text{C}$) and chromatographed on neutral alumina (activity 1). The yellow band which eluted with petrol containing 10% ether was collected and evaporated to dryness to give the product (350 mg, 55%) as an air-sensitive yellow solid: ^1H NMR (C_6D_6 , 100 MHz) δ 4.46 (s, 3, C_6H_3), 3.79–3.21 (m, 4, dicp), 2.75–1.95 (m, 8, dicp), 1.71 (s, 9, $\text{C}_6\text{H}_3\text{Me}_3$); ^{13}C NMR (C_6D_6) δ 92.7, 83.7, 17.8 (mesitylene), 59.5, 59.3, 56.7, 55.5, 52.0, 47.2, 44.4, 44.2, 33.7, 27.7 (dicp). Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{Os}$: C, 51.6; H, 5.5; mol wt, 444. Found: C, 51.1; H, 5.4; mol wt (mass spectrometry), 444.

(η -Hexamethylbenzene)(2,3,5- η -3a,4,6,7,7a-pentahydro-4,7-methano-1*H*-inden-5-yl)ruthenium(II) Hexafluorophosphate, $[\text{Ru}(\text{C}_{10}\text{H}_{13})(\text{C}_6\text{Me}_6)]\text{PF}_6$. A solution of 60% aqueous HPF_6 was added dropwise to a solution of $\text{Ru}(\text{C}_6\text{Me}_6)(\text{C}_{10}\text{H}_{12})$ (100 mg, 0.25 mmol) in diethyl ether (10 mL) to give immediately a pale yellow solid. When further addition of acid gave no more precipitate, the solid was filtered off, washed with ether, and dried in vacuo. The yield was 65 mg (45%): ^1H NMR (CD_2Cl_2 , 100 MHz) δ 4.40 (m, 2), 3.75 (m, 1), 3.52 (m, 1), 2.68–1.60 (complex overlapping m, 7), (dicp) 2.08 (s, 18, C_6Me_6), -0.09 (m, 1, H^{6a}) -10.13 (d, 1, $J = 18$ Hz, H^{6b}); ^{13}C NMR (CD_2Cl_2 and CDCl_3) δ 105.0 (s, CMe), 15.9 (q, $J = 128.8$ Hz, CMe) (C_6Me_6), 87.1 (d, $J = 165$ Hz), 78.0 (d, $J = 161$ Hz), 75.4 (d, $J = 169$ Hz), 62.8 (d, $J = 144$ Hz), 56.9 (d, $J = 138$ Hz, C^8), 52.5 (d, $J = 139$ Hz), 43.6 (d, $J = 132$ Hz), 39.4 (d, $J = 146$ Hz), 33.0 (t, $J = 129$ Hz, C^1), 2.52 (dd, $J = 159$, 78 Hz, C^6) (dicp). Anal. Calcd for $\text{C}_{22}\text{H}_{31}\text{F}_6\text{Ru}$: C, 48.8; H, 5.8. Found: C, 47.9; H, 5.9.

(η -Mesitylene)(2,3,5- η -3a,4,6,7,7a-pentahydro-4,7-methano-1*H*-inden-5-yl)osmium(II) Hexafluorophosphate, $[\text{Os}(\text{C}_{10}\text{H}_{13})(\text{C}_6\text{H}_3\text{Me}_3)]\text{PF}_6$, 2. A solution of $\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{C}_{10}\text{H}_{12})$ (500 mg, 1.13 mmol) in diethyl ether (10 mL) was treated with an excess of 60% aqueous HPF_6 . The yellow precipitate which formed immediately was collected by filtration, washed with ether, and dried in vacuo. The yield was 525 mg (80%). An analytically pure, orange crystalline solid was obtained by recrystallization from dichloromethane/ether: ^1H NMR (CD_2Cl_2 , 200 MHz) δ 5.87 (s, 3, C_6H_3), 4.97 (dd, 1, $J = 4.8$, 3.3 Hz, H^3), 4.85 (m, 1, H^5), 4.65 (m, 1, H^2), 3.50 (m, 1, H^4), 3.04–2.90 (m, 2, dicp protons, assignment unknown), 2.71 (m, 1, H^{3a}), 2.65–2.15 (complex m, 4, dicp protons, assignment unknown), 2.26 (s, 9, C_6Me_3), 0.10 (16-line m, 1, H^{6a}), -10.08 (dd, 1, $J = 16.5$, 4.5 Hz, H^{6b}) (the results of decoupling experiments are summarized in Table I); ^{13}C NMR (CDCl_3) δ 103.3 (s, CMe), 87.3 (d, $J = 173$ Hz, CH), 18.2 (q, $J = 129$ Hz, Me) (mesitylene), δ 73.0 (d, $J = 165$ Hz, C^3), 62.5 (d, $J = 145$ Hz), 58.6 (d, $J = 165$ Hz, C^2), 58.6 (t, $J = 135$ Hz, C^8), 53.3 (d, $J = 143$ Hz), 51.8 (d, $J = 135$ Hz), 43.4 (d, $J = 135$ Hz), 37.2 (d, $J = 147$ Hz), 32.5 (t, $J = 133$ Hz, C^1), -3.30 (dd, $J = 160$, 66 Hz, C^6) (dicp). Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{F}_6\text{Os}$: C, 38.8; H, 4.3; P, 5.3. Found: C, 38.8; H, 4.3; P, 5.2.

(η -Cyclopentadienyl)(2,3,5- η -3a,4,6,7,7a-pentahydro-4,7-methano-1*H*-inden-5-yl)rhodium(III) Hexafluorophosphate,

$[\text{Rh}(\text{C}_{10}\text{H}_{13})(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$. This was prepared similarly to the (hexamethylbenzene)ruthenium complex by addition of 60% aqueous HPF_6 in excess to a solution of $\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{C}_{10}\text{H}_{12})$ (350 mg, 1.17 mmol) in ether (15 mL). After being washed with ether and dried in vacuo, the air-stable, orange solid product was obtained in 40% yield: ^1H NMR (CD_2Cl_2 , 200 MHz) δ 5.68 (s, 5, C_5H_5), 6.17 (m, 2), 5.60 (m, 1), 3.83 (m, 1), 2.89 (m, 1), 2.8–2.2 (br m, 6) (dicp), 0.65 (10-line m, 1, H^6), -7.63 (dd, 1, $J_{6a,6b} = 20.2$ Hz, $J_{\text{RhH}} = 12.1$ Hz, H^{6b}); ^{13}C NMR (CD_2Cl_2) δ 91.5 (dd, $J_{\text{CH}} = 183$ Hz, $J_{\text{RhC}} = 6$ Hz, C_5H_5), 94.0 (d, partially obscured by C_5H_5 resonance, $J_{\text{CH}} \approx 150$ Hz, $J_{\text{RhC}} = 10$ Hz, C^5), 81.0 (d, $J_{\text{CH}} = 172$ Hz, $J_{\text{RhC}} = 13$ Hz, C^2 or C^3), 79.4 (dd, $J_{\text{CH}} = 170$ Hz, $J_{\text{RhC}} = 7$ Hz, C^3 or C^2), 57.6 (t, $J = 136$ Hz, C^8), 63.1 (d, $J = 154$ Hz), 51.3 (d, $J = 148$ Hz), 41.5 (d, $J = 141$ Hz), 38.9 (d, $J = 144$ Hz) (C^{3a} , C^4 , C^7 , C^{7a}), 32.0 (t, $J = 130$ Hz, C^8), 2.90 (dd, $J = 159$ Hz, 81 Hz, C^6). Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{F}_6\text{PRh}$: C, 40.4; H, 4.1; P, 6.9. Found: C, 40.7; H, 4.0; P, 7.3.

(2,3,5- η -3a,4,6,7,7a-pentahydro-4,7-methano-1*H*-inden-5-yl)(η -pentamethylcyclopentadienyl)rhodium(III) Hexafluorophosphate, $[\text{Rh}(\text{C}_{10}\text{H}_{13})(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$. This was prepared similarly as an orange solid in 45% yield from $\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{C}_{10}\text{H}_{12})$ and 60% aqueous HPF_6 : ^1H NMR (CD_2Cl_2 , 200 MHz) δ 1.77 (s, 15, C_5Me_5), 5.00 (m, 1), 4.79 (m, 2), 3.71 (m, 1), 2.97 (m, 1), 2.6–2.1 (br m, 6) (dicp), 0.41 (m, 1, H^6), -6.83 (dd, 1, $J_{6a,6b} = 19.1$ Hz, $J_{\text{RhH}} = 10.3$ Hz, H^{6b}); ^{13}C NMR (CD_2Cl_2) δ 102.9 (d, $J_{\text{RhC}} = 5.3$ Hz, C_5Me_5), 9.1 (q, $J = 130$ Hz, C_5Me_5), 101.0 (dd, $J_{\text{CH}} = 165$ Hz, $J_{\text{RhC}} = 11$ Hz, C^5), 88.6 (dd, $J_{\text{CH}} = 167$ Hz, $J_{\text{RhC}} = 8$ Hz), 86.0 (dd, $J_{\text{CH}} = 174$ Hz, $J_{\text{RhC}} = 14$ Hz) (C^2 , C^3), 55.2 (t, $J = 135$ Hz, C^8), 62.2 (d, $J_{\text{CH}} = 145$ Hz), 53.1 (partly obscured by CD_2Cl_2 resonance), 42.4 (d, $J = 142$ Hz), 38.9 (d, $J = 146$ Hz) (C^{3a} , C^4 , C^7 , C^{7a}), 32.5 (t, $J = 131$ Hz, C^1), 6.1 (dd, $J = 152$ Hz, 83 Hz, C^6). Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{F}_6\text{PRh}$: C, 46.5; H, 5.5; P, 6.0. Found: C, 46.4; H, 5.4; P, 6.2.

(2,3,5- η -3a,4,6,7,7a-pentahydro-4,7-methano-1*H*-inden-5-yl)(η -pentamethylcyclopentadienyl)iridium(III) Hexafluorophosphate, $[\text{Ir}(\text{C}_{10}\text{H}_{13})(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$. Dropwise addition of 60% aqueous HPF_6 to $\text{Ir}(\eta\text{-C}_5\text{Me}_5)(\text{C}_{10}\text{H}_{12})$ (300 mg, 0.65 mmol) dissolved in ether (15 mL) gave the product as a pale yellow solid, which was washed with ether and dried in vacuo. The yield was 330 mg (85%). Recrystallization from dichloromethane/ether gave large yellow prisms: ^1H NMR (CD_2Cl_2 , 200 MHz) δ 1.85 (s, 15, C_5Me_5), 4.55 (m, 1), 4.48 (m, 1), 4.40 (m, 1), 3.54 (m, 1), 3.13 (m, 1), 2.86 (m, 2), 2.7–2.2 (m, 4) (dicp), 0.22 (m, 1, H^6), -9.52 (dd, 1, $J_{6a,6b} = 16.1$ Hz, $J_{5,6a} = 2.9$ Hz, H^{6b}); ^{13}C NMR (CD_2Cl_2) δ 98.9 (C_5Me_5), 8.7 (q, $J = 129$ Hz, C_5Me_5), 83.2 (d, $J = 167$ Hz), 67.8 (d, $J = 165$ Hz), 63.4 (d, $J = 167$ Hz) (C^2 , C^3 , C^5), 58.7 (t, $J = 137$ Hz, C^8), 60.5 (d, $J = 146$ Hz), 53.0 (partly obscured by CD_2Cl_2 resonance), 43.6 (d, $J = 139$ Hz), 37.3 (d, $J = 148$ Hz) (C^{3a} , C^4 , C^7 , C^{7a}), 32.1 (t, $J = 135$ Hz, C^1), 9.0 (dd, $J = 165$ Hz, 50 Hz, C^6). Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{F}_6\text{PIr}$: C, 39.7; H, 4.7; P, 5.1. Found: C, 39.2; H, 4.5; P, 5.8.

(η -Mesitylene)(*tert*-butyl isocyanide)(2,3,5- η -3a,4,6,7,7a-pentahydro-4,7-methano-1*H*-inden-5-yl)osmium(II) Hexafluorophosphate, $[\text{Os}(\text{C}_{10}\text{H}_{13})(\text{C}_6\text{H}_3\text{Me}_3)(\text{CN-}t\text{-Bu})]\text{PF}_6$. A solution of $[\text{Os}(\text{C}_{10}\text{H}_{13})(\text{C}_6\text{H}_3\text{Me}_3)]\text{PF}_6$ (300 mg, 0.51 mmol) in dichloromethane (10 mL) was treated with a threefold excess of *tert*-butyl isocyanide (0.175 mL) and set aside for 5 h. The original orange-yellow color of the solution faded considerably. Solvent was removed in vacuo, and the residual yellow oil was washed with ether to give the pale yellow solid product (245 mg, 70%). This was recrystallized from dichloromethane/ether to give air-stable crystals: IR (Nujol) 2150 cm^{-1} [$\nu(\text{CN})$]. ^1H NMR (CD_2Cl_2 , 200 MHz) δ 5.74 (s, 3, C_6H_3), 2.20 (s, 9, $\text{C}_6\text{H}_3\text{Me}_3$), 1.59 (s, 9, *t*-Bu), 5.21 (t, 1, $J = 4.7$ Hz), 4.74 (dd, 1, $J = 5.4$, 4.0 Hz, H^2 , H^3), 3.5–1.0 (complex overlapping m, remaining dicp protons). Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{NF}_6\text{Os}$: C, 42.9; H, 5.1; N, 2.1; P, 4.6. Found: C, 43.1; H, 5.2; N, 2.3; P, 4.5.

The analogous hexamethylbenzene ruthenium compound was prepared in 48% yield similarly from $[\text{Ru}(\text{C}_{10}\text{H}_{13})(\text{C}_6\text{Me}_6)]\text{PF}_6$ and *t*-BuNC in dichloromethane: IR (Nujol) 2142 cm^{-1} [$\nu(\text{CN})$]; ^1H NMR (CD_2Cl_2 , 100 MHz) δ 2.12 (s, 18, C_6Me_6), 1.59 (s, 9, *t*-Bu), 4.21 (m, 2), 2.8–1.0 (overlapping m, 11, dicp); ^{13}C NMR (CD_2Cl_2) δ 108.6 (s, CMe), 16.0 (q, $J = 129$ Hz, Me) (C_6Me_6), δ 30.8 (q, $J = 129$ Hz, *t*-Bu), 58.7 (s, CMe), 153.9 (br s, CN) (*t*-BuNC), δ 91.4 (d, $J = 162$ Hz), 82.7 (d, $J = 168$ Hz), 61.7 (d, $J = 149$ Hz), 55.0 (d, $J = 127$ Hz), 42.8 (d, $J = 133$ Hz), 39.1, 38.2, 35.6, 31.4 (t, $J = 127.5$ Hz, C^1) (dicp). Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{NF}_6\text{Ru}$: C, 51.9;

Table II. Details of X-ray Data Collection for [Os(C₁₀H₁₃)(C₆H₃Me₃)]PF₆

	P2 ₁ /n	P2 ₁
wavelength, Å	0.7107	0.7107
monochromator	graphite	graphite
scan type ^{a, b}	θ-2θ	θ-2θ
2θ _{max} , deg	50	60
total reflctns ^c	3833	7585
forms recorded	±h, ±k, ±l	±h, ±k, ±l
unique (I > 3σ)	2150	3065
reflectns ^d		
R _s ^e	0.031	0.033
std reflctns	600, 061, 018	520, 040, 104
periodicity	~110 ref (2 h)	~110 ref (2 h)
indicated degradatn	<3%	<3%
crystal dimens, mm	0.06 × 0.19 × 0.13	0.12 × 0.11 × 0.12
μ(Mo Kα), cm ⁻¹	65.4	67.7
transmission factors	0.453-0.699	0.462-0.535

^a Scan velocities were 3 °min⁻¹ 2θ. ^b Backgrounds were measured with crystal and counter stationary for 7 s at each scan extremity. ^c For the P2₁ modification ±h, ±k, ±l data were measured twice: there are 5038 unique reflections (±h, ±k, ±l) to 2θ = 60°. ^d In point groups 2/m for 2a and 2 for 2b. ^e R_s = Σσ_s(F_o)/Σ|F_o| where σ_s(F_o) is the error contribution from counting statistics only.

H, 6.5; N, 2.2; P, 5.0. Found: C, 51.7; H, 6.5; N, 2.1; P, 5.1.

Collection and Reduction of X-ray Intensity Data. Well-formed crystals of a mixture containing both the centrosymmetric (2a) and noncentrosymmetric (2b) crystalline modifications of [Os(C₁₀H₁₃)(C₆H₃Me₃)]PF₆ (2) were obtained by slow recrystallization from dichloromethane under argon. The separate modifications were not distinguishable macroscopically.

Crystal Data. 2a: C₁₉H₂₅F₆POs, fw 588.6, monoclinic, space group P2₁/n, a = 11.584 (2) Å, b = 12.235 (2) Å, c = 13.990 (2) Å, β = 88.40 (2)°, V_{calcd} = 1982.0 Å³, ρ_{calcd} = 1.97 g cm⁻³, Z = 4, F(000) = 1136, μ(Mo Kα) = 65.4 cm⁻¹, t = 21 (1) °C.

2b: C₁₉H₂₅F₆POs, fw 588.6, monoclinic, space group P2₁, a = 12.484 (2) Å, b = 10.124 (2) Å, c = 7.611 (1) Å, β = 95.54 (2)°, V_{calcd} = 957.4 Å³, ρ_{calcd} = 2.04 g cm⁻³, Z = 2, F(000) = 568, μ(Mo Kα) = 67.7 cm⁻¹, t = 21 (1) °C.

Reflection intensities for both 2a and 2b were recorded on a Philips PW1100/20 automatic four-circle diffractometer operating in θ-2θ scan mode with graphite-monochromated Mo Kα radiation. The experimental details are summarized in Table II, and data reduction procedures followed those which we have described elsewhere. Isotropic crystal degradation of ca. 3% during data collection, as indicated from measurement of the "standard" reflections, was observed for each modification and data were corrected accordingly. Data were also corrected for specimen absorption effects (SHELX)²⁰ but not for extinction. The resultant |F_o| values were assigned weights w ∝ σ(F_o)⁻² with p² = 0.002 (modified by subsequent refinement to 0.007 for 2a and 0.001 for 2b).

Solution and Refinement of the Structures. The structures were solved readily by conventional Patterson and Fourier synthesis techniques. Atomic scattering factors, together with anomalous dispersion corrections, were taken from ref 22. Refinement was by full-matrix least-squares analysis, minimizing Σw(|F_o| - |F_c|)², with anisotropic thermal parameters specified for all non-hydrogen atoms. Hydrogen atoms, other than those on the mesitylene methyl groups, were located by calculation (C-H = 0.95 Å assumed). Group isotropic thermal parameters (1 for mesitylene and 1 for dicyclopentadiene H atoms) were refined. Methyl H atoms were not included in the scattering models at any time. At convergence (2b values given in parentheses) R = 0.042 (0.041), R_w = 0.055 (0.041), shift/error ratios were uniformly

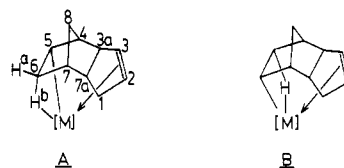


Figure 1. Two possible structures for protonated dicyclopentadiene complexes. Structure A is the one actually adopted.

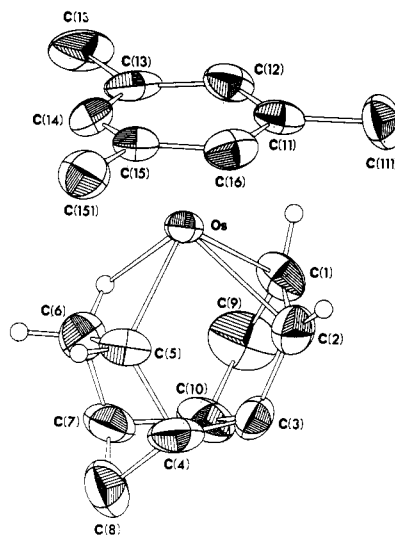


Figure 2. Molecular structure of [Os(2,3,5-η-C₁₀H₁₃)(η-C₆H₃Me₃-1,3,5)]PF₆ (2a). Hydrogen atom numbering follows that of the attached carbon atoms.

Table III. Atom Coordinates for 2a (Values Multiplied by 10⁴)

	x	y	z
Os	54 (0)	2083 (0)	2313 (0)
C(1)	-110 (14)	758 (11)	3365 (12)
C(2)	747 (14)	1503 (26)	3697 (12)
C(3)	301 (12)	2166 (28)	4455 (10)
C(4)	262 (26)	3386 (29)	4207 (11)
C(5)	-11 (13)	3498 (14)	3163 (11)
C(6)	-1255 (12)	3116 (27)	3186 (12)
C(7)	-1528 (15)	2927 (28)	4241 (12)
C(8)	-824 (13)	3838 (27)	4654 (15)
C(9)	-1118 (28)	853 (20)	4066 (28)
C(10)	-975 (29)	1904 (29)	4580 (14)
C(11)	1279 (12)	1082 (14)	1433 (9)
C(12)	197 (12)	823 (15)	1137 (10)
C(13)	-647 (13)	1603 (20)	886 (10)
C(14)	-258 (27)	2684 (28)	839 (10)
C(15)	841 (14)	3001 (14)	1027 (10)
C(16)	1602 (12)	2209 (27)	1381 (10)
C(111)	2145 (12)	249 (14)	1791 (13)
C(131)	-1855 (14)	1268 (20)	604 (13)
C(151)	1215 (29)	4217 (27)	927 (12)
P	5154 (3)	2256 (4)	2818 (3)
F(1)	6196 (13)	2596 (20)	2227 (14)
F(2)	5459 (14)	3189 (11)	3512 (11)
F(3)	4061 (14)	1977 (27)	3444 (14)
F(4)	4842 (13)	1314 (13)	2111 (11)
F(5)	4360 (13)	3039 (10)	2237 (11)
F(6)	5876 (14)	1494 (13)	3399 (12)

less than 0.16 (0.26), and difference Fourier electron density excursions were less than ±1.2 (±1.9) e Å⁻³, with the larger excursions all occurring within ca. 1 Å of the metal centres. Neither data set showed evidence of extinction, and no corrections were applied. Application of Hamilton's R factor ratio test²³ to the possible enantiomers of 2b (ratio = 1.0074) allows choice of that reported here with better than 99.5% confidence. Molecules in the crystal analyzed have the absolute configuration shown in

(20) Sheldrick, G. M. "SHELX-76", Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

(21) (a) Busing, W. R.; Levy, H. A. *J. Chem. Phys.* 1957, 26, 563. (b) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* 1967, 6, 197.

(22) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(23) Hamilton, W. C. *Acta Crystallogr.* 1965, 18, 502.

Table IV. Atom Coordinates for 2b
(Values Multiplied by 10⁴)

	x	y	z
Os	-2762 (0)	-2499 (0)	-574 (0)
C(1)	-4201 (11)	-1709 (27)	443 (21)
C(2)	-3945 (11)	-977 (14)	-902 (20)
C(3)	-4766 (24)	-1300 (36)	-2534 (38)
C(4)	-4173 (12)	-1832 (28)	-4036 (29)
C(5)	-3256 (9)	-2522 (52)	-3205 (13)
C(6)	-3845 (12)	-3848 (15)	-2441 (24)
C(7)	-4995 (20)	-3601 (30)	-3009 (31)
C(8)	-4944 (13)	-2858 (25)	-4748 (20)
C(9)	-5234 (10)	-2565 (42)	9 (29)
C(10)	-5412 (9)	-2562 (49)	-1972 (20)
C(11)	-1592 (28)	-1302 (30)	1363 (31)
C(12)	-1830 (9)	-2281 (20)	2137 (13)
C(13)	-1750 (28)	-3726 (20)	1267 (38)
C(14)	-1226 (29)	-3649 (38)	-364 (30)
C(15)	-1011 (7)	-2573 (34)	-1170 (12)
C(16)	-1298 (26)	-1285 (23)	-376 (32)
C(111)	-2007 (20)	36 (30)	2166 (48)
C(131)	-1782 (28)	-5017 (39)	2328 (33)
C(151)	-520 (9)	-2417 (34)	-2914 (27)
P	-8364 (2)	-2524 (14)	-6880 (4)
F(1)	-8046 (7)	-2599 (22)	-4860 (10)
F(2)	-9242 (13)	-1401 (27)	-6758 (39)
F(3)	-9218 (28)	-3550 (21)	-6541 (25)
F(4)	-7497 (14)	-3435 (20)	-7162 (32)
F(5)	-7525 (28)	-1292 (28)	-7034 (37)
F(6)	-8739 (9)	-2323 (32)	-8861 (11)

Figure 2. Final atomic coordinates, together with estimated standard errors, are listed in Tables III and IV. Listings of hydrogen atom coordinates (not refined), anisotropic thermal parameters, and observed and calculated structure factor amplitudes have been included in the supplementary material. Computational details are given in ref 24.

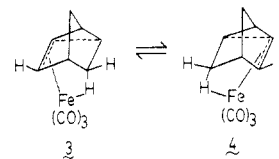
Results and Discussion

The zerovalent metal complexes of dicyclopentadiene (dicp) $M(\eta\text{-arene})(\text{dicp})$ ($M = \text{Ru}$, arene = C_6Me_6 ; $M = \text{Os}$, arene = 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$) are prepared by heating a mixture of the appropriate (arene)metal dichloride with dicp and anhydrous Na_2CO_3 in 2-propanol. After purification by chromatography the yields are ca. 30% and 50% for ruthenium and osmium, respectively. A similar procedure has been used by Maitlis et al.¹⁷ to prepare the rhodium(I) complex $\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{dicp})$ from $[\text{RhCl}_2(\eta\text{-C}_5\text{Me}_5)]_2$, and we have also made the iridium(I) analogue $\text{Ir}(\eta\text{-C}_5\text{Me}_5)(\text{dicp})$ in 90% yield from $[\text{IrCl}_2(\eta\text{-C}_5\text{Me}_5)]_2$. The $(\eta\text{-cyclopentadienyl})\text{rhodium(I)}$ compound $\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{dicp})$ has been mentioned as one product from the reaction of dicp with the 1,3-cycloheptadiene complex $[\text{RhCl}(\text{1,3-C}_7\text{-H}_{10})]_2$ in the presence of isopropylmagnesium bromide.¹⁸ We prepared it in high yield by treatment of $[\text{RhCl}(\text{dicp})]_2$ with $\text{C}_5\text{H}_5\text{Na}$. All the dicyclopentadiene complexes are yellow solids which are soluble in most organic solvents; the arene dicp complexes are appreciably more air-sensitive than the corresponding C_5H_5 or C_5Me_5 dicp complexes. They are monomeric by mass spectrometry, and their ^1H NMR spectra show complex multiplets in the region δ 4.0–1.95 due to the dicp protons in addition to the expected singlets for the arene or cyclopentadienyl protons. There are no peaks in the ^1H and ^{13}C NMR spectra which can

be assigned to a free olefin, so the dicyclopentadiene must be present in its endo form, acting as a bidentate, chelating ligand.

Solutions of the dicyclopentadiene complexes in ether react with 60% aqueous HPF_6 to give yellow precipitates of the monoprotonated salts which are readily soluble in dichloromethane and chloroform. The rhodium, iridium, and osmium salts are air-stable as solids but somewhat air-sensitive in solution; the ruthenium complex is air-sensitive even as a solid. The (arene)ruthenium and -osmium salts revert to the parent zerovalent metal complex on treatment with aqueous Na_2CO_3 .

The ^1H NMR spectra of all the monoprotonated complexes show a doublet in the metal hydride region at ca. δ -10 with a coupling of ca. 20 Hz. This doublet is absent from the spectra of the monodeuterated complexes prepared by use of DPF_6 . The magnitude of the coupling is at the upper end of the range quoted for geminal CH_2 groups²⁷ and is a clear indication that the hydride ligand bridges the metal atom and one of the dicyclopentadiene carbon atoms. The hydride resonances observed in the ^1H NMR spectra of $\text{Fe}(\text{CO})_3(\eta\text{-C}_4\text{H}_6)$ and of $\text{Fe}(\text{CO})_3(\eta\text{-C}_4\text{H}_4)$ dissolved in FSO_3H also show couplings of 22 and 29 Hz, respectively, suggesting that Fe–H–C bridged species are present.^{5,28} Protonated (norbornadiene)iron tricarbonyl exhibits a triplet hydride resonance ($J = 13$ Hz), an observation which is compatible with a pair of rapidly equilibrating M–H–C structures 3 and 4.^{29,30} In the com-



pound of empirical formula $\text{C}_{21}\text{H}_{25}\text{ClRu}$ obtained by reduction of $[\text{RuCl}_2(\text{nbd})]_n$ with zinc dust in ethanol, which is known from X-ray crystallographic study to contain a Ru–H–C interaction, the hydride resonance appears as a doublet ($J = 14$ Hz), apparently owing to a three-bond interproton coupling.³¹

In the spectra of the $(\eta\text{-C}_6\text{H}_3\text{Me}_3)\text{Os}$ and $(\eta\text{-C}_5\text{Me}_5)\text{Ir}$ complexes each component of the doublet shows an additional splitting of ca. 3 Hz, probably arising from the three-bond coupling $J_{5,6}$ (see below). The doublet hydride resonance of the $(\eta\text{-C}_6\text{Me}_6)\text{Ru}$ complex shows some broadening which may be due to long-range coupling, while the corresponding signal in the spectra of the $(\eta\text{-C}_5\text{H}_5)\text{Rh}$ and $(\eta\text{-C}_5\text{Me}_5)\text{Rh}$ complexes appears as a doublet of doublets (each with additional fine structure) owing to coupling with ^{103}Rh of ca. 10 Hz.

The spectroscopic data for the protonated dicp complexes do not establish conclusively which of the four possible carbon atoms of the dicp moiety is involved in the M–H–C interaction. The 5,6 double bond in the norbornene fragment of free dicp is known to be more reactive than the 2,3 double bond toward hydrogen, phenyl azide, and nitrosyl chloride.³² Thus, coordinated dicyclopentadiene is likely to be protonated at the 5,6 double

(24) Computations were carried out with both ANUCRYS²⁵ and SHELX²⁰ programs on the UNIVAC 1100/82 computer of the Australian National University Computer Services Centre. The molecular diagrams were drawn with ORTEP.²⁶

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bond, but this could still give rise to two possible structures A and B (Figure 1). There is no evidence from the NMR spectra that solutions of the protonated dicp complexes contain more than one species and the X-ray study of [Os(C₁₀H₁₃)(η -C₆H₃Me₃)]PF₆ (see below) shows that structure A is adopted, the metal-carbon σ -bond being on the same side of the dicp moiety as C³ and the M-H-C fragment being on the same side as C². It is of interest that the 5,6 double bond of coordinated dicp in the complexes MCl₂(dicp) (M = Pt, Pd) also undergoes nucleophilic attack by OMe⁻ and, in the resulting platinum complex [PtCl(dicp-OMe)]₂, the metal-carbon σ -bond is also on the same side of the dicp moiety as C³.^{33,34}

The ¹H NMR spectra of all the protonated dicp complexes show a one-proton multiplet in the region δ -0.09 to +0.65 which is assigned to the proton H^{6a}. Decoupling experiments show that H^{6a} is coupled to the bridging hydride proton H^{6b} ($J_{HH} \approx 20$ Hz). In the case of [Os(C₁₀H₁₃)(C₆H₃Me₃)]PF₆, irradiation of the H^{6a} resonance at δ 0.10 also collapses a one-proton multiplet at δ 4.85 to a doublet, showing that this must be due to the proton H⁵ on the carbon atom bound to osmium. The decoupling experiments summarized in Table I establish that the olefinic protons H² and H³ of [Os(C₁₀H₁₃)(C₆H₃Me₃)]PF₆ resonate at δ 4.65 and 4.97, respectively. Other assignments are given in the Experimental Section.

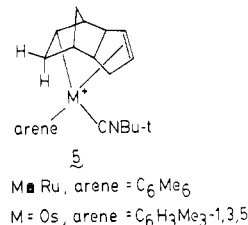
A characteristic feature of the gated ¹³C NMR spectra of the protonated dicp complexes which is diagnostic of a bridging M-H-C system is a doublet of doublets in the region δ -3 to +10 due to C⁶. The pattern arises from coupling with the terminal and bridging hydrogen atoms and the coupling constants ($J_{CH^a} \approx 160$ Hz, $J_{CH^b} = 50$ -80 Hz) are comparable with those reported for other M-H-C complexes.^{1,3-5,28,30} The coupling constant to the bridging hydride proton J_{CH^b} decreases in the order [Rh(C₁₀H₁₃)(η -C₆Me₅)]⁺ (83 Hz) \approx [Rh(C₁₀H₁₃)(η -C₅H₅)]⁺ (81 Hz) > [Ru(C₁₀H₁₃)(η -C₆Me₅)]⁺ (78 Hz) > [Os(C₁₀H₁₃)(η -C₆H₃Me₃)]⁺ (66 Hz) > [Ir(C₁₀H₁₃)(η -C₅Me₅)]⁺ (50 Hz). Thus the magnitude of J_{CH^b} is less for the 5d elements than for the corresponding 4d elements, suggesting that the C-H(bridge) bond is stronger for the latter than for the former. Conversely, the M-H interaction is stronger for the third-row than for the second-row elements, in line with the trend for terminal hydrides.

We have not attempted to assign completely the ¹³C NMR spectra of the protonated dicp complexes, though resonances due to the methylene carbon atoms C¹ and C⁸ are evident at δ 55-60 and 30-35, respectively. In the spectrum of [Rh(C₁₀H₁₃)(η -C₅H₅)]PF₆ three of the signals appear as doublets ($J \approx 7$ -13 Hz) owing to coupling with ¹⁰³Rh. The doublets at δ 81.0 and 79.0 have C-H coupling constants of ca. 170 Hz and are assigned to the olefinic carbon atoms C² and C³ (or C³ and C²), while the doublet at δ 94.0 has a J_{CH} value of ca. 150 Hz and presumably is due to the σ -bonded carbon atom C⁵. The corresponding signals in [Rh(C₁₀H₁₃)(η -C₅Me₅)]PF₆ are at δ 88.6 and 86.0 (C² and C³) and at δ 101.0 (C⁵), the J_{CH} value for the last peak (165 Hz) being larger than for the corresponding C₅H₅ compound.

Attempts to locate bands arising from the M-H-C interaction in the IR spectra of the protonated dicp complexes have been unsuccessful. Specifically, there are no bands in the 2500-2700 cm⁻¹ region assignable to a mod-

ified C-H stretching vibration cf. 2580 cm⁻¹ for C₂₁H₂₅-ClRu,³¹ 2605 cm⁻¹ for [TaCl₃(CHCMe₃)(PMe₃)₂],³⁵ and 2704/2664 cm⁻¹ for Mo{Et₂B(pyrazolate)₂}(η -C₃H₅)-(CO)₂.^{36,37}

Since the bridging C-H bond in the protonated dicp complexes can be regarded as a two-electron donor giving Ru(II), Os(II), Rh(III), and Ir(III) their preferred 18-electron configuration, one might expect the bridge to be cleaved by better donors. However, in surprising contrast to the Fe{P(OMe)₃}(dienyl) cations,³ the (arene)ruthenium and -osmium compounds do not react with CO under ambient conditions. They are also unaffected by trimethyl phosphite, even in large excess, but they do react with an excess of *tert*-butyl isocyanide to give stable, pale yellow 1:1 adducts [M(C₁₀H₁₃)(η -arene)(CN-*t*-Bu)]PF₆ (M = Ru, arene = C₆Me₅; M = Os, arene = C₆H₃Me₃). Although



the ¹H and ¹³C NMR spectra are very complex, the signals characteristic of the M-H-C interaction in the starting materials are absent, and the IR spectra show a typical ν (CN) band at ca. 2150 cm⁻¹. These data are consistent with structure 5.

Crystal and Molecular Structures of [Os(C₁₀H₁₃)(C₆H₃Me₃)]PF₆. Except for three short H...F contacts (2.42 and 2.54 Å, **2a**; 2.20 Å, **2b**), interion distances in both structures are consistent with normal van der Waals separations. Stereoscopic diagrams showing the crystal packing arrangements have been deposited. The stereochemical arrangement in a single cation from **2a** is shown in Figure 2.^{38,39} The cation conformations in **2a** and **2b** are virtually indistinguishable, and drawings differ, essentially, only in the relative magnitudes and dimensions of the thermal ellipsoids. Vibration amplitudes for both structures are relatively large with ($U_{max}^{1/2}$) values ranging up to 0.45 (0.51) Å for C and to 0.58 (0.56) Å for F atoms (**2b** values in parentheses). Bond lengths and bond angles, together with standard error estimates, are listed in Table V. Inspection of the table confirms, for reasons which are not entirely clear, that the values for **2b** are both less precise and intrinsically less reliable [e.g., C-C(benzene) = 1.20 (4) Å] than those for **2a**.⁴¹ Therefore, unless otherwise indicated, subsequent discussion will pertain exclusively to the geometry of **2a** ($P2_1/n$).

As shown in Figure 2, the cations comprise osmium bound both to η^6 -mesitylene and to a dicyclopentadiene fragment attached via an η^2 -olefin bond from C(1)-C(2), a σ -bond from C(5), and a three-center-two-electron bond involving (6B) (vide infra). The metal-arene bonding is

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(38) Most hydrogen atoms have been omitted for clarity.

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(40) Data have not been analyzed, and bond lengths and angles have not been corrected, for libration effects.

(41) The root-mean-square deviation of 20 C-C distances from their expectation values from these values in **2a** is 0.035 Å (cf. a mean least-squares error estimate of 0.025 Å) and in **2b** is 0.092 Å (cf. 0.038 Å).

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Table V. Selected Bond Distances (Å) and Angles (deg) for [Os(2,3,5- η -C₁₀H₁₃)(η -C₆H₃Me₃-1,3,5)]PF₆ (**2a** and **2b**)

	2a	2b		2a	2b
Distances					
Os-C(1)	2.19 (2)	2.18 (2)	C(7)-C(8)	1.51 (3)	1.53 (4)
Os-C(2)	2.23 (2)	2.13 (2)	C(8)-C(4)	1.50 (2)	1.48 (3)
Os-C(5)	2.10 (2)	2.04 (1)	C(9)-C(1)	1.51 (3)	1.56 (3)
Os-C(6)	2.30 (2)	2.31 (2)	C(10)-C(3)	1.52 (3)	1.59 (5)
Os-C(11)	2.22 (1)	2.32 (3)	C(10)-C(7)	1.49 (3)	1.44 (5)
Os-C(12)	2.26 (2)	2.28 (1)	C(10)-C(9)	1.49 (3)	1.50 (3)
Os-C(13)	2.26 (2)	2.18 (2)	C(11)-C(12)	1.37 (2)	1.20 (4)
Os-C(14)	2.23 (2)	2.24 (2)	C(12)-C(13)	1.42 (3)	1.61 (4)
Os-C(15)	2.29 (2)	2.28 (1)	C(13)-C(14)	1.40 (3)	1.46 (4)
Os-C(16)	2.19 (1)	2.20 (3)	C(14)-C(15)	1.37 (3)	1.29 (5)
C(1)-C(2)	1.44 (2)	1.33 (2)	C(15)-C(16)	1.41 (3)	1.50 (5)
C(2)-C(3)	1.42 (3)	1.57 (3)	C(16)-C(11)	1.43 (2)	1.41 (4)
C(3)-C(4)	1.53 (3)	1.52 (4)	C(111)-C(11)	1.53 (2)	1.59 (5)
C(4)-C(5)	1.51 (2)	1.44 (4)	C(131)-C(13)	1.52 (2)	1.54 (4)
C(5)-C(6)	1.51 (2)	1.66 (6)	C(151)-C(15)	1.56 (3)	1.52 (2)
C(6)-C(7)	1.52 (3)	1.48 (3)			
Angles					
C(1)-Os-C(2)	37.8 (6)	35.9 (6)	C(7)-C(6)-C(5)	104 (2)	102 (2)
C(1)-Os-C(6)	90.4 (7)	89.0 (7)	C(6)-C(7)-C(8)	99 (2)	102 (2)
C(2)-Os-C(5)	77.3 (7)	75.7 (15)	C(6)-C(7)-C(10)	111 (2)	111 (2)
C(5)-Os-C(6)	39.9 (6)	44.4 (16)	C(10)-C(7)-C(8)	105 (2)	99 (3)
Os-C(1)-C(2)	73 (1)	70 (1)	C(4)-C(8)-C(7)	92 (2)	96 (2)
Os-C(1)-C(9)	116 (1)	114 (2)	C(1)-C(9)-C(10)	107 (2)	105 (2)
C(9)-C(1)-C(2)	106 (2)	114 (2)	C(3)-C(10)-C(7)	102 (2)	103 (1)
Os-C(2)-C(1)	70 (1)	74 (1)	C(3)-C(10)-C(9)	104 (2)	104 (3)
Os-C(2)-C(3)	110 (1)	110 (1)	C(9)-C(10)-C(7)	121 (2)	122 (3)
C(3)-C(2)-C(1)	111 (2)	108 (2)	C(12)-C(11)-C(16)	117 (2)	125 (3)
C(2)-C(3)-C(4)	114 (2)	110 (2)	C(12)-C(11)-C(111)	124 (2)	114 (3)
C(2)-C(3)-C(10)	107 (2)	105 (2)	C(111)-C(11)-C(16)	119 (2)	118 (3)
C(10)-C(3)-C(4)	101 (2)	102 (2)	C(11)-C(12)-C(13)	124 (2)	121 (2)
C(3)-C(4)-C(5)	108 (2)	106 (2)	C(12)-C(13)-C(14)	115 (2)	111 (2)
C(3)-C(4)-C(8)	107 (2)	100 (2)	C(12)-C(13)-C(131)	122 (2)	123 (2)
C(8)-C(4)-C(5)	100 (2)	106 (3)	C(131)-C(13)-C(14)	123 (2)	122 (3)
Os-C(5)-C(4)	118 (1)	126 (2)	C(13)-C(14)-C(15)	124 (2)	125 (3)
Os-C(5)-C(6)	77 (1)	77 (1)	C(14)-C(15)-C(16)	118 (2)	118 (1)
C(6)-C(5)-C(4)	100 (1)	101 (2)	C(14)-C(15)-C(151)	121 (2)	128 (3)
Os-C(6)-C(5)	63 (1)	59 (1)	C(151)-C(15)-C(16)	121 (2)	113 (3)
Os-C(6)-C(7)	123 (1)	125 (2)	C(11)-C(16)-C(15)	121 (2)	118 (3)

just marginally asymmetric, with Os-C ranging from 2.19 (1) to 2.29 (2) Å [2.19 (2) to 2.31 (3) Å for **2b**] and an Os-ring perpendicular distance of 1.753 (1) Å [1.749 (1) Å for **2b**]. These values agree well with those observed in the ruthenium(II)-arene complexes RuCl₂(η -C₆H₆)-(PMePh₂) [2.19 (1)-2.27 (1) and 1.69 Å] and RuCl₂(η -C₆H₄-1-Me-4-CHMe₂)(PMePh₂) [2.21 (1)-2.26 (1) and 1.72 Å].⁴² However, they are significantly greater than those occurring in the (arene)osmium dichloride dimer [OsCl₂(η -C₆H₄-1-Me-4-CHMe₂)₂] [2.15-2.19 and 1.637 (2) Å].⁴³ The smaller arene-osmium distance in the dimer (Δ = 0.11 Å) probably reflects, primarily, the high electronegativity of the trans (chloride) ligands but also, perhaps, the presence of fewer, and less unfavorable, intramolecular nonbonding interactions. For **2a** the principal nonbonding interactions include C(1)···C(11) (3.13 Å), C(1)···C(12) (3.13 Å), C(5)···C(15) (3.18 Å), H(1)···C(11) (2.43 Å), and H(1)···C(12) (2.45 Å). In the dimer there are just three short Cl···C contacts (3.24-3.30 Å) and no short Cl···H contacts.

The Os-C(5) distance [2.10 (2) Å] compares well with the two other values that have been reported for Os(II)-C σ -bonds in mononuclear octahedral complexes, viz., 2.13 (2) Å in *cis*-OsH(2-C₁₀H₇)(Me₂PCH₂CH₂PMe₂)₂⁴⁴ and 2.18 (2) Å (mean of two values) in *cis*-Os(CH₂C₆F₅)₂(CO)₄.⁴⁵

Although no structural data for mononuclear osmium(II)-olefin complexes are available for comparison, the Os-C(1) and Os-C(2) distances in **2a** [average 2.21 (2) Å] agree well with reported Ru(II)-olefin distances (2.17-2.29 Å) in a range of octahedral ruthenium complexes containing ethylene,⁴⁶ 1,5-cyclooctadiene,⁴⁷⁻⁴⁹ norbornadiene,^{47,50,51} or 1-3:6,7- η -C₈H₉,⁵² ruthenium-ligand and osmium-ligand bond lengths are expected to be similar. The Os-C(olefin) distances [Os-C(1) and Os-C(2)] also agree well with those observed in trinuclear carbonyl clusters, e.g., 2.21 (2) and 2.25 (2) Å to the terminal carbon atoms of transoid butadiene in Os₃(CO)₁₀(*s-trans*-C₄H₆).⁵³

Although the hydrogen atoms were not located directly from difference syntheses, the approximate location of the added proton [H(6B)] can be inferred with considerable

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certainty, both from the bonding geometry about C(6) and from R factor analysis. The observed single-bond distance to C(5) [1.51 (2) Å] confirms unambiguously that C(6) and C(5) are both sp^3 hybridized. Furthermore, whereas the Os–C(6) distance [2.30 (2) Å] is too great for a direct Os–C σ -bond, the lengthening of 0.20 Å (0.26 Å in **2b**) relative to Os–C(5) is entirely consistent with the presence of a two-electron–three-center C–H–M bond, similar to those in $[Fe\{P(OMe)_3\}_3(\eta^3-C_8H_{13})]BF_4$ ³ and $Mn(CO)_3(\eta^3-C_6H_5Me)$.⁶ In the latter complexes the metal–carbon distances in the C–H–M moiety are lengthened by 0.16 and 0.14 Å, respectively, vis à vis the M–C distances to the remote terminal carbon atoms of the η^3 -allyl moieties. With H(6B) tetrahedrally disposed at 0.95 Å from C(6), the calculated Os–H distance is 1.81 Å (1.90 Å for **2b**) and the C–H–Os angle is 110° (104° for **2b**). These values are comparable with the observed M–H distances and C–H–M angles in $[Fe\{P(OMe)_3\}_3(\eta^3-C_8H_{13})]BF_4$ [Fe–H = 1.874 (3) Å, C–H–Fe = 99.4 (2)°; neutron diffraction analysis]³ and in $Mn(CO)_3(\eta^3-C_6H_5Me)$ [Mn–H = 1.86 (2) Å, C–H–Mn = 100 (1)°, X-ray diffraction;^{6a} Mn–H = 1.84 (1) Å; neutron diffraction analysis^{6b}]. In contrast, a similarly disposed H atom (tetrahedral, C–H = 0.95 Å) on C(5) results in an unacceptably short Os–H contact (ca. 1.43 Å). Moreover the C–H internuclear separation cannot be significantly less than 1.08 Å and, in a bridging environment, may be substantially greater, the corresponding observed values in the iron cyclooctenyl and manganese 6-*endo*-methylcyclohexenyl complexes being 1.164 (3)³ and 1.19 (1) Å,^{6b} respectively. In contrast to the neutron scattering result, the 1.07 (2) Å C–H (bridging) distance observed in the manganese complex by X-ray diffraction analysis^{6a} probably represents an upper limit for X-ray determined (inter electron density centroid) separations. However, whereas increasing the assumed C–H(bridging) separation to 1.1–1.2 Å (from 0.95 Å) serves to generate even less favorable contacts to a C(5) hydrogen atom substituent [Os–H = ca. 1.3 Å], the geometry of the proposed C(6)–H(6B)–Os moiety becomes no less favorable [Os–H = ca. 1.75 Å; C–H–Os = ca. 102°]. That the proposed location of H(6B) in **2** is not grossly in error is also strongly supported by R factor analysis. Omission of H(6B) from the scattering model increases R_w from 0.0554 to 0.0559 for **2a**

and from 0.0406 to 0.0408 for **2b**. The R factor ratios are each significant at the 99.5% confidence level.²³ The proposed C–H–Os interaction in **2** is appreciably greater than those suggested for $Mo\{Et_2B(pyrazolate)_2\}(\eta^3-C_3H_4Ph-2)(CO)_2$ [Mo–C = 3.055 (7) Å; Mo–H(estimated) = 2.15 Å]³⁷ and for $C_{21}H_{25}ClRu$ [Ru–C = 2.749 (2) Å, Ru–H = 2.10 (3) Å].³¹

Bond distances and angles in the coordinated dicyclopentadiene moiety are unexceptional and, except in the immediate vicinity of C(5) and C(6), are similar to those in $PdCl_2(endo-dicp)$.⁵⁴ In the latter, tilting of the norbornene double bond brings C(5) closer to the metal than C(6) [Pd–C(5) = 2.19 (1) Å; Pd–C(6) = 2.28 (1) Å], though the difference in M–C bond lengths is smaller than in the osmium complex. It is clear from this comparison that the same carbon atom of coordinated dicyclopentadiene, C⁶ in Figure 1 (C(6) in Figure 2), is susceptible to nucleophilic attack in the palladium(II) complex and to electrophilic attack (protonation) in the osmium(0) complex.

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Registry No. 1, 77-73-6; 2, 94957-48-9; 5 (M = Os, arene = $C_6H_3Me_3$ -1,3,5), 94978-20-8; 5 (M = Ru, arene = C_6Me_6), 94978-22-0; $[IrCl_2(\eta-C_5Me_5)]_2$, 12354-84-6; $Rh(\eta-C_5H_5)(\eta-C_{10}H_{12})$, 55834-67-8; $Rh(\eta-C_5Me_5)(\eta-C_{10}H_{12})$, 33363-21-2; $Ir(\eta-C_5Me_5)(\eta-C_{10}H_{12})$, 94957-49-0; $Ru(\eta-C_6Me_6)(\eta-C_{10}H_{12})$, 94957-50-3; $Os(\eta-C_6H_3Me_3$ -1,3,5)($\eta-C_{10}H_{12}$), 94978-23-1; $[Ru(\eta-C_6Me_6)(C_{10}H_{13})]PF_6$, 94957-52-5; $[Rh(\eta-C_5H_5)(C_{10}H_{13})]PF_6$, 94957-54-7; $[Rh(\eta-C_5Me_5)(C_{10}H_{13})]PF_6$, 94957-56-9; $[Ir(\eta-C_5Me_5)(C_{10}H_{13})]PF_6$, 94957-58-1; $[RhCl(\eta-C_{10}H_{12})]_2$, 12131-71-4; $(NH_4)_2IrCl_6$, 16940-92-4; C_5HMe_5 , 41539-64-4; $[RhCl(C_2H_4)]_2$, 12081-16-2; C_5H_5Na , 4984-82-1; $[RhCl_2(\eta-C_5Me_5)]_2$, 12354-85-7; $[RuCl_2(\eta-C_6Me_6)]_2$, 67421-02-7; $[OsCl_2(\eta-C_6H_3Me_3$ -1,3,5)]₂, 94957-59-2; OsO_4 , 20816-12-0; 1,3,5-trimethyl-1,4-cyclohexadiene, 4074-23-1.

Supplementary Material Available: Tables of structure factors, atom coordinates (including hydrogen atoms), and isotropic thermal parameters and molecular packing diagrams for **2a** and **2b** (38 pages). Ordering information is given on any current masthead page.

(54) Wright, L. L.; Wing, R. M.; Rettig, M. F. *J. Am. Chem. Soc.* **1982**, 104, 610.