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Ring-Methyl Activation in Pentamethylcyclopentadienyl Complexes. 3. Synthesis and Reactions of (η^4-Tetramethylfulvene)(η^5-cyclopentadienyl)rhodium and -iridium

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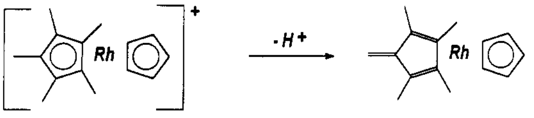
$[Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)]^+$ (**1a**) was deprotonated (by potassium *tert*-butoxide) to give the neutral tetramethylfulvene complex $[Rh(\eta^4\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]$ (**2a**), which was a good nucleophile toward Me_3SiCl, $CH_2{=}CHCH_2Br$, $PhCH_2Br$, Cl_2, I_2, CO_2 (+MeI), and Ph_2CO, giving $[Rh(\eta^5\text{-}C_5Me_4CH_2X)(\eta^5\text{-}C_5H_5)]^+$ (X = Me_3Si–, $CH_2{=}CHCH_2$–, $PhCH_2$–, Cl, I, MeO_2C–, and $Ph_2C(OH)$–, respectively). The complex **2a** also yielded **1a** both on protonation and on treatment with the ferrocenium ion in THF. Similar reactions were carried out on $[Ir(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)]^+$ (**1b**), deprotonated by lithium diisopropylamide in THF, yielding $[Ir(\eta^5\text{-}C_5Me_4CH_2X)(\eta^5\text{-}C_5H_5)]^+$ (X = Me_3Si–, $PhCH_2$–, or $Ph_2C(OH)$–) with Me_3SiCl, $PhCH_2Br$, or Ph_2CO; these reactions presumably proceeded via $[Ir(\eta^4\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]$ (**2b**). While both **2a** and **2b** reacted with MeI, **2a** gave a mixture of complexes, $[Rh(C_5H_5)(C_5Me_nEt_{5-n})]^+$ (**7a**, n = 1–5), whereas the iridium complex **2b** gave just $[Ir(\eta^5\text{-}C_5Me_4Et)(\eta^5\text{-}C_5H_5)]^+$. Possible mechanisms for this process are reviewed.

Recent studies in our laboratories have shown that the C–H bonds of ring methyls in pentamethylcyclopentadienyl complexes of iridium,[1,2] rhodium,[3] and ruthenium[4] can successfully be activated. Although detailed studies will be needed before mechanisms can be defined, it is already clear that at least two processes are possible: (a) via an oxygen activation and (b) by deprotonation by a base. Thus, the ruthenium(III) complex $[\{Ru(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$ reacted with oxygen, giving the Ru(IV) μ-oxo complex, $[\{Ru(\eta^5\text{-}C_5Me_5)Cl_2\}_2(\mu\text{-}O)]$, which then spontaneously lost water to give the (tetramethylfulvene)ruthenium(II) complex, $[\{Ru(\eta^6\text{-}C_5Me_4CH_2)Cl_2\}_2]$.[4] By contrast, the iridium complexes $[Ir(\eta^5\text{-}C_5Me_5)(Me)(CO)(Ph)]$ and $[Ir(\eta^5\text{-}C_5Me_5)Me_4]$ are deprotonated by *sec*-butyllithium; reaction with the appropriate electrophile then gave $[Ir(\eta^5\text{-}C_5Me_4CH_2X)(Me)(CO)(Ph)]$ (X = CH_2Ph, $C(OH)(R)Ph$, $CH{=}CH_2$, COPh, COOR, $SiMe_3$) and $[Ir(\eta^5\text{-}C_5Me_4CH_2X)Me_4]$ (X = Et, $SiMe_3$), respectively, in high yields. Although the intermediates in the iridium reactions have not yet been characterized, we presume that an anionic species such as $Li[Ir(\eta^5\text{-}C_5Me_4CH_2)(Me)(CO)(Ph)]$, is formed, which can then react (e.g., with organic halides, X–Y) to give the products.

In a preliminary communication we have also described the ready deprotonation of the cationic rhodium sandwich complex $[Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)]^+$ (**1a**) to give the neutral tetramethylfulvene complex, $[Rh(\eta^4\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]$ (**2a**).[3] We here give details of this reaction and of those of **2a** with electrophiles, as well as of parallel reactions of the iridium analog, $[Ir(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)]^+$ (**1b**).

Results and Discussion

A. Rhodium Complexes Related to $[Rh(\eta^4\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]$ (2a). (i) Synthesis of $[Rh(\eta^5\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]$ (2a). The deprotonation of the pale yellow **1a** to give the red-brown **2a** proceeded best with potassium *tert*-butoxide in THF at room temperature. Although sensitive to air and moisture, complex **2a** was reasonably thermally stable under an inert atmosphere, allowing characterization by elemental analysis and NMR spectroscopy. The NMR spectra show the presence of doublets (coupling to ^{103}Rh, I = $^1/_2$, 100%), due to a symmetrical η^5-C_5H_5 (^{1}H, δ 4.75, J(RhH) 1 Hz; ^{13}C, δ 84.1, J(RhC) 5Hz), and two sets of methyl singlets (^{1}H, δ 1.50 and 1.70; ^{13}C, δ 11.9 and 12.8) as well as three types of quaternary C atoms (^{13}C: δ 70.4, J(RhC) 11 Hz; 91.5 J(RhC) 12 Hz; 94.3), and a $CH_2{=}$ (^{1}H, δ 3.39; ^{13}C, δ 69.0) due to the η^n-$C_5Me_4{:}CH_2$ ligand. The ^{1}H signal of the C_5H_5 ring is at a lower frequency (higher field) by comparison with the cationic complex **1a** ($\Delta\delta$ 0.7 ppm), confirming that **2a** has no positive charge. Since two of the three sets of quaternary carbons show coupling to



1a *2a*

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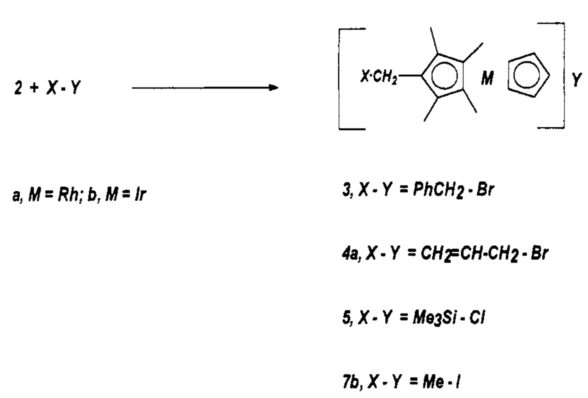
^{103}Rh, while the third and CH_2= do not, this strongly suggests that the tetramethylfulvene is η^4-bonded with one ring carbon and the attached CH_2= not coordinated. The presence of an uncoordinated double bond in **2a** was confirmed by the band at 1607 cm^{-1} in the IR spectrum.

A single crystal X-ray structure determination of **2a** has not been possible, but a structure determination of the related (indenyl)(6,6-diphenylfulvene)rhodium showed that the fulvene is η^4- and the indenyl is η^5-bonded to the rhodium.[5] Deprotonation reactions analogous to that which occurs in **1** → **2** have been observed for (η^6-hexamethylbenzene)iron[6] and -manganese[7] cations (giving η^5-pentamethylbenzyl complexes) and a (pentamethylcyclopentadienyl)iridium, which yielded an (η^4-tetramethylfulvene)iridium complex.[8]

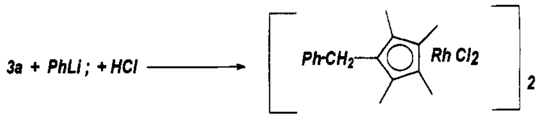
(ii) Reactions of [Rh(η^5-C_5Me_4:CH_2)(η^5-C_5H_5)] (2a) with Organic Halides (X–Y). The tetramethylfulvene in complex **2a** behaved conventionally, as a nucleophile toward electrophilic reagents; for example, organic halides (X–Y, hexane solution) reacted to give substituted derivatives of tetramethylrhodocenium (**3a–5a**) in 50–70% yields.



The complexes were characterized as the hexafluorophosphate salts (Y = PF_6); the NMR spectra showed the presence of singlets due to the symmetrical η^5-C_5H_5, and two sets of methyl singlets and a CH_2 due to the C_5Me_4-CH_2– ligand (^{1}H, δ 2.12, 2.15, and 2.08, for example in **5a**). In this case 7–8-Hz couplings to ^{103}Rh were found for all the C_5 ring carbons, showing that both rings are η^5-bonded; the CH_2X was not coupled.

Although base promoted substitution reactions of H in the methyls of pentamethylcyclopentadienyl complexes have been found for iridium[1,2] and cobalt[9,10] complexes, this and some related reactions which we have recently discovered for ruthenium,[4] appear to be the first examples of the synthesis of substituted pentamethylcyclopentadienyl complexes from isolated tetramethylfulvene complexes.

The synthetic utility of such reactions is increased since the C_5H_5 ring can be displaced. This was accomplished by reaction with PhLi followed by hydrolysis and treatment with gaseous HCl to give the chloride dimer complexes; thus **6a** was obtained in 45% yield from **3a**.



6a

By contrast to its reaction with other halides, that of **2a** with MeI was more complex. It gave an inseparable mixture composed of mono- and polyethyl cationic complexes, [Rh(C_5H_5)($C_5Me_nEt_{5-n}$)]$^+$ (**7a**, n = 1–5). The reaction did not depend on the solvent, and the same mixture was obtained when toluene, THF, CH_2Cl_2, or neat MeI was used. The same mixture was also obtained when pentamethylrhodocenium was reduced by Na/Hg in THF in the presence of MeI. The ^{1}H NMR spectrum of the product showed several overlapping triplets and quartets of differing intensities, arising from the presence of several different Et– groups. Four different Cp resonances were also visible, suggesting that at least four different complexes had been formed. The clearest information on the nature of the product came from the positive FAB mass spectrum, which showed peaks at m/z 359 (n = 1; relative intensity, 5%), 345 (n = 2; 24%), 331 (n = 3; 63%), 317 (n = 4; 100%), and 303 (n = 5; 35%). In addition, some of the pentamethylrhodocenium, **1a**, is also present. This information indicates that all six species [Rh(C_5H_5)($C_5Me_nEt_{5-n}$)]$^+$ (**7a**, n = 0–5) are probably present, though it is not clear whether their relative amounts are reliably given by the relative intensities quoted.

Further evidence comes from the analogous iridium reaction. The microanalysis, NMR, and positive FAB-mass spectrum of the isolated product from reaction of MeI and **2b** indicated the presence of one species, [Ir(C_5H_5)(C_5Me_4Et)]$^+$, **7b**; however, the EI mass spectrum showed that some of the disubstituted [Ir(C_5H_5)(C_5Me_3-Et_2)]$^+$ was also formed.

The reaction of **2a** with MeI is different not only from the other reactions of **2a** but also from the reactions of MeI with η^5-pentamethylbenzyl complexes of iron[2] and manganese[3] where only monoethyl substituted complexes (e.g., **8**) were obtained.

$$[\mathrm{Fe}(\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{Me_5C_6{=}CH_2})] + \mathrm{MeI} \rightarrow \underset{\mathbf{8}}{[\mathrm{Fe}(\mathrm{C_5H_5})(\eta^6\text{-}\mathrm{Me_5C_6Et})]^+}$$

$$[\mathrm{Mn}(\eta^5\text{-}\mathrm{Me_5C_6{=}CH_2})(\mathrm{CO})_3] + \mathrm{MeI} \rightarrow [\mathrm{Mn}(\eta^6\text{-}\mathrm{Me_5C_6Et})(\mathrm{I})(\mathrm{CO})_2] + [\mathrm{Mn}(\eta^6\text{-}\mathrm{Me_6C_6})(\mathrm{CO})_3]^+$$

(iii) Reactions of [Rh(η^4-C_5Me_4:CH_2)(η^5-C_5H_5)] with Halogens and Other Oxidizing Agents. When a hexane solution of **2a** was treated with gaseous Cl_2, a yellow precipitate, presumably the chloride salt, **9a** (Y = Cl), formed immediately; this was converted into the hexafluorophosphate **9a** (Y = PF_6) which was characterized and shown to contain the η^5-(chloromethyl)tetramethylrhodocenium cation.

$$\underset{\mathbf{2a}}{[\mathrm{Rh}(\eta^4\text{-}\mathrm{C_5Me_4{:}CH_2})(\eta^5\text{-}\mathrm{C_5H_5})]} + \mathrm{Cl_2} \rightarrow \underset{\mathbf{9a}}{[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{C_5Me_4CH_2Cl})]\mathrm{Cl}}$$

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A somewhat related reaction has been found in the ruthenium system[4]

$$[Ru(\eta^4\text{-}C_5Me_4{:}CH_2)Cl_2(Me_2SO)] + 2HCl \rightarrow [Ru(\eta^5\text{-}C_5Me_4CH_2Cl)Cl_3(Me_2S)] + H_2O$$

which proceeded easily and in high yield despite the complicated redox and hydrogen transfer processes which are involved.

A reaction similar to the formation of **9a** also occurred between **2a** and iodine, where the product was the η^5-(iodomethylene)tetramethylrhodocenium cation **10a**. However, since the counteranion was always I_3^-, the reaction

$$\underset{\textbf{2a}}{[Rh(\eta^4\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]} + 2I_2 \rightarrow \underset{\textbf{10a}}{[Rh(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_4CH_2I)]I_3}$$

required 2 equiv of I_2 to obtain good yields; smaller quantities of iodine gave lower amounts of the triiodide salt. Neither the simple iodide salt nor any other product was observed.

The iron complex $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6Me_5{=}CH_2)]$ has been reported[6] to react with iodine, giving $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_5CH_2I)]^+$ when a ratio of iron complex to I_2 of 1:1 was used, but a dimer complex $[\{Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_5\text{-}CH_2\text{-})\}_2]^{2+}$ either using a 2:1 stoichiometry or by reacting the neutral methylene complex with the iodoiodide. No reactions of this type could be induced with **2a** and **10a**, suggesting that the C—I bond in complex **10a** is less reactive than in the iron complex.

The tetramethylfulvene complex **2a** was also easily oxidized with ferrocenium hexafluorophosphate in THF to give pentamethylrhodocenium hexafluorophosphate (**1a**) in 78% yield.

$$\underset{\textbf{2a}}{[Rh(\eta^4\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]} + [Fe(\eta^5\text{-}C_5H_5)_2]PF_6 \rightarrow \underset{\textbf{1a}}{[Rh(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]PF_6} + Fe(\eta^5\text{-}C_5H_5)_2$$

The reaction presumably proceeds via a primary electron transfer to give the unstable cation radical $[Rh(C_5H_5)(Me_4C_5{=}CH_2)]^+$, which abstracts $H^\bullet$ from the THF solvent. A somewhat analogous oxidation of $[Fe(C_5H_5)(Me_4C_5{=}CH_2)]$ by TCNQ to pentamethylferrocenium has been reported.[6,11]

(iv) Reactions of $[Rh(\eta^4\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]$ (2a) with Carbon Dioxide. Complex **2a** also reacted with dry gaseous carbon dioxide to give an unstable zwitterionic complex, **11a**, which decarboxylated easily to pentamethylrhodocenium, **1a**.

$$\underset{\textbf{2a}}{[Rh(\eta^4\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]} + CO_2 \rightarrow \underset{\textbf{11a}}{[Rh^+(\eta^5\text{-}C_5Me_4CH_2CO_2^-)(\eta^5\text{-}C_5H_5)]} \rightarrow \textbf{1a}$$

Owing to its instability, attempts to isolate **11a** were unsuccessful and only mixtures of **1a** and **11a** were obtained, as indicated by the NMR spectra and by the presence of a band at 1605 cm^{-1} in the IR spectrum due to $\nu(CO_2^-)$.[6] An aqueous solution of the mixture showed pH = 7, and attempts to protonate the zwitterion (using strong acids such as BF_3·(etherate) in $CHCl_3$, or HPF_6 in water) led to immediate decarboxylation to **1a**.

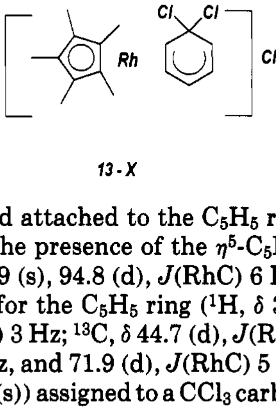
However **11a** was successfully trapped as the stable methyl ester **12a**, by adding methyl iodide to the solution after carbon dioxide had been passed through it, and characterized as the ester hexafluorophosphate salt.

$$\underset{\textbf{11a}}{[Rh^+(\eta^5\text{-}C_5Me_4CH_2CO_2^-)(\eta^5\text{-}C_5H_5)]} + MeI \rightarrow \underset{\textbf{12a}}{[Rh(C_5H_5)(C_5Me_4CH_2CO_2Me)]^+}$$

(v) Protonation Reactions of $[Rh(\eta^4\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]$ (2a). Complex **2a** underwent protonation readily to give pentamethylrhodocenium, **1a**. This reaction even occurred with water to give a substance, the NMR spectrum of which showed the presence of the $[Rh(C_5H_5)(C_5Me_5)]^+$ cation and which appeared to be an aquated hydroxide thereof, but which gave poor microanalyses. On addition of KPF_6, $[Rh(C_5H_5)(C_5Me_5)]PF_6$ was isolated in 87% overall yield.

A very unexpected reaction occurred between **2a** and chloroform involving H transfer to the $\eta^4\text{-}C_5Me_4{:}CH_2$. The product is **13a**, a neutral adduct (**2a** + $CHCl_3$) in which the H had apparently added to the methylene, giving an $\eta^5\text{-}C_5Me_5$, while the CCl_3 had attached to the C_5H_5 ring.

13a



13-X

The NMR spectra showed the presence of the $\eta^5\text{-}C_5Me_5$ ring (^{1}H, δ 1.74 (s); ^{13}C, δ 10.9 (s), 94.8 (d), J(RhC) 6 Hz), as well as three resonances for the C_5H_5 ring (^{1}H, δ 3.04 (m), 4.61 (m), 3.91 (t), J(HH) 3 Hz; ^{13}C, δ 44.7 (d), J(RhC) 12 Hz), 75.3 (d), J(RhC) 7 Hz, and 71.9 (d), J(RhC) 5 Hz) and a resonance (^{13}C, δ 105.9 (s)) assigned to a CCl_3 carbon. These resonances are in positions very similar to those observed by Buhro et al. for the $\eta^4\text{-}C_5H_5CCl_3$ ligand in $[Re(NO)(PPh_3)(PPhCl_2)(\eta^4\text{-}C_5H_5CCl_3)]$ (^{13}C, δ 44.2, 45.1 (2 × dd, J(PC)), 72.2 (dd, J(PC)), 81.3, 82.2 (2 × s), and 115.5 (CCl_3; dd, J(PC)),[12] and therefore we suggest that the same ligand (but in a more symmetrical environment, and without coupling to ^{31}P, of course) is also present in **13a**.

We exclude the alternative formulation $[Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5CCl_2)]Cl$, **13-X**, with an η^5-dichlorocyclohexadienyl ring since that complex should be ionic and the chloride should be easily exchanged for other anions.

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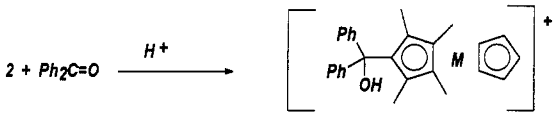
This was not the case; **13a** was insoluble in water and decomposed in other solvents (such as methanol, acetone, and even deuteriochloroform), to give $[Rh(C_5H_5)(C_5Me_5)]^+$; this is consistent with the formulation suggested but is improbable for a cyclohexadienyl.

The complex $[Re(NO)(PPh_3)(PPhCl_2)(\eta^4\text{-}C_5H_5CCl_3)]$ was formed by a reaction of related stoichiometry, combining $[Re(NO)(PPh_3)(PPhCl)(\eta^5\text{-}C_5H_5)]$ with CCl_4.[12] $[Mn(CO)_3(C_6Me_5{:}CH_2)]$ also added a number of halocarbons to both the metal and to the exocyclic methylene;[7] however, with $CDCl_3$ it gave $[Mn(CO)_2(Cl)(C_6Me_5CH_2CDCl_2)]$.

(vi) Reaction with Benzophenone. The neutral complex **2a** also reacted with benzophenone as electrophile giving, after hydrolysis, the tertiary alcohol **14a**; isolation and purification of the complex was difficult, hence the low yield.



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B. Iridium Complexes Related to $[Ir(\eta^4\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]$ (2b). The base of choice for a useful selectivity in the deprotonation of $[Ir(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)]^+$, **1b**, was lithium diisopropylamide (LDA) in cyclohexane/THF, at −70 °C, ratio 1.2:1, Li:Ir. The white suspension of **1b** dissolved to give a clear yellow solution, which was then treated with the desired electrophile at low temperatures. The reaction mixture was allowed to warm up and was then worked up after addition of excess ammonium hexafluorophosphate. The following electrophilic reagents gave the respective products in moderate yields: benzyl bromide (**3b**, 23%), trimethylchlorosilane (**5b**, 56%), methyl iodide (**7b**, 49%), and benzophenone (**14b**, 47%).

$$\underset{\mathbf{1b}}{[Ir(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)]PF_6} \rightarrow \underset{\mathbf{2b}}{[Ir(\eta^4\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]}$$

$$\underset{\mathbf{2b}}{[Ir(\eta^4\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]} + \text{X–Y};\ NH_4PF_6 \rightarrow \underset{\mathbf{3b,\ 5b,\ 7b}}{[Ir(\eta^5\text{-}C_5Me_4CH_2X)(\eta^5\text{-}C_5H_5)]PF_6}$$

X–Y = $PhCH_2$–Br (**3b**), Me_3Si–Cl (**5b**), Me–I (**7b**)

The reactions leading to **3b** and **5b** were similar to those already described for rhodium; the products were again identified by microanalyses and their spectra. In each case the NMR spectra showed the presence of a $\eta^5\text{-}C_5H_5$ ring and the characteristic 1:2:2 pattern of the methyls and the carbons for a $\eta^5\text{-}C_5Me_4CH_2X$ ring, as well as the CH_2 resonances and those due to X. However, the reaction with methyl iodide, which leads cleanly to the monoethyl complex **7b**, contrasts sharply with the rhodium system which gives the mixture **7a** described above.

The products obtained from some reactions of the deprotonated pentamethyliridocenium, **1b**, with an electrophile were sometimes mixtures where the electrophile had added at either the Cp* or the Cp ring. We presume that some bases are able to deprotonate either the $\eta^5\text{-}C_5Me_5$ or the $\eta^5\text{-}C_5H_5$ ring and that the products arise from both intermediates. For example, in the reaction of complex **1b** with *sec*-butyllithium followed by trimethylchlorosilane (where the products are easily isolated and identified), the NMR spectra of the crude product mixture indicated the presence of some substitution at the $\eta^5\text{-}C_5H_5$ ring and also of disubstitution at the $\eta^5\text{-}C_5Me_5$ ring. Apparently similar lemon-yellow solutions were formed on reaction of colorless **1b** with all the bases; however, attempts to isolate and characterize $[Ir(\eta^4\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]$, the iridium analog of **2a**, from the reaction of **1a** with potassium *tert*-butoxide were unsuccessful.

C. Mechanistic Considerations. We have shown that the methyl CH's in the cationic complexes $[M(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)]PF_6$ (M = Rh or Ir) can be activated by deprotonation. The key intermediate, $[M(\eta^4\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)]$, **2a**, was isolated and characterized for M = Rh; it reacted smoothly with different electrophiles such as organic halides or carbonyl compounds, giving products (tetramethylrhodocenium complexes) bearing a variety of substituents, such as **3a**–**5a** and **14a**, in 50–70% yields. The iridium complex reacted similarly, but with greater difficulty, to give tetramethyliridocenium cations with side chains (**3b**, **5b**, **7b**, and **14b**), though in rather lower yield. These reactions are broadly similar to ones we have already described for the complexes $[Ir(\eta^5\text{-}C_5Me_5)(CO)(Me)(Ph)]$ and $[Ir(\eta^5\text{-}C_5Me_5)(Me)_4]$.[1,2] Although a number of related reactions have previously been developed,[13] there has been little discussion of mechanisms which, we therefore anticipated, would involve deprotonation followed by nucleophilic substitution at carbon by **2a** or **2b**.

However, such a simplistic view was ruled out by the results of reactions (i) with different bases and (ii) with methyl iodide as electrophile. The sensitivity of the reactions to the nature of the organometallic base used to deprotonate was unexpected; thus, of several tried, potassium *tert*-butoxide was generally the best for the rhodium compounds, while lithium diisopropylamide was better for the iridium analogs. In many cases, no yields at all of the desired products were obtained with other bases. Reaction of chlorotrimethylsilane with the product of deprotonation of the iridium cation by lithium diisopropylamide gave a clean reaction with attack at the C_5Me_5 ring, while addition of the same reagent to the product of deprotonation by *sec*-butyllithium gave a mixture where attack at both the C_5Me_5 and the C_5H_5 rings had occurred.

The differences between **2a** and **2b** in their reactions with methyl iodide were also surprising. Thus, while the iridium species **2b** reacted smoothly with MeI to give one product, **7b**, the rhodium complex **2a** gave a range, $[Rh(C_5H_5)(C_5Me_nEt_{5-n})]^+$ (**7a**, n = 1–5), as well as $[Rh(C_5H_5)(C_5Me_5)]^+$. There seem to have been few other reports of such multiple alkylations, possibly because of the difficulties in separating and characterizing the products, difficulties which have also severely complicated our investigations. Very recently, however, an apparently similar series of products was briefly noted, where polysubstitution appears to have taken place during deprotonation of the 17-electron decamethylferrocenium, and subsequent reaction with an electrophile.[14] This may indicate that odd-electron species generate polysubstitutions, which may in turn suggest that an electron transfer

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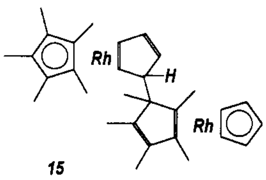
[13] See, for example: Astruc, D. *Acc. Chem. Res.* **1986**, *19*, 377 *Synlett* **1991**, 369; *Top. Curr. Chem.* **1991**, *160*, 47.

[14] Novikova, L N.; Zagorevskii, D V.; Ustynyuk, N A. *J. Organomet. Chem.* **1993**, *460*, C6.

(probably to a 19-electron intermediate) is involved in the reactions discussed here.[15]

It seems likely that the reactions of both the pentamethylrhodocenium and -iridocenium cations **1a** and **1b** with organometallic bases involve electron transfer processes at a key early stage. We have, in a separate investigation, examined the electrochemistry of **1a**,[16] where cyclic voltammetry showed that pentamethylrhodocenium is reduced to the 19-electron Rh(II) radical $[\mathrm{Rh}(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)]$ in a reaction which is reversible only below −35 °C. The radical species is very reactive, and bulk electrolysis at the first plateau potential gave a product in high yield which was characterized as the *dimer* of pentamethylrhodocene, **15**, this was also obtained by reaction of **1a** with excess Na–Hg in THF. However, we have not yet been successful in converting either **2a** into **15** (for example, with $SnBu_3H$) or carrying out the reverse reaction.



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The reduction potentials $[\mathrm{M}(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)]^+/[\mathrm{M}(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)]$, M(III)/M(II), are larger for Ir (−2.03 V) than for Rh (−1.15 V). Thus, if the first stage of the reaction with an organometallic base is an electron transfer, it will be more difficult for Ir than for Rh. A possible scheme for such a process (m′y is the organometallic base; M = Rh or Ir) is

$$[\mathrm{M}(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)]^+ + \mathrm{m'y} \rightarrow [\mathrm{M}(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)] + [\mathrm{m'y}]^+$$

$$[\mathrm{m'y}]^+ \rightarrow \mathrm{m'}^+ + \mathrm{y}^\bullet$$

$$[\mathrm{M}(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)] + \mathrm{y}^\bullet \rightarrow [\mathrm{M}(\eta^5\text{-}C_5Me_4{:}CH_2)(\eta^5\text{-}C_5H_5)] + \mathrm{Hy}$$

or, alternatively, to explain substitution at the Cp ring

$$[\mathrm{M}(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)] + [\mathrm{m'y}]^+ \rightarrow [\mathrm{M}(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_4\mathrm{m'y})] + \mathrm{H}^+$$

The reactions of **2a** (and **2b**) with electrophiles may also involve electron transfer steps,[17] and we have considered a number of possibilities. One is that a radical chain process takes place which involves 19-electron species, e.g., $[\mathrm{Rh^{II}}(C_5Me_4CH_2Me)(C_5H_5)]$, formed as in

$$[\mathrm{Rh^{I}}(C_5Me_4CH_2)(C_5H_5)] + \mathrm{MeI} \rightarrow [\mathrm{Rh^{II}}(C_5Me_4CH_2Me)(C_5H_5)] + \mathrm{I}^\bullet$$

$$[\mathrm{Rh^{II}}(C_5Me_4Et)(C_5H_5)] + \mathrm{I}^\bullet \rightarrow [\mathrm{Rh^{I}}(C_5Me_3Et{:}CH_2)(C_5H_5)] + \mathrm{HI}$$

$$[\mathrm{Rh^{I}}(C_5Me_3Et{:}CH_2)(C_5H_5)] + \mathrm{MeI} \rightarrow [\mathrm{Rh^{II}}(C_5Me_3Et_2)(C_5H_5)] + \mathrm{I}^\bullet$$

$$[\mathrm{Rh^{II}}(C_5Me_3Et_2)(C_5H_5)] + \mathrm{I}^\bullet \rightarrow [\mathrm{Rh^{III}}(C_5Me_3Et_2)(C_5H_5)]^+\mathrm{I}^-$$

However this would imply a stability of the 19-electron rhodocene (Rh(II)) species toward I•, HI, and MeI and of the 18-electron fulvene (Rh(I)) complexes toward HI and I• which is unlikely, based on our working experience.

A variant on this is

$$[\mathrm{Rh^{I}}(C_5Me_4CH_2)(C_5H_5)] + \mathrm{MeI} \rightarrow [\mathrm{Rh^{II}}(C_5Me_4CH_2Me)(C_5H_5)] + \mathrm{I}^\bullet$$

$$[\mathrm{Rh^{II}}(C_5Me_4Et)(C_5H_5)] + \mathrm{MeI} \rightarrow [\mathrm{Rh^{I}}(C_5Me_3Et{:}CH_2)(C_5H_5)] + \mathrm{MeH} + \mathrm{I}^\bullet$$

$$[\mathrm{Rh^{I}}(C_5Me_3Et({:}CH_2))(C_5H_5)] + \mathrm{MeI} \rightarrow [\mathrm{Rh^{II}}(C_5Me_3Et_2)(C_5H_5)] + \mathrm{I}^\bullet$$

$$[\mathrm{Rh^{II}}(C_5Me_3Et_2)(C_5H_5)] + \mathrm{I}^\bullet \rightarrow [\mathrm{Rh^{III}}(C_5Me_3Et_2)(C_5H_5)]^+\mathrm{I}^-$$

or

$$[\mathrm{Rh^{I}}(C_5Me_4CH_2)(C_5H_5)] + \mathrm{MeI} \rightarrow [\mathrm{Rh^{II}}(C_5Me_3({:}CH_2)_2)(C_5H_5)] + \mathrm{MeH} + \mathrm{I}^\bullet$$

$$[\mathrm{Rh^{II}}(C_5Me_3({:}CH_2)_2)(C_5H_5)] + \mathrm{MeI} \rightarrow [\mathrm{Rh^{II}}(C_5Me_3Et({:}CH_2))(C_5H_5)] + \mathrm{I}^\bullet$$

$$[\mathrm{Rh^{II}}(C_5Me_3Et({:}CH_2))(C_5H_5)] + \mathrm{MeI} \rightarrow [\mathrm{Rh^{II}}(C_5Me_3Et_2)(C_5H_5)] + \mathrm{I}^\bullet$$

$$[\mathrm{Rh^{II}}(C_5Me_3Et_2)(C_5H_5)] + \mathrm{I}^\bullet \rightarrow [\mathrm{Rh^{III}}(C_5Me_3Et_2)(C_5H_5)]\mathrm{I}$$

Nineteen electron species and an unusual cleavage of MeI are part of both these processes, and methane should be observed as a stoichiometric byproduct. An examination of the gaseous products from the reaction of **2a** with CD_3I did indeed show that CD_3H and CD_4 were formed, but the yield was minute, only ca. 1% of the total reactants. This appears to rule out any such processes playing a significant role.

One final possibility we have considered is that **2a** (or **2b**) acts as a base, eliminating HI from the alkyl halide. In the case of MeI this would leave methylene, $:CH_2$, which can then insert into C–H bonds in the manner of a carbene,

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[15] We have also checked that $[\mathrm{Rh}(C_5H_5)(C_5Me_nEt_{5-n})]^+$ (**7a**, n = 0–5) do not arise directly from the cationic complexes: separate experiments showed that $[\mathrm{Rh}(C_5H_5)(C_5Me_5)]^+\mathrm{I}^-$ does not react with MeI or with MeI in the presence of I_2. Further, the same mixture **7a**, is obtained in a variety of solvents and in neat methyl iodide itself.

[16] Gusev, O. V.; Denisovich, L. I.; Peterleitner, M. G.; Rubezhov, A. Z.; Ustynyuk, N. A.; Maitlis, P. M. *J. Organomet. Chem.* **1993**, *452*, 219.

[17] Such considerations may underlie the formation of the polyethyl complexes **7a**. Furthermore, the fact that only monosubstituted species are formed with other electrophilic reagents implies that only a monometalated species is initially present; if this were not the case, then other electrophiles ought to give rise to polysubstituted products, too. Aspects of the chemistry of 19-electron radical species have recently been reviewed (Astruc, D. *Acc. Chem. Res.* **1991**, *24*, 36), but rather few of their reactions with electrophiles have so far been investigated.

$$[Rh^{I}(C_5Me_4CH_2)(C_5H_5)] + CH_3I \rightarrow [Rh^{III}(C_5Me_5)(C_5H_5)]I + :CH_2$$

$$[Rh^{I}(C_5Me_4CH_2)(C_5H_5)] + :CH_2 \rightarrow [Rh^{II}(C_5Me_3Et(:CH_2))(C_5H_5)]$$

$$[Rh^{II}(C_5Me_3Et(:CH_2))(C_5H_5)] + CH_3I \rightarrow [Rh^{III}(C_5Me_4Et)(C_5H_5)]I + :CH_2$$

$$[Rh^{III}(C_5Me_4Et)(C_5H_5)]I + :CH_2 \rightarrow [Rh^{III}(C_5Me_3Et_2)(C_5H_5)]I$$

For the reaction of the higher alkyl iodides one would anticipate that loss of HI would yield the olefin

$$[Rh^{I}(C_5Me_4CH_2)(C_5H_5)] + RCH_2CH_2I \rightarrow [Rh^{III}(C_5Me_5)(C_5H_5)]I + RCH{=}CH_2$$

In fact, reaction of the tetramethylfulvene complex with ethyl, isopropyl, or allyl iodide all gave just pentamethylrhodocenium, which is consistent with such a path. On balance, this last proposal seems to be the most consistent with our present results, but more data are needed to probe the problem further.

Experimental Section

All reactions were carried out using standard Schlenk techniques under nitrogen or argon. Tetrahydrofuran (THF), toluene, and diethyl ether were freshly distilled over sodium/benzophenone prior to use. Solutions of lithium diisopropylamide (LDA; 1.5 M in cyclohexane), *sec*-butyllithium (1.2 M in ether), and potassium *tert*-butoxide (solid) were used as supplied by Aldrich. ^1H and ^{13}C NMR spectra were measured on a Bruker AM 250 spectrometer, and IR spectra on a Perkin-Elmer 1600 spectrometer. Microanalyses were carried out by the University of Sheffield Microanalysis Service.

[Rh(η^4-$C_5Me_4CH_2$)(η^5-C_5H_5)] (2a). THF (10 mL) was added to a mixture of solid $[Rh(C_5Me_5)(C_5H_5)]PF_6$ (**1a**, 100 mg, 0.22 mmol) and solid *t*-BuOK (50 mg, 0.45 mmol). The solution became red-brown and was stirred (10 min/20 °C); the solvent was then removed in vacuo and hexane (10 mL) was added, to give a suspension which was stirred (10 min) and then filtered through Hyflo-supercel. Solutions of complex **2a** prepared in this way were used for most of the subsequent reactions. An analytically pure sample of **2a** was obtained by concentrating the solution to 5 mL and cooling to −78 °C. Yield: 43 mg (64%). Anal. Calcd for **2a**, $C_{15}H_{19}Rh$: C, 59.6; H, 6.3. Found: C, 58.8; H, 6.6. IR spectrum (heptane): $\nu(>C{=}CH_2)$ 1607 cm^{-1}. ^1H NMR (C_6D_6): δ 1.50 (s, 2CH_3, 6H), 1.70 (s, 2CH_3, 6H), 3.39 (s, CH_2, 2H), 4.75 (d, C_5H_5, 5H, *J*(RhH) = 1 Hz). ^{13}C NMR (C_6D_6): δ 11.9 (2*C*H_3), 12.8 (2*C*H_3), 69.1 (*C*H_2), 70.4 (d, 2*C*Me, *J*(RhC) 11 Hz), 84.1 (d, C_5H_5, *J*(RhC) 5 Hz), 91.5 (d, 2*C*Me, *J*(RhC) 12 Hz), 94.3 (Me_4C_4*C*$=CH_2$).

Reaction of 2a with $[Fe(C_5H_5)_2]^+PF_6^-$ To Give [Rh(η^5-C_5Me_5)(η^5-C_5H_5)] (1a). The solution of **2a** in THF was added to solid $[Fe(C_5H_5)_2]^+PF_6^-$ (75 mg, 0.22 mmol) by cannula, and the resultant mixture was stirred (2 h/20 °C). The solvent was removed in vacuo, and the solid residue was washed with diethyl ether (3 × 10 mL) and water (5 × 20 mL) and crystallized from CH_2Cl_2/Et_2O (yield 70 mg, 78%) of $[Rh(C_5H_5)(C_5Me_5)]PF_6$, **1a**, identified by ^1H NMR spectroscopy (CD_3COCD_3): δ 2.12 (s, C_5Me_5, 15H), 5.54 (d, C_5H_5, 5H, *J*(RhH) 1 Hz).

Reactions of 2a with XY (XY = $C_6H_5CH_2Br$, $CH_2{=}CHCH_2Br$, or Me_3SiCl). The halide XY (0.50 mmol) was added to a hexane solution of **2a** cooled to 0 °C, and the mixture was stirred (2 h/0 °C) until a colorless solution was obtained (except for $CH_2{=}CHCH_2Br$, which was less reactive and needed 8 h/20 °C). Stirring was continued until the product had fully precipitated; it was then filtered off, washed with Et_2O (3 × 10 mL), dissolved in water (20 mL), filtered, and reacted with a solution of NH_4PF_6 (200 mg in 10 mL of water). The resultant precipitate was filtered off, washed with water (2 × 10 mL), and crystallized from CH_2Cl_2/Et_2O to give $[Rh(C_5H_5)(C_5Me_4CH_2X)]^+PF_6^-$.

[Rh(η^5-$C_5Me_4CH_2CH_2Ph$)(η^5-C_5H_5)]PF_6 (3a). Yield: 84 mg (72%). Anal. Calcd for $C_{22}H_{26}F_6PRh$: C, 49.1; H, 4.9. Found: C, 49.3; H, 4.9. ^1H NMR ($CDCl_3$): δ 1.86 (s, 2CH_3, 6H), 2.11 (s, 2CH_3, 6H), 2.76 (m, CH_2CH_2Ph, 4H), 5.48 (d, C_5H_5, 5H, *J*(RhH) 1 Hz), 6.9–7.3 (m, Ph, 5H). ^{13}C NMR (CD_3COCD_3): δ 10.4 (2*C*H_3), 10.6 (2*C*H_3), 28.1 (CH_2*C*H_2Ph), 36.5 (*C*H_2CH_2Ph), 89.1 (d, C_5H_5, *J*(RhC) 6 Hz), 102.3 (d, *C*Me, *J*(RhC) 8 Hz), 104.5 (d, 2*C*Me, *J*(RhC) 8 Hz), 106.0 (d, 2*C*Me, *J*(RhC) 10.0 Hz); Ph δ 127.2 (CH), 129.3 (2CH), 129.7 (2CH), 141.2 (*C*).

[Rh(C_5H_5)($C_5Me_4CH_2CH_2CH{=}CH_2$)]PF_6 (4a). Yield: 57 mg (53%). Anal. Calcd for $C_{18}H_{24}F_6PRh$: C, 44.3; H, 4.95. Found: C, 44.5; H, 4.85. ^1H NMR ($CDCl_3$): δ 2.11 (s, 2CH_3, 6H), 2.14 (s, 2CH_3, 6H), 2.0–2.2 (m, CH_2*C*$H_2CH{=}CH_2$, 2H), 2.5–2.7 (m, *C*$H_2CH_2CH{=}CH_2$, 2H), 4.9–5.1 (m, $=CH_2$, 2H), 5.52 (d, C_5H_5, 5H, *J*(RhH) 1 Hz), 5.6–5.8 (m, CH_2CH_2*C*$H{=}CH_2$, 1H). ^{13}C NMR (CD_3COCD_3): δ 10.6 (4CH_3), 25.2 ($CH_2CH_2CH{=}CH_2$), 34.8 ($CH_2CH_2CH{=}CH_2$), 89.1 (d, C_5H_5, *J*(RhC) 7 Hz), 102.2 (d, 4*C*Me, *J*(RhC) 8 Hz), 104.0 (*C*Me), 116.4 ($=CH_2$), 137.7 (CH_2CH_2*C*$H{=}CH_2$).

[Rh(C_5H_5)($C_5Me_4CH_2SiMe_3$)]PF_6 (5a). Yield: 64 mg (55%). Anal. Calcd for $C_{18}H_{28}F_6PRhSi$: C, 41.5; H, 5.4. Found: C, 41.5; H, 5.3. ^1H NMR: δ 0.00 (s, $SiMe_3$, 9H), 2.08 (s, CH_2SiMe_3, 2H), 2.12 (s, 2CH_3, 6H), 2.15 (s, 2CH_3, 6H), 5.50 (d, C_5H_5, 5H, *J*(RhH) 1 Hz). ^{13}C NMR: δ −0.9 ($SiMe_3$), 10.6 (2*C*H_3), 11.3 (2*C*H_3), 16.2 (*C*H_2), 88.0 (d, C_5H_5, *J*(RhC) 8 Hz), 99.0 (d, *C*Me, *J*(RhC) 8 Hz), 101.0 (d, 2*C*Me, *J*(RhC) 8 Hz), 107.6 (d, 2*C*Me, *J*(RhC) 7 Hz).

[Rh(C_5H_5)($C_5Me_nEt_{5-n}$)]PF_6 (7a). MeI (20 μL, 0.30 mmol) was added to a hexane solution of **2a** cooled to 0 °C; the reaction was carried out and worked up as described above, to yield, after crystallization from CH_2Cl_2/Et_2O, 61 mg of a mixture of cationic complexes, $[Rh(C_5H_5)(C_5Me_nEt_{5-n})]PF_6$, **7a**. Mass spectrum (+FAB): *m/z* 359 $[Rh(C_5H_5)(C_5MeEt_4)]^+$ (5%), 345 $[Rh(C_5H_5)(C_5Me_2Et_3)]^+$ (24%), 331 $[Rh(C_5H_5)(C_5Me_3Et_2)]^+$ (62%), 317 $[Rh(C_5H_5)(C_5Me_4Et)]^+$ (100%), 303 $[Rh(C_5H_5)(C_5Me_5)]^+$ (35%). ^1H NMR (CD_3COCD_3): δ 1.11 (t, CH_2*C*H_3, 3H), 2.19 (s, 2CH_3, 6H, *J* 7 Hz), 2.21 (s, 2CH_3, 6H), 2.61 (q, *C*H_2CH_3, 2H, *J* 7 Hz), 5.74 (d, C_5H_5, 5H, *J*(RhH) 1 Hz); $[Rh(C_5H_5)(C_5Me_4Et)]^+PF_6^-$. Other signals: δ 1.12 (t, *J* 7 Hz), 1.16 (t, *J* 7 Hz), 2.20 (s), 2.22 (s), 2.27 (s), 2.29 (s), 2.58 (q, *J* 7 Hz), 2.64 (q, *J* 7 Hz), 5.75 (d, *J*(RhH) 1 Hz), 5.78 (d, *J*(RhH) 1 Hz), 5.79 (d, *J*(RhH) 1 Hz).

[{($C_5Me_4CH_2CH_2Ph$)$RhCl_2$}$_2$] (6a). Lithium phenyl (0.5 mL of a 1.8 M solution in cyclohexane/ether) was added to a suspension of $[Rh(C_5H_5)(C_5Me_4CH_2CH_2Ph)]PF_6$ (**3a**, 135 mg, 0.25 mmol) in Et_2O (10 mL), and the mixture was stirred (0.5 h/20 °C). Water (0.5 mL) was then added, the solution was filtered, and a stream of HCl gas was passed through this solution (5 min). Workup gave $[\{(C_5Me_4CH_2CH_2Ph)RhCl_2\}_2]$, **6a**; yield 45 mg (45%). Anal. Calcd for $C_{34}H_{42}Cl_4Rh_2$: C, 51.15; H, 5.3; Cl, 25.8. Found: C, 50.6; H, 5.1; Cl, 18.3. ^1H NMR ($CDCl_3$): δ 1.35 (s, 2CH_3, 6H), 1.54 (s, 2CH_3, 6H), 2.5–2.8 (m, CH_2CH_2Ph, 4H), 6.8–7.2 (m, Ph, 5H).

[Rh(η^5-$C_5Me_4CH_2Cl$)(η^5-C_5H_5)]PF_6 (9a). A slow stream of chlorine gas was passed through a solution of **2a** in hexane (5 min). A yellow solid precipitated immediately, which was filtered off, washed (Et_2O; 3 × 10 mL) and dissolved in water (20 mL). After addition of NH_4PF_6 and crystallization this gave 56 mg (53%) of **9a**. Anal. Calcd for $C_{15}H_{19}ClF_6PRh$: C, 37.3; H, 4.0; Cl, 7.3. Found: C, 37.4; H, 4.0; Cl, 7.6. ^1H NMR (CD_3COCD_3): δ 2.26 (s, 2CH_3, 6H), 2.28 (s, 2CH_3, 6H), 4.79 (s, CH_2Cl, 2H), 5.83 (d, C_5H_5, 5H, *J*(RhH) 1Hz). ^{13}C NMR (CD_3COCD_3): δ 10.2 (2*C*H_3), 10.6 (2*C*H_3), 36.2 (*C*H_2), 89.6 (d, C_5H_5, *J*(RhC) 7 Hz), 97.0 (d, *C*Me, *J*(RhC) 12 Hz), 102.5 (d, 2*C*Me, *J*(RhC) 7 Hz), 104.3 (d, 2*C*Me, *J*(RhC) 7 Hz).

$\mathrm{[Rh(\eta^5\text{-}C_5Me_4CH_2I)(\eta^5\text{-}C_5H_5)]I_3}$ (10a). A solution of iodine (114 mg, 0.45 mmol) in hexane (30 mL) was added to a hexane solution of **2a** at −78 °C. The dark yellow-brown solid which precipitated was filtered off, washed with $\mathrm{Et_2O}$ and water, and crystallized from $\mathrm{CH_2Cl_2/Et_2O}$ to give **10a** (108 mg, 60%). Anal. Calcd for $\mathrm{C_{15}H_{19}I_4Rh}$: C, 22.25; H, 2.4; I, 62.7. Found: C, 22.5; H, 2.25; I, 62.4. ^{1}H NMR ($\mathrm{CD_3COCD_3}$): δ 2.22 (s, 2$\mathrm{CH_3}$, 6H), 2.27 (s, 2$\mathrm{CH_3}$, 6H), 4.54 (s, $\mathrm{CH_2I}$), 5.83 (d, $\mathrm{C_5H_5}$, 5H, *J*(RhH) 1 Hz). ^{13}C NMR ($\mathrm{CD_3COCD_3}$): δ 10.6 (2*C*$\mathrm{H_3}$), 10.9 (2*C*$\mathrm{H_3}$), 30.5 (*C*$\mathrm{H_2}$), 89.6 (d, *C*$_5$H$_5$, *J*(RhC) 7 Hz), 99.5 (d, *C*Me, *J*(RhC) 10 Hz), 101.9 (d, 2*C*Me, *J*(RhC) 7 Hz), 103.8 (d, 2*C*Me, *J*(RhC) 7 Hz).

$\mathrm{[Rh(\eta^5\text{-}C_5Me_4CH_2CO_2)(\eta^5\text{-}C_5H_5)]}$ (11a). A stream of dry $\mathrm{CO_2}$ was passed through a hexane solution of **2a** (5 min/20 °C). The pale yellow precipitate was filtered off, washed with $\mathrm{Et_2O}$, and crystallized from $\mathrm{CH_2Cl_2/Et_2O}$ to give 40 mg of a mixture of $\mathrm{[Rh(C_5H_5)(C_5Me_5)]^+}$, **1a**, and $\mathrm{[Rh(C_5H_5)\{C_5Me_4(CH_2CO_2)\}]}$, **11a**, ratio 1.0:1.2 by ^{1}H NMR spectroscopy. IR, $\nu(\mathrm{CO_2})$ ($\mathrm{CH_2Cl_2}$): 1608 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.88 (s, 2$\mathrm{CH_3}$, 6H), 2.00 (s, 2$\mathrm{CH_3}$, 6H), 3.12 (s, $\mathrm{CH_2CO_2}$), 5.22 (d, 5H, *J*(RhH) 1 Hz; $\mathrm{[Rh(C_5}\mathit{H}_5\mathrm{)\{C_5Me_4(CH_2CO_2)\}]}$), 1.95 (s, $\mathrm{C_5Me_5}$, 15H), 5.44 (d, 5H, *J*(RhH) 1 Hz; $\mathrm{[Rh(C_5}\mathit{H}_5\mathrm{)(C_5Me_5)]^+}$).

$\mathrm{[Rh(\eta^5\text{-}C_5Me_4CH_2CO_2Me)(\eta^5\text{-}C_5H_5)]PF_6}$ (12a). A stream of dry $\mathrm{CO_2}$ was passed through a hexane solution of **2a** (5 min/20 °C); after removal of volatiles, the residue was dissolved in $\mathrm{CH_2Cl_2}$ (10 mL) and MeI (500 μL) added. The solution was stirred, $\mathrm{Et_2O}$ added, and the precipitate filtered off, which, after treatment with a solution of $\mathrm{NH_4PF_6}$ gave $\mathrm{[Rh(C_5H_5)\{C_5Me_4(CH_2CO_2Me)\}]PF_6}$, **12a**, crystallized from $\mathrm{CH_2Cl_2/Et_2O}$ (yield 56 mg, 50%). Anal. Calcd for $\mathrm{C_{17}H_{22}F_6O_2PRh}$: C, 40.3; H, 4.4. Found: C, 40.3; H, 4.2. IR $\nu(\mathrm{CO_2})$ ($\mathrm{CH_2Cl_2}$): 1740 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.11 (s, 2$\mathrm{CH_3}$, 6H), 2.16 (s, 2$\mathrm{CH_3}$, 6H), 3.57 (s, $\mathrm{CH_2CO_2Me}$, 2H), 3.70 (s, $\mathrm{CO_2CH_3}$, 3H), 5.55 (d, $\mathrm{C_5H_5}$, 5H, *J*(RhH) 1 Hz). ^{13}C NMR ($\mathrm{CD_3COCD_3}$): δ 10.5 (2*C*$\mathrm{H_3}$), 10.6 (2*C*$\mathrm{H_3}$), 28.8 (*C*$\mathrm{H_2}$), 52.5 ($\mathrm{CO_2}$*C*$\mathrm{H_3}$), 89.4 (d, *C*$_5$H$_5$, *J*(RhC) 7 Hz), 98.0 (d, *C*Me, *J*(RhC) 14 Hz), 103.1 (d, 2*C*Me, *J*(RhC) 8 Hz), 103.4 (d, 2*C*Me, *J*(RhC) 7 Hz), 169.9 (*C*$\mathrm{O_2}$Me).

Reaction of Complex 2a with $\mathrm{H_2O}$. Water (50 μL, 2.78 mmol) was added to a solution of **2a** in hexane. The mixture was stirred at room temperature, and the precipitate was filtered off, washed with ether, and crystallized from $\mathrm{CH_2Cl_2/Et_2O}$. Yield: 47 mg. Anal. Calcd for $\mathrm{C_{15}H_{21}ORh\cdot 2H_2O}$: C, 50.6; H, 7.1. Found: C, 50.9; H, 6.0. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.52 (broad s, $\mathrm{H_2O}$, large), 2.16 (s, 5Me, 15H), 5.70 (d, $\mathrm{C_5H_5}$, 5H, *J*(RhH) 1 Hz). Reaction with $\mathrm{KPF_6}$ gave **1a** as the hexafluorophosphate (87% yield).

$\mathrm{[Rh(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_5CCl_3)]}$ (13a). Chloroform (500 μL) was added to a solution of **2a** in hexane and the mixture was stirred (2 h/20 °C) to give a yellow solution. This was filtered, concentrated to 5 mL, and cooled to −80 °C, to give bright yellow crystals of **13a** (62 mg, 67%). Anal. Calcd for $\mathrm{C_{16}H_{20}Cl_3Rh}$: C, 45.6; H, 4.8. Found: C, 45.5; H, 4.8. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.74 (s, $\mathrm{C_5Me_5}$, 15H), 3.04 (m, 2H), 3.91 (t, $\mathrm{>C(H)CCl_3}$, 1H, *J* 3 Hz), 4.61 (m, 2H). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 10.9 ($\mathrm{C_5}\mathit{Me}_5$), 44.7 (d, 2*C*H, *J*(RhC) 12 Hz), 71.9 (d, >*C*$\mathrm{HCCl_3}$, *J*(RhC) 5 Hz), 75.3 (d, 2*C*H, *J*(RhC) 7 Hz), 94.8 (d, *C*$_5$Me$_5$, *J*(RhC) 6 Hz), 105.9 ($\mathrm{CCl_3}$).

$\mathrm{[(C_5Me_5)Ir(C_5H_5)][PF_6]}$ (1b). White crystals of $\mathrm{[Ir(C_5Me_5)(C_5H_5)]PF_6}$, (yield 1.10 g, 81%; ^{1}H NMR ($\mathrm{CD_3COCD_3}$) δ 5.78 (s, $\mathrm{C_5H_5}$), 2.30 (s, $\mathrm{C_5Me_5}$); mass spectrum (+FAB): *m*/*z* 393 $\mathrm{[Ir(C_5Me_5)(C_5H_5)]^+}$) were made from freshly distilled cyclopentadiene (4.36 g, 33 mmol), and $\mathrm{[\{(C_5Me_5)IrCl_2\}_2]}$ (1.0 g, 1.255 mmol) as previously described.[18]

$\mathrm{[Ir\{C_5Me_4(CH_2SiMe_3)\}(C_5H_5)]PF_6}$ (5b). A solution of lithium diisopropylamide (1.5 M in cyclohexane; 220 μL, 0.330 mmol; ratio Ir:LDA = 1.2) was added to a suspension of $\mathrm{[Ir(C_5Me_5)(C_5H_5)]PF_6}$ (**1b**, 0.145 g, 0.275 mmol) in dry THF (20 mL) at −70 °C. The white suspension slowly dissolved to a clear lemon yellow solution (30 min/−70 °C). On addition of $\mathrm{ClSiMe_3}$ (85 μL, 660 mmol, ratio Ir:$\mathrm{ClSiMe_3}$ = 1:2.5) the yellow solution turned colorless (5 min/−70 °C). After warming to room temperature, the solvent was removed in vacuo and the residue was converted into the hexafluorophosphate and crystallized from $\mathrm{Cl_2CH_2}$/diethyl ether to yield cream colored needles of $\mathrm{[Ir(C_5Me_4(CH_2SiMe_3))(C_5H_5)]PF_6}$, **5b** (yield 94 mg, 56%). Anal. Calcd for $\mathrm{C_{18}H_{28}F_6IrPSi}$: C, 35.5; H, 4.6. Found: C, 35.3; H, 4.4. ^{1}H NMR spectrum ($\mathrm{CD_3COCD_3}$), δ: 5.73 (s, $\mathrm{C_5H_5}$); 2.32, 2.31 (2 × s, 2 × Me, $\mathrm{C_5Me_4}$); 2.22 (s, 2H, $\mathrm{CH_2}$); 0.05 (s, 9H, $\mathrm{SiMe_3}$). ^{13}C NMR (acetone-*d*$_6$), δ: 102 (s, $\mathrm{C_{3,4}}$ $\mathrm{C_5Me_4R}$); 95.3 (s, $\mathrm{C_{2,5}}$, $\mathrm{C_5Me_4R}$); 93.5 (s, $\mathrm{C_{3,4}}$, $\mathrm{C_5Me_4R}$); 81.8 (s, $\mathrm{C_5H_5}$); 15.5 (s, $\mathrm{CH_2}$–Si); 11.4, 10.5 (s, $\mathrm{C_5Me_4R}$), −0.8 (s, $\mathrm{Si(CH_3)_3}$). Mass spectrum (+FAB): *m*/*z* 465 $\mathrm{[Ir(C_5Me_4SiMe_3)(C_5H_5)]^+}$.

$\mathrm{[Ir(C_5Me_4(CH_2CH_3))(C_5H_5)][PF_6]}$ (7b). This was made in the same way as above, from **1b** (140 mg, 0.260 mmol) and methyl iodide (65 μL, 1.04 mmol, ratio Ir:MeI = 1.4). After workup the product was crystallized from $\mathrm{CH_2Cl_2/Et_2O}$ as white crystals of $\mathrm{[Ir(C_5Me_4Et)(C_5H_5)]PF_6}$, **7b** (yield 71 mg, 49%). Anal. Calcd for $\mathrm{C_{16}H_{22}F_6IrP}$: C, 35.0; H, 3.85. Found: C, 34.8; H, 4.0. ^{1}H NMR, δ ($\mathrm{CD_3COCD_3}$): 5.79 (s, 5H, $\mathrm{C_5H_5}$), 2.58 (quartet, 2H, $\mathrm{CH_2CH_3}$, *J* 8 Hz); 2.30 (s, 12H, $\mathrm{C_5Me_4R}$), 1.12 (t, 3H (*J* 8 Hz), $\mathrm{CH_3CH_2}$). Mass spectrum (EI): *m*/*z* 421 and 435 $\mathrm{[(C_5Me_4Et)Ir(C_5H_5)]^+}$, 435 $\mathrm{[(C_5Me_3Et_2)Ir(C_5H_5)]^+}$. Mass spectrum (+FAB): *m*/*z* = 407 (base peak, $\mathrm{[(C_5Me_4Et)Ir(C_5Me_5)]^+}$).

$\mathrm{[Ir(C_5Me_4CH_2CH_2Ph)(C_5H_5)]PF_6}$ (3b). This was prepared similarly in 23% yield. Anal. Calcd for $\mathrm{C_{22}H_{26}F_6IrP}$: C, 42.1; H, 4.2. Found: C, 41.1; H, 3.9. ^{1}H NMR ($\mathrm{CD_3COCD_3}$): δ 7.23 (m, $\mathrm{C_5}\mathit{H}_5$), 5.78 (s, 5H, $\mathrm{C_5}\mathit{H}_5$), 2.84 (m), 2.29 (s, 6H, $\mathrm{C_5}\mathit{Me}_4\mathrm{R}$), 2.14 (s, 6H, $\mathrm{C_5}\mathit{Me}_4\mathrm{R}$). ^{13}C NMR, δ (acetone-*d*$_6$): 141.2 (s, $\mathrm{C_{ipso}}$, Ph), 129.6 (s, $\mathrm{C_{meta}}$, Ph), 129.2 (s, $\mathrm{C_{ortho}}$, Ph), 127.1 (s, $\mathrm{C_{para}}$, Ph), 97.8 (s, $\mathrm{C_1}$, $\mathrm{C_5Me_4R}$); 96.1 (s, $\mathrm{C_{2.5}}$, $\mathrm{C_5Me_4R}$), 95.5 (s, $\mathrm{C_{3,4}}$, $\mathrm{C_5Me_4R}$), 81.8 (s, $\mathrm{C_5H_5}$), 36.7 (s, $\mathrm{CH_2}$–Ph); 28.0 (s, $\mathrm{CH_2}$–$\mathrm{CH_2}$), 10.4, 10.2 (s, $\mathrm{C_5Me_4R}$).

$\mathrm{[Rh\{C_5Me_4(CH_2CPh_2OH)\}(C_5H_5)]PF_6}$ (14a). This complex was made from benzophenone (73 mg, 0.4 mmol), complex **1a** (205 mg, 0.38 mmol) in THF (3 mL), and LDA (0.32 mmol) in cyclohexane (at −45 °C). The crude product was dissolved in a mixture of saturated aqueous $\mathrm{NH_4Cl}$, EtOH, and acetone (ratio 2:3:5; 20 mL), and chromatographed on silica gel (60/0.040–0.063 mm/9385, Merck) as a chloride. After addition of a solution of $\mathrm{NH_4PF_6}$ the precipitate was crystallized several times, to yield 40 mg (28%) of complex **14a**. Anal. Calcd for $\mathrm{C_{28}H_{30}F_6OPRh}$: C, 53.35; H, 4.8. Found: C, 52.95; H, 5.1. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 1.59 (s, 6H, 2 $\mathrm{CH_3}$), 2.07 (s, 6H, 2 $\mathrm{CH_3}$), 2.35 (s, 1H, OH), 3.49 (s, 2H, $\mathrm{CH_2}$), 5.44 (d, $\mathrm{C_5H_5}$, *J*(H–Rh) 1 Hz), 7.29 (m, 10H, 2Ph). Mass spectrum (+FAB): *m*/*z* 485 (100%) [M − $\mathrm{PF_6}$]. IR ν(OH): 3590 cm^{-1}.

$\mathrm{[Ir\{C_5Me_4(CH_2CPh_2OH)\}(C_5H_5)]PF_6}$ (14b). This complex was prepared similarly from benzophenone (278 mg, 1.53 mmol), complex **1b** (205 mg, 0.38 mmol) in THF (20 mL), and LDA (0.73 mmol) in cyclohexane (at −70 °C), yield: 129 mg (47%). Anal. Calcd for $\mathrm{C_{28}H_{30}F_6IrOP}$: C, 47.45; H, 4.2. Found: C, 46.7; H, 4.2. Mass spectrum (+FAB): *m*/*z* 575 $\mathrm{[(C_5Me_4CH_2CPh_2OH)Ir(C_5H_5)]^+}$ (base peak). ^{1}H NMR (acetone-*d*$_6$): δ 7.37 (m, 4H, $\mathrm{C_6}\mathit{H}_5$), 7.28 (m, 6H, $\mathrm{C_6}\mathit{H}_5$), 5.77 (s, 5H, $\mathrm{C_5}\mathit{H}_5$), 4.90 (s, 1H, O*H*), 3.66 (s, 2H, CH_2–R), 2.25 (s, 6H, $\mathrm{C_5}\mathit{Me}_4\mathrm{R}$), 1.94 (s, 6H, $\mathrm{C_5}\mathit{Me}_4\mathrm{R}$). ^{13}C NMR (acetone-*d*$_6$): δ 147.8 ($\mathrm{C_{ipso}}$, Ph), 128.6 (s, $\mathrm{C_{meta}}$, Ph), 127.8 (s, $\mathrm{C_{para}}$, Ph), 127.7 (s, $\mathrm{C_{ortho}}$, Ph), 96.9 (s, $\mathrm{C_{2,5}}$, $\mathrm{C_5Me_4R}$), 96.5 (s, $\mathrm{C_1}$, $\mathrm{C_5Me_5}$), 96.2 (s, $\mathrm{C_{3,4}}$, $\mathrm{C_5Me_4R}$), 81.8 (s, *C*$_5$H$_5$), 79.7 (s, *C*$\mathrm{Ph_2(OH)}$), 39.0 (s, $\mathrm{CH_2}$–R), 11.4, 10.4 (s, $\mathrm{C_5}\mathit{Me}_4\mathrm{R}$).

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