Mono- and Bis(pentaisopropylcyclopentadienyl) Cobalt and Rhodium Sandwich Complexes and Other Decabranched Cyclopentadienyl Complexes

Dirk Buchholz, Bruno Gloaguen, Jean-Luc Fillaut, Michel Cotrait, and Didier Astruc*

Dedicated to Professor Henri Brunner on the occasion of his 60th birthday

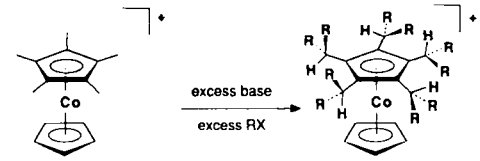
Abstract: The acidity of methyl protons in the 18-electron cationic complexes $[MCp^*Cp]^+PF_6^-$ and $[MCp_2^*]^+PF_6^-$ (M = Co or Rh, Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5) has been used for novel syntheses of starburst organometallic complexes. $[CoCp^*Cp]^+PF_6^-$ was deprotonated at $-30\,^\circ C$ with Si_2Me_6NK (1 equiv) in THF to give the fulvene complex $[Co^ICp(\eta^4$-$C_5Me_4CH_2)]$. This was not stable at $20\,^\circ C$, but was characterized by ^1H and ^{13}C NMR at $-30\,^\circ C$. The complexes $[MCp^*Cp]^+PF_6^-$ (M = Co or Rh) reacted with excess base (KOH or *t*BuOK) and alkyl halides (RX = CH_3I, C_2H_5I, CH_2=$CHCH_2Br$, or $PhCH_2Br$) to give decasubstituted complexes (i.e., two hydrogens of each methyl group are replaced by two R groups). Distinct *endo* and *exo* alkyl groups are observed in the new complexes by NMR at room temperature. Coalescence occurs at higher temperatures; this indicates that the bulky alkyl groups are rotating. The calculated activation parameters ($\Delta G^\ddagger$) are 71.3 ± 0.8, 70.3 ± 0.8, and $81.0\pm0.8\,kJ\,mol^{-1}$ for $[Co(C_5iPr_5)Cp]^+PF_6^-$, $[Rh(C_5iPr_5)$-$Cp]^+PF_6^-$ (in $C_6D_5NO_2$), and $[Co\{C_5$-$(CHEt_2)_5\}Cp]^+PF_6^-$ (in *o*-$C_6H_4Cl_2$), respectively. The single directionality of these ligands is confirmed by the X-ray crystal structure of $[Co(C_5iPr_5)Cp]^+PF_6^-$. This structure clearly shows the "paddle wheel" conformation adopted in the C_5iPr_5 ligand, due to steric hindrance between adjacent isopropyl groups and the staggered conformation of the two rings. The relative E° values measured by cyclic voltammetry show that the electron-donating properties of the new $C_5(CHR_2)_5$ ligand are between those of C_5H_5 and C_5Me_5. With the decamethylcobalticinium salt $[CoCp_2^*]^+PF_6^-$, the permethylation reactions with base and CH_3I did not go to completion, even under forcing conditions and with repeated reaction (the maximum number of methyl groups introduced was 14). On the other hand, $[RhCp_2^*]^+PF_6^-$, in which the distance between rings is larger than in the Co analogue, reacted with excess KOH and CH_3I to give $[Rh(C_5iPr_5)_2]^+PF_6^-$ in 55% yield; only one diastereoisomer was detected by NMR ($\Delta G^\ddagger = 85.5\pm0.8\,kJ\,mol^{-1}$ in $C_6D_5NO_2$). The C_5iPr_5 sandwich complexes are extremely robust, even at the 19-electron (Co^{II}) stage. The 20-electron K^+ salt of the Co^I anion was regiospecifically protonated by H_2O at the Cp ligand to give $[Co(C_5iPr_5)(\eta^4$-$C_5H_6)]$ and was decomplexed at $190\,^\circ C$ to $K^+(C_5iPr_5)^-$.

Keywords
cobalt compounds · cyclopentadienyl ligands · metallocenes · peralkylations · rhodium compounds

Introduction

The pentamethylcyclopentadienyl (Cp*) ligand has occupied a central position in organometallic chemistry and catalysis for the last fifteen years, since it has become easily available.[1-3] A number of other interesting pentasubstituted cyclopentadienyl ligands C_5R_5 are also known.[4-7] Metallocenes pose specific problems with respect to their chirality[8] and have proven valuable in material sciences[9, 10] and catalysis.[11] We envisaged using the common Cp* ligand as a starting point for the direct synthesis of polysubstituted bulky ligands by reaction with an excess of base and an alkyl halide. We reported in preliminary communications that two of the hydrogens on each methyl group could be substituted by alkyl groups in one-pot reactions of metallicinium complexes $[MCp^*Cp]^+$ (M = Co and Rh) to give pentaisopropylcyclopentadienyl cobalt and rhodium complexes and longer decabranched Cp analogues (Scheme 1).[12] The reaction consists of the deprotonation of a methyl substituent activated by the cationic $CoCp^+$ moiety and subsequent alkylation of the exocyclic methylene; this deprotonation–alky-

[*] Prof. D. Astruc, Dr. D. Buchholz, Dr. B. Gloaguen, Dr. J.-L. Fillaut
Laboratoire de Chimie Organique et Organométallique
URA CNRS N°35, Université Bordeaux I
351, cours de la Libération, F-33405 Talence Cédex (France)
Telefax: Int. code +(33) 5684 6646
e-mail: astruc@cribx1.u-bordeaux.fr
M. Cotrait
Laboratoire de Cristallographie et Physique Cristalline
ERS CNRS N°133, Université Bordeaux I



Scheme 1. Peralkylation of $[CoCp^*Cp]^+$ (R = CH_3, C_2H_5, CH_2=$CHCH_2$, or $PhCH_2$).

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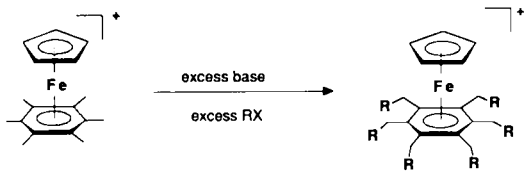
lation sequence is then repeated in situ until steric bulk inhibits further reaction.[13, 14] This starburst reaction[15–23] is an extension of the $FeCp^+$-induced hexaalkylation of hexamethylbenzene (Scheme 2)[24, 25] to organocobalt chemistry. The major difference between C_5-ring and C_6-ring chemistry is that the latter leads to monosubstitution at each methyl group (except with allyl),[22] whereas the former consistently leads to disubstitution, as will be shown here.



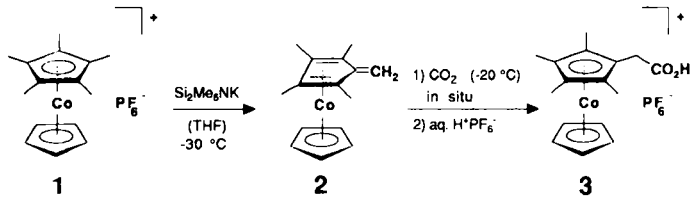
Scheme 2. Hexaalkylation of $[FeCp(C_6Me_6)]^+$ (R = alkyl, e.g., CH_3; CH_2Ph).

In addition to being novel, the decasubstituted cyclopentadienyl (Cp) ligands form complexes that show a remarkable directionality;[26] this is even true of pentaisopropyl Cp. The peralkylation and perfunctionalization reactions thus provide an original route to new chiral molecules and to organometallic molecular "trees".[16, 17] In this paper, we report the details of the permethylation, perethylation, perallylation, and perbenzylation of $[CoCp^*Cp]^+PF_6^-$. The X-ray crystal structure of the 1,2,3,4,5-pentaisopropylcobalticinium salt and the extension of the permethylation reaction to complexes of other metals, in particular to cationic rhodium sandwich complexes, are discussed. We address the problems of permethylating 18-electron cationic decamethyl sandwich complexes, the mechanism involving fulvene complexes, and the decomplexation of the pentaisopropyl Cp ligand. Independently of our work, Sitzman has published the synthesis and characterization of $[Mo(C_5iPr_5)(CO)_3CH_3]$, the only other organometallic complex known to contain this ligand.[27] Interesting features of the $C_5iPr_5^{\cdot}$ radical have also been reported [Eq. (1)].[28, 29]

$$C_5iPr_5^-Li^+ \xrightarrow{FeCl_2} C_5iPr_5^{\cdot} \quad (1)$$

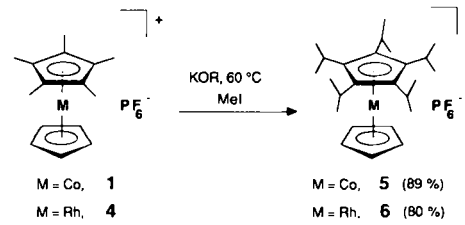
Results and Discussion

1. Acidity of pentamethylcobalticinium hexafluorophosphate (1): Cobalticinium complex **1** is readily available by the Kölle method.[30] It could be deprotonated at low temperature with 1 equiv *t*BuOK or Me_6Si_2NK in THF to give a red, neutral complex **2** (Scheme 3). However, this complex was not stable at room temperature. Deprotonation at −30 °C (Me_6Si_2NK), evaporation of the solvent at this temperature, and subsequent dissolution in $[D_8]$toluene allowed the characterization of the tetramethylfulvene Co^I complex **2** by ^1H and ^{13}C NMR. A singlet is observed for the exocyclic methylene protons at $\delta = 3.6$ and a ^{13}C signal at $\delta = 68.2$ appears as a triplet in the off-resonance spectrum. The ^1H signal at $\delta = 4.41$, attributed to the C_5H_5 ring, is at higher field ($\Delta\delta = 0.7$ ppm) than the corresponding signal for the cationic species **1**. This also suggests that a neutral tetramethylfulvene complex is formed by deprotonation of the cobalt sandwich. This deprotonation reaction is analogous to the long-known deprotonation of $[FeCp(C_6Me_6)]^+PF_6^-$ to give $[FeCp\{\eta^5\text{-}(C_6Me_5CH_2)\}]$.[31] More recently, analogous deprotonations of $[Mn(C_6Me_6)(CO)_3]^+$[32] and $[IrCp^*Cp]^+$[33] complexes have been reported. Reaction of **2** with CO_2 yielded the acid **3**.[34] This reaction shows the nucleophilic properties of **2**.



Scheme 3. Acidity of **1**.

2. Decamethylation of $[MCp^*Cp]^+PF_6^-$ (M = Co or Rh): The complex **1** and its rhodium analogue **4**[35] reacted with excess (20 equiv) *t*BuOK and CH_3I in THF at 60 °C for 14 h to give pure 1,2,3,4,5-pentaisopropylmetallicinium hexafluorophosphates **5** and **6**, respectively, as indicated by the ^1H NMR spectra of the reaction products (Scheme 4). The complex **5** was recrystallized from acetone/alcohol (1/1) to give yellow crystals in 81% yield. It should be noted that *t*BuOK reacts faster with CH_3I than with **1** or **4** at room temperature; however, at 60 °C, the opposite is true. Slow addition of CH_3I at 60 °C gave efficient permethylation. In an alternative procedure, powdered KOH and DME (1,2-dimethoxyethane) were used; this prevented the side reaction from competing. The latter procedure was found to be more straightforward, and high yields of **5** (89%) and **6** (80%) were obtained.



Scheme 4. Decamethylation of $[MCp^*Cp]^+$ (R = H or *t*Bu).

Crystals of **5**, obtained as indicated above, allowed the determination of the X-ray crystal structure. The *x/a*, *y/b*, *z/c* fractional coordinates and the B_{eq} (Å^2) factors are given in ref. [58]. The SNOOPI representation[36] of complex **5** is shown in Figure 1 (middle). The projection of the structure on the *yz* plane is shown in Figure 1 (bottom). The main characteristics of the structure are summarized in Table 1 and selected bonds and angles are given in Table 2. The most important feature is that the five isopropyl groups in the C_5iPr_5 radical are oriented in the same direction in a "paddle wheel" type arrangement.[28] This is illustrated by the fact that the internal C-C-C angles such as C(21)-C(11)-C(12) are close to 130°, whereas the external C-C-C angles such as C(21)-C(11)-C(15) are close to 120°. This feature is attributed to the steric hindrance between adjacent isopropyl groups. The two Cp rings are also staggered in order to minimize contact between the methyl groups and the C–H bonds of the unsubstituted Cp. Moreover, the atoms C(21)–C(25) are 0.15 Å above the mean C_5iPr_5 plane; the C–*i*Pr bonds are bent away from cobalt. The cobalt atom and the centroids of the two five-membered rings lie in a straight line; the distance to the substituted Cp is slightly larger (1.684(2) Å) than to the unsubstituted Cp (1.656(2) Å). The cyclopentadienyl rings are perfectly parallel to each other and separated by 3.34 Å.

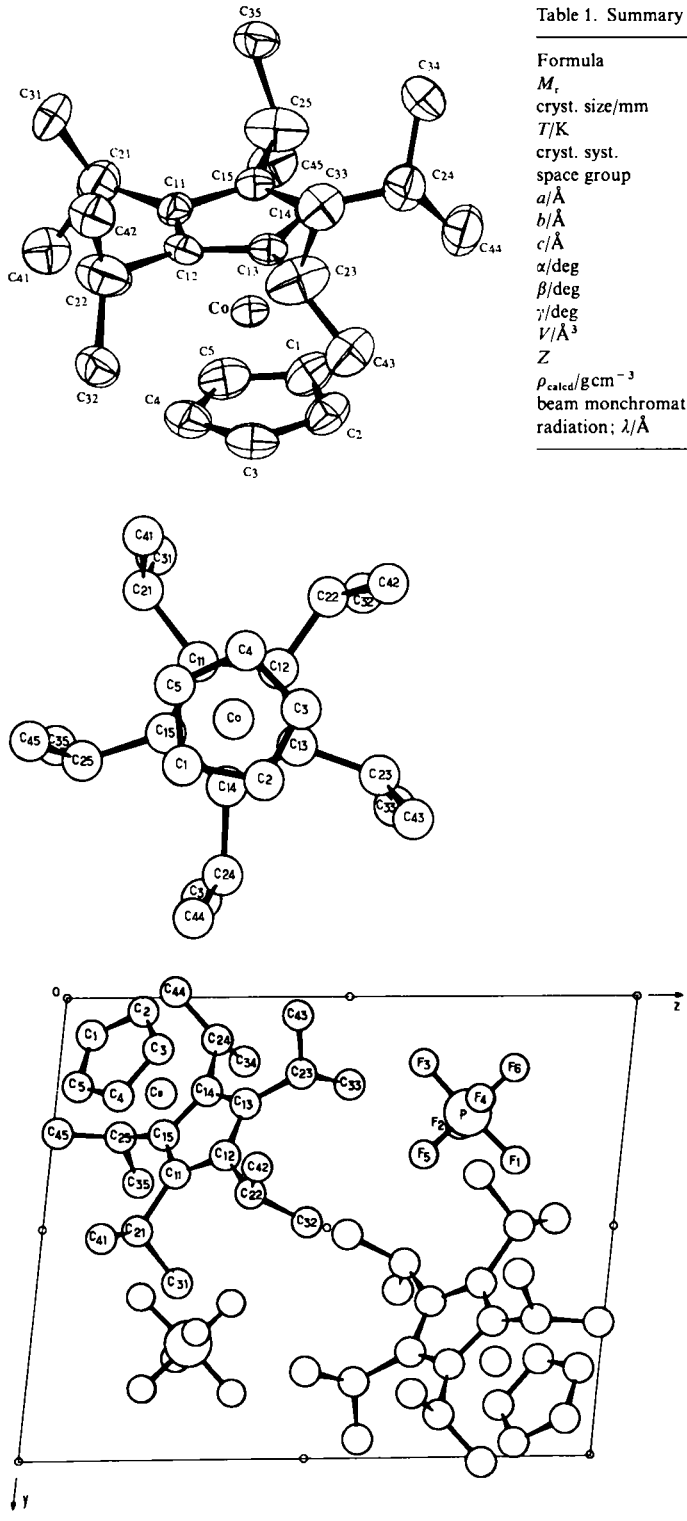


Fig. 1. Crystal structure of **5**. Top: perspective view (thermal ellipsoids at the 50% probability level); middle: top view (SNOOPI drawing); and bottom: projection of the unit cell on the *yz* plane along the *x* axis.

Table 1. Summary of crystal data of **5**.

Formula	$C_{25}H_{40}Co^+PF_6^-$	abs. coeff./cm^{-1}	63.9
M_r	544.5	$F(000)$	560
cryst. size/mm	0.2 × 0.3 × 0.6	scan type	$\omega-2\theta$
T/K	293	range/deg	1–65
cryst. syst.	triclinic	scan width/deg	1.2 + 0.14 tanθ
space group	(no. 2)	detector aperture/mm	1.6 + 1.7 tanθ
a/Å	9.536 (1)	index ranges	$0\le h\le 11$, $-12\le k\le 12$,
b/Å	10.802 (1)		$-15\le l\le 15$
c/Å	13.230 (1)	no. of reflns collected	4431
α/deg	95.670 (6)	no. of reflns observed	2444
β/deg	100.692 (5)	criterion for observed reflns	$I>3\sigma(I)$
γ/deg	93.256 (5)	no. of refined parameters	361
V/Å^3	1328.5	refinement method	full-matrix least-squares on F
Z	2	R	0.068
ρ_{calcd}/gcm^{-3}	1.361	Rw	0.074
beam monchromator	graphite	goodness-of-fit on F	1.45
radiation; λ/Å	$Cu_{K\alpha}$; 1.54178	weighting scheme w	1.0 $(\sigma(F)^2 + 0.00432F^2)$

Table 2. Selected bond lengths (Å) and angles (°) of **5** (standard deviations in parentheses [a]).

Co–C1	2.06(1)	C11–C21	1.54(1)
Co–C2	2.07(1)	C12–C22	1.54(1)
Co–C3	2.05(1)	C13–C23	1.52(1)
Co–C4	2.05(1)	C14–C24	1.51(1)
Co–C5	2.04(1)	C15–C25	1.51(1)
Co–C11	2.050(8)	C21–C31	1.51(2)
Co–C12	2.044(8)	C22–C32	1.50(2)
Co–C13	2.046(8)	C23–C33	1.49(2)
Co–C14	2.040(8)	C24–C34	1.48(2)
Co–C15	2.048(8)	C25–C35	1.47(2)
C1–C2	1.45(1)	C21–C41	1.48(2)
C1–C5	1.39(1)	C22–C42	1.51(2)
C2–C3	1.40(1)	C23–C43	1.43(2)
C3–C4	1.40(1)	C24–C44	1.48(2)
C4–C5	1.39(1)	C25–C45	1.45(2)
C11–C12	1.43(1)	P–F1	1.54(1)
C11–C15	1.42(1)	P–F2	1.51(1)
C12–C13	1.41(1)	P–F3	1.54(1)
C13–C14	1.42(1)	P–F5	1.42(1)
C14–C15	1.41(1)	P–F6	1.53(1)
C2-C1-C5	106.6(9)	C15-C14-C24	128.3(8)
C1-C2-C3	106.5(9)	C11-C15-C25	123.8(8)
C2-C3-C4	109.6(9)	C11-C21-C31	109.2(8)
C1-C4-C5	107.3(9)	C12-C22-C32	115.5(9)
C1-C5-C4	110.0(9)	C13-C23-C33	110.5(9)
C12-C11-C15	107.6(7)	C14-C24-C34	114(1)
C11-C12-C13	108.3(7)	C15-C25-C35	112.6(9)
C12-C13-C14	107.6(7)	C11-C21-C41	117.9(9)
C13-C14-C15	108.3(7)	C12-C22-C42	109.2(9)
C11-C15-C14	108.2(7)	C13-C23-C43	119.8(9)
C11-C12-C22	118.1(8)	C14-C24-C44	119(1)
C12-C13-C23	121.7(8)	C15-C25-C45	119.8(9)
C13-C14-C24	123.0(8)	C31-C21-C41	115.1(9)
C14-C15-C25	123.9(8)	C32-C22-C42	109.2(9)
C15-C11-C21	119.7(8)	C33-C23-C43	116(1)
C12-C11-C21	132.4(8)	C34-C24-C44	118(1)
C13-C12-C22	133.2(8)	C35-C25-C45	119(1)
C14-C13-C23	130.4(8)		

[a] The PF_6^- has its usual geometry with a mean bond length P–F of 1.53 Å, excluding the abnormally short P–F5 bond. The high thermal motion of the fluorine atoms (B_{eq} between 14 and 22 Å^2) contrasts with low B_{eq} (4.8 Å^2) of the P atom and implies some libration of the PF_6^- anion. This results in some imprecision in bond lengths and angles.

3. Decaalkylation and Decafunctionalization of [CoCp*-Cp]$^+PF_6^-$ (1): The decamethylation of **1** could be extended to other organic halides, namely, ethyl iodide, allyl bromide, and benzylbromide. *t*BuOK must be avoided with organic halides bearing a β hydrogen atom, since dehydrohalogenation is then much faster than the reaction with the organometallic complex.[37] This is particularly true of alkyl iodides. In these cases, KOH can be used. The reaction of **1** with ethyl iodide and KOH was carried out at 80 °C in DME (2 d) or neat (1 d), and 1,2,3,4,5-penta(pent-3-yl)cobalticinium hexafluorophosphate (**7**, Scheme 5) was obtained in 61% and 70% yield, respectively, as yellow needles after workup and recrystallization from THF/ether (1/1) (coalescence temperature $T_c = 100$ °C at 80 MHz; $\Delta G^{\neq} = 81.0 \pm 0.8$ kJ mol^{-1} for the ro-

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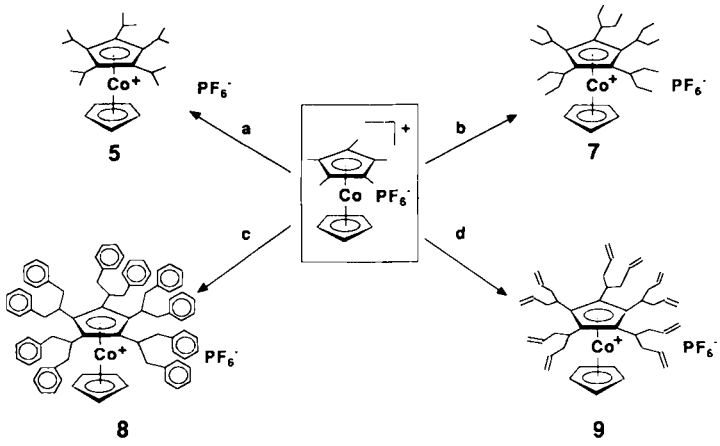
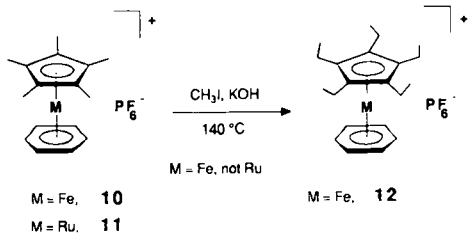


Scheme 5. Decaalkylation and decafunctionalization of **1**: a) MeI, *t*BuOK, THF; b) EtI, KOH, DME; c) $PhCH_2Br$, *t*BuOK, THF; d) C_3H_5Br, *t*BuOK, THF.

tation of the alkyl groups). Reaction of **1** with $PhCH_2Br$/*t*BuOK at 75 °C gave the decabenzylated complex **8** in 45% yield after one day, whereas decaallylation required the use of KOH at a significantly higher temperature (110 °C) and gave only 15% yield of **9** after 10 h. Attempted decabenzylation under the same conditions (KOH, DME, 110 °C) resulted in low yields (10%). Reduced yields are due to the moderate stability of bulky complexes under the conditions required to complete the decafunctionalization. Decomplexed organic ligands can be extracted from the organic phase and consist mainly of decasubstituted cyclopentadienes. The decafunctional cobalticinium derivatives **8** and **9** are relatively unstable, whereas the pentaisopropylmetallicinium complexes of Co and Rh, **5** and **6**, are robust (vide infra).

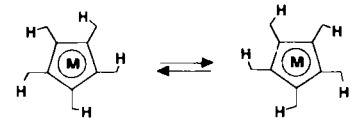
The relative ease of disubstituting each methyl group in $[MCp^*Cp]^+$ contrasts with the classical monosubstitution of $[FeCp(C_6Me_6)]^+$. This can be explained in terms of the greater angle between the Cp* centroid and the two adjacent substituents (72°) compared to the corresponding angle in C_6Me_6 (60°). The 12° difference thus enables additional substitution to take place. Note that monosubstitution at each Me of Cp* in cationic sandwich complexes is far from straightforward, and attempts to achieve this gave statistical mixtures of tetra, penta, and hexa substitution.

The polymethylation of the rather unreactive complex $[FeCp^*C_6H_6]^+PF_6^-$[14] must be carried out at around 140 °C in an autoclave with KOH and CH_3I, and the pentaethylcyclopentadienyl complex **12** is obtained in impure form. Under these conditions, the Ru analogue **11** did not react (Scheme 6). The reduced reactivity of **10** and **11** is attributed to the shift of the positive charge towards the "even" (η^6) benzene ligand;[37–39] thus the methyl substituents of **10** and **11** are less acidic than in **1** and **4**. For the same reason, the methyl substituents of $[FeCp(C_6Me_6)]^+$ are more acidic than those of **1** and **4**.[40] The acidity of the methyl groups is therefore not the determining factor for the relative degree of substitution in the alkylations of $[FeCp(C_6Me_6)]^+$ and **1**, although it is decisive for the relative reactivities of **1** (or **4**) and **10** (or **11**).



Scheme 6. Polymethylation of **10**; the Ru analogue **11** did not react under the same conditions.

4. Directionality and "*endo–exo*" Interconversion Observed by NMR: The room temperature ^1H and ^{13}C NMR spectra of the decaalkyl- or decafunctional metallicinium complexes **5–9** show very distinct patterns for the *endo* and *exo* branches on the same alkyl chain attached to Cp. The five substituents at Cp, including the tertiary CH groups at the branching point of each substituent, appear equivalent (C_5 symmetry). These features show that the five substituents adopt a single directionality, either clockwise or counterclockwise.[26] This is confirmed by the interconversion of the two "enantiomers" at high temperature, observed by ^1H NMR for **5**, **6**, and **7** (Scheme 7). For **8** and **9**, the interconversion would be observed at a temperature higher than the decomposition temperature. Interconversion becomes more difficult as the bulkiness of the substituents increases—the opposite trend was noted above for the decomplexation reaction.



Scheme 7. Clockwise and counterclockwise directionalities of the methine C–H bonds in **5–9**; the interconversion of these enantiomers is fast only at high temperatures (alkyl substituents are omitted for clarity).

The variable-temperature NMR experiments were carried out at 80 MHz in $1,2\text{-}Cl_2C_6H_4$[12] or at 200 MHz in $C_6D_5NO_2$ (Fig. 2). At 80 MHz, the methyl region shows a coalescence at 65 °C for **5** and 100 °C for **7**. At 200 MHz, coalescence is observed at 77 °C for **5** and 60 °C for **6**. The calculated activation parameters ($\Delta G^{\neq}$) are 71.3 ± 0.8, 70.3 ± 0.8, and 81.0 ± 0.8 kJ mol^{-1} for **5**, **6**, and **7**, respectively.[41] The lower coalescence temperature for the rhodium complex **6** as compared to its cobalt analogue **5** may be attributed to the larger separation between the two rings in **6** than in **5**, due to the fact

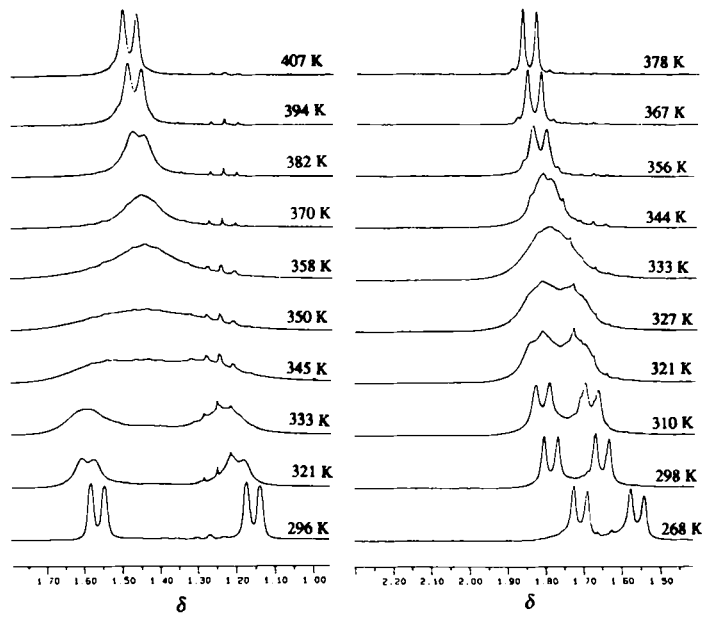


Fig. 2. Variable-temperature ^1H NMR spectra of **5** (left) and **6** (right) at 200 MHz in $C_6D_5NO_2$.

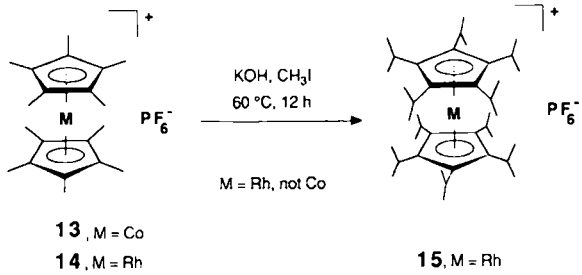
that rhodium is larger than cobalt. This would be in accordance with the staggered conformation found in the X-ray crystal structure of **5** (Fig. 1). However, it should be noted that the $\Delta G^{\ddagger}$ values for **5** and **6** are very close to each other and even perhaps within experimental error (errors in the coalescence temperatures lead to very small errors in $\Delta G^{\ddagger}$). In any case, if the metal effect is significant, it is very small. Thus, when the C_5iPr_5 faces a Cp ligand, the influence of the metal (first or second row) is very weak, and the rotational barrier reflects the steric bulk within the C_5iPr_5 ligand.

These NMR data confirm that the conformations with a single directionality are the most stable ones, whereas other conformations with mixed directionality of the C–H bonds have a higher energy. Molecular mechanics calculations have shown that, as a rule, rotation of simple alkyl groups attached to planar frameworks, such as in hexaisopropylbenzene and [Cr(hexadimethylsilylbenzene)$(CO)_3$], takes place by a stepwise, uncorrelated mechanism.[26] Thus, whereas the free ligands are not chiral, the complexes of this series exhibit metallocenic chirality[8] at low temperatures, imposed by the single directionality.

5. Decamethylation of Both Rings of the Decamethylrhodicinium Cation—One-Pot Formation of 20 C–C Bonds: The permethylation of both rings of the 18-electron monocationic decamethylmetallicinium complexes of Co and Rh was a challenge. The main questions were 1) whether the permethylation of one ring would sterically inhibit permethylation of the other and 2) assuming that permethylation of both rings were possible, what would be the influence of the directionality of the first ring on that of the second.

The polymethylation of the decamethylcobalticinium salt **13**[30] was attempted under various conditions. However, the reaction always remained incomplete even under the most forcing conditions. The products resulting from incomplete permethylation, obtained by using KOH in DME or *t*BuOK (neat) and CH_3I, were extracted and submitted to the reaction again in order to increase the degree of permethylation. Saturation was observed when around 14 methyl groups had been introduced. We were forced to conclude that a clean product could not be obtained, let alone the decaisopropylcobalticinium product. We then switched to the previously unknown rhodium analogue $[RhCp_2^*]^+PF_6^-$ (**14**). This complex was made in 40% yield from $[RhCp^*Cl_2]_2$ and LiCp* at −10 °C in ether (15 h),[42] and its X-ray crystal structure shows a perfectly staggered conformation.[43] The reaction of **14** with CH_3I and KOH in DME at 60 °C for two days afforded $[Rh(C_5iPr_5)_2]^+PF_6^-$ (**15**) in 55% yield (Scheme 8).

The ^1H NMR spectrum of **14** at 200 MHz in $C_6D_5NO_2$ shows distinct *endo* and *exo* methyl groups characterized by two doublets, at $\delta = 1.17$ and 1.34, which coalesce at 135 °C without decomposition. It also shows a septet of ten equivalent methine protons ($\delta = 2.88$). The coalescence temperature (135 °C, $C_6D_5NO_2$) and rotational barrier of the isopropyl groups ($\Delta G^{\ddagger} = 85.5 \pm 0.8$ kJ mol^{-1}) are, as expected, higher than those of **5** and **6**, owing to the larger steric constraints. The ^1H and ^{13}C NMR data show the presence of only one diastereoisomer (in detectable amounts). Models and attempts to solve its X-ray crystal structure[43] indicate that the directionalities of the two rings are most probably opposite in the stable diastereoisomer (**B** in Fig. 3).



Scheme 8. Decamethylation of both rings in **14**; the Co analogue **13** failed to give a clean product, and a maximum of 14 Me groups were introduced.

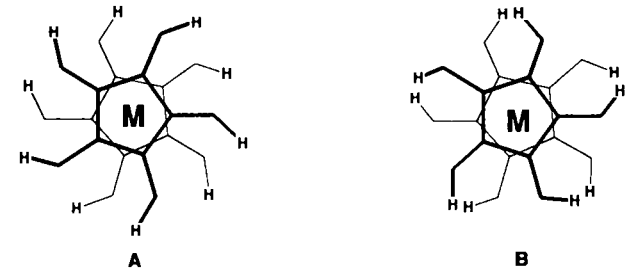


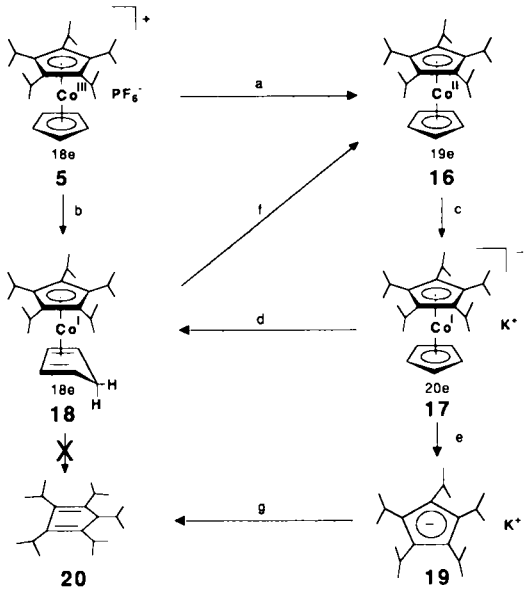
Fig. 3. The two possible conformations of decaisopropylmetallocenes (the methyl substituents are omitted for clarity; here, M = Rh^+): **A**: clockwise/clockwise, **B**: clockwise/counterclockwise.

6. Chemistry of Pentaisopropylcobalticinium Hexafluorophosphate (5): The electronic effect of pentasubstitution can be examined by recording the E° values of the Co^{III}/Co^{II} and Co^{II}/Co^{I} redox couples by cyclic voltammetry.[44] Table 3 compares the E° values of various cobalticinium cations. The electronic effects of CHR_2 (R = Me, Et) are between those of H and Me.[45, 46] Both waves are chemically and electrochemically reversible for **5**, whereas the second wave is not chemically reversible for **7** ($i_a/i_c = 0.8$ at −30 °C, $i_a/i_c = 0$ at 20 °C; scan rate = 400 mV s^{-1}). It thus appears that, for complexes containing a bulky $C_5(CHR_2)_5$ ligand, reduction to the 20-electron anionic Co^I sandwich complex is a suitable means of achieving decomplexation (as an alternative to thermal decomposition, see Section 3) to obtain the free ligand. Neutral 19-electron Co^{II} sandwich complexes, such as **16** (Scheme 9), can be synthesized by one-electron reduction of the Co^{III} cations by using one equivalent of the electron-reservoir complex $[Fe^ICp(C_6Me_6)]$ or Na/Hg in THF. Further reduction to the 20-electron anion **17** was achieved by using a potassium mirror. Hydrolysis of **17** resulted in regiospecific reduction of the unsubstituted cyclopentadienyl ligand to give the Co^I complex **18**, which was fully characterized. Heating **17** at 190 °C gave the potassium salt of the pentaisopropylcyclopentadienyl anion (**19**), which was characterized by the ^1H NMR spectrum (500 MHz) of the known diene **20**,[27, 28] obtained by protonation with water and extraction with ether (Scheme 9).

Table 3. E° values (in V vs. SCE, Hg cathode, DMF, nBu_4NBF_4, 0.1 M, −30 °C) for $[Co(C_5R_5)Cp]^+PF_6^-$, where R = H, CH_3 (**1**), *i*Pr (**5**), and $CHEt_2$ (**7**).

	$[CoCp_2]^+PF_6^-$	**1** [31]	**5**	**7**
$E^\circ(Co^{III}/Co^{II})$	−0.89 [47, 48]	−1.17	−0.96	−1.00
$E^\circ(Co^{II}/Co^{I})$	−1.88 [49, 50]	−2.19	−2.11	−2.10

0947-6539/95/0106-0378 $ 30.00+.25/0 Chem. Eur. J. 1995, 1, No. 6



Scheme 9. Chemistry of **5**: a) $[Fe^{I}Cp(C_6Me_6)]$ or Na/Hg, THF, 20 °C; b) $NaBH_4$ or $LiAlH_4$, THF, 20 °C; c) K, DME, 20 °C; d) H_2O, 20 °C; e) 190 °C; f) 150 °C; g) H_2O, 20 °C.

Conclusion

1. The methyl group of a Cp* ligand in cationic 18-electron sandwich complexes could be deprotonated by *t*BuOK to give a characterizable tetramethylfulvalene neutral cobalt complex.

2. The acidity of the methyl groups of the Cp* ligand in $[MCp^*Cp]^+$ (M = Co, Rh) allowed the formation of ten C–C bonds in a one-pot reaction, by reaction with excess KOR′ (R′ = H or *t*Bu) and an organic halide RX (RX = MeI, EtI, $CH_2{=}CHCH_2Br$, $PhCH_2Br$) to give $[M\{C_5(CHR_2)_5\}Cp]^+$.

3. The first mono- and bis(pentaisopropylcyclopentadienyl) sandwich complexes were made in this way. Other sandwich complexes with new decasubstituted cyclopentadienyl ligands $C_5(CHR_2)_5$, including decafunctional ones, have also been synthesized. These decafunctional cobalticinium derivatives are new highly-branched cores, which can be used for the construction of molecular "trees". Decomplexation of all the ligands has been shown to be feasible under various conditions, depending on the bulkiness of the substituents. With the decamethylrhodicinium cation, 20 C–C bonds were formed in a one-pot reaction, whereas the Co analogue failed to react in the same way, because of the steric constraints between the two rings.

4. The X-ray crystal structure of pentaisopropylcobalticinium hexafluorophosphate and variable-temperature NMR studies show the single directionality in all the new ligands of the sandwich complexes, as well as the interconvertibility of the two directionalities at high temperature for the C_5iPr_5 and $C_5\{CH(pent\text{-}3\text{-}yl)_2\}_5$ ligands. The NMR data of decaisopropylrhodicinium complex show the presence of only the most stable diastereoisomer.

5. The basic organometallic chemistry and electrochemistry of the pentaisopropylcobalticinium salt show that it is an extremely robust complex in its three oxidation states, although decomplexation could be achieved at high temperatures in the 20-electron anion; the protonation of this anion was completely regiospecific.

Experimental Section

Deprotonation of $[CoCp^*Cp]^+PF_6^-$ (1): At −30 °C, a solution of Me_6Si_2NK (200 mg, 1.10^{-3} M) in THF was added to a THF suspension of **1** (405 mg, 1.10^{-3} M). The reaction mixture immediately turned red. The solvent was removed in vacuo at −5 °C, and the residue extracted with pentane. The pentane was removed in vacuo to give the crude product **2** in 70% yield. The deprotonated complex **2** rapidly decomposed to a brown mixture at room temperature under argon. ^1H NMR (250 MHz, $[D_8]$toluene, −30 °C): δ = 4.41 (s, 5H, Cp), 3.62 (t, 2H, CH_2), 2.03 (s, 6H, 2 CH_3), 1.80 (s, 6H, 2 CH_3); ^{13}C NMR (62.9 MHz): δ = 12.59 and 13.31 (CH_3), 57.19 and 58.87 (*C*–Me), 68.24 (C=*C*H_2), 81.12 (C_5H_5), 88.52 (*C*–Me), 137.74 (*C*=CH_2; cf. δ = 140 for $[FeCp\{C_6Me_5(=CH_2)\}]$ ref. [31]).

1,2,3,4,5-Pentaisopropylmetallicinium hexafluorophosphates 5 and 6 [12]: Complex **1** (544 mg, 1.00 mmol) or **4** (588 mg, 1.00 mmol) was mixed with powdered KOH (2.24 g, 40 mmol) and dried at 60 °C in a Schlenk tube in vacuo for 3 h. CH_3I (5.68 g, 40 mmol) was then mixed with deoxygenated DME (20 mL). This solution was added through a cannula to the solids, and the reaction mixture was kept at 60 °C for 1 d. The volatile components were then evaporated in vacuo, and the remaining solids dissolved in CH_2Cl_2 and water. The aqueous phase was neutralized with aqueous HCl and washed several times with small amounts of CH_2Cl_2. The combined extracts were shaken with an aqueous solution of 5% HPF_6, filtered over Na_2CO_3, and dried with Na_2SO_4. After removal of the solvent in vacuo, the crude reaction product was dissolved in a small amount of acetone, ethanol added, and the solvent mixture evaporated until crystallization occurred. A few drops of acetone were used to redissolve the traces of precipitated product, and the complex was allowed to crystallize at −20 °C to yield 89% of **5** and 80% of **6**, respectively. **5**: Anal (%) calcd for $CoC_{25}H_{40}PF_6$: C 55.15, H 7.40; found: C 55.13, H 7.16. Cyclic voltammetry (Hg, 20 °C, DMF, 0.1 M nBu_4NBF_4, 400 mVs^{-1}) Co^{III}/Co^{II}: E° = −0.96 V vs. SCE, i_a/i_c = 1.0; $E_{pa}-E_{pc}$ = 80 mV, n = 1; Co^{II}/Co^{I}: E° = −2.19 V vs. SCE, i_a/i_c = 0.8, n = 1. **6** (acetone solvate): Anal (%) calcd for $RhC_{25}H_{40}PF_6\cdot(CH_3)_2CO$: C 52.01, H 7.17; found: C 52.12, H 6.81.

1,2,3,4,5-Pentakis(1-ethylpropyl)cobalticinium hexafluorophosphate (7): A procedure analogous to that described above for the synthesis of **5** and **6** was applied to **1** (2.00 g), EtI (31.0 g), and KOH (11.10 g). Recrystallization from THF/ether gave 2.37 g of **7** (70% yield) as yellow needles. ^1H NMR (250 MHz, $CDCl_3$, TMS): δ = 5.49 (s, 5H, Cp), 2.84 (m, 5H, CH), 2.10 and 1.94 (m, 10H, CH_2 *exo*), 1.41 and 1.32 (m, 10H, CH_2 *endo*), 1.20 and 1.01 (t, 30H, CH_3 *exo* and *endo*); ^{13}C NMR (62.9 MHz): 109.0 (quaternary C), 85.0 (Cp), 39.7 (CH), 33.2 and 30.3 (CH_2 *exo* and *endo*), 16.7 and 14.0 (CH_3 *exo* and *endo*). Anal (%) calcd for $C_{35}H_{60}CoPF_6$: C 61.38, H 8.88; found: 61.43, H 8.77. Cyclic voltammetry (Hg, 20 °C, DMF, 0.1 M nBu_4NBF_4, 400 mVs^{-1}) Co^{III}/Co^{II}: E° = −1.00 V vs. SCE, i_a/i_c = 0.8, $E_{pa}-E_{pc}$ = 85 mV, n = 1; Co^{II}/Co^{I}: E° = −2.10 V vs. SCE, i_a/i_c = 0, n = 1.

1,2,3,4,5-Pentakis(1-benzyl-2-phenylethyl)cobalticinium hexafluorophosphate (8): A mixture of **1** (2.00 g, 4.95 mmol), *t*BuOK (22.17 g, 198 mmol), and $PhCH_2Br$ (28.1 g, 198 mmol) in THF (30 mL) was stirred at 75 °C for 1 d. A workup procedure analogous to that described for **5** and **6** gave a yellow oil. This was washed with ether, and a solid powder was thus obtained, which was recrystallized from acetone/alcohol (1/1) to give 2.90 g of yellow-brown crystals (45% yield). Anal (%) calcd for $C_{85}H_{80}CoPF_6$: C 78.20, H 6.18, Co 4.51; found: C 78.31, H 6.07, Co 4.59. ^1H NMR (250 MHz, $CDCl_3$, TMS): δ = 7.37 (m, 50H, Ph), 6.18 (s, 5H, Cp), 3.56 (sept, 5H, CH), 3.37 (m, 20H, *exo* and *endo* CH_2); ^{13}C NMR (62.38 MHz): δ = 128.7 (quaternary C of Ph rings), 108.5 (C_5R_5), 86.3 (Cp), 44.2 and 41.6 (*exo* and *endo* CH_2), 38.5 (CH).

Synthesis of 1,2,3,4,5-pentakis(1-allyl-but-3-enyl)cobalticinium hexafluorophosphate (9): The same procedure as described for the synthesis of **5** and **6** was applied to **1** (2.00 g, 4.95 mmol), KOH (11.10 g, 198 mmol), and $CH_2{=}CHCH_2Br$ (23.96 g, 1.98 mmol) at 110 °C for 24 h and gave a brown oil. After washing with pentane (150 mL) and ether (4 × 50 mL) yellow-brown microcrystals were filtered off (0.597 g, 15% yield). Anal. (%) calcd for $C_{45}H_{60}CoPF_6$: C 67.13; H 7.52; found: C 67.11, H 7.53. ^{13}C NMR (62.38 MHz, $CDCl_3$, TMS): δ = 134.9 and 136.4 (*exo* and *endo* $CH_2{=}CH$), 117.4 and 116.1 (*exo* and *endo* $CH_2{=}CH$), 107.6 (C_5R_5), 85.7 (Cp), 43.05 and 41.14 (*exo* and *endo* CH_2), 35.3 (CH).

Attempts at permethylating decamethylcobalticinium (13): Complex **13** (1.00 g, 2.1 mmol) was stirred with KOH (8.80 g, 160 mmol) and dried at 60 °C in a Schlenk tube in vacuo for 3 h. CH_3I (11.36 g, 80 mmol) was then mixed with deoxygenated DME (25 mL). This solution was added through a cannula to the mixture of solids. The reaction mixture was heated to 60 °C for 1 d, then extracted as described for **8**. The percentage of homologated methyl groups was determined by determining the ratio between the signal of the CH + CH_2 groups and the signal of the remaining methyl groups in the ^1H NMR spectra. In the first reaction, a little under half the methyl groups were homologated. The PF_6^- salts of the mixture of the resulting complexes were combined and treated again in the same way. This procedure was repeated six times, but only 69% homologation was achieved, which corresponds to the introduction of about 14 methyl groups (see Scheme 8).

Synthesis of decamethylrhodicinium hexafluorophosphate (14): *n*BuLi (1 mL, 1.60 mmol, 1.60 M in *n*-hexane) was added dropwise with a syringe to a cooled solution (−80 °C) of Cp*H (220 mg, 1.62 mmol) in THF (20 mL). The stirred reaction mixture was allowed to warm up to room temperature over 4 h to yield a white suspension of Cp*Li. This was transferred through a cannula to a suspension of $[Cp^*RhCl_2]_2$ (0.46 g, 0.75 mmol) in THF (30 mL) at −10 °C. A color change from red to turquoise was observed during reaction (12 h). The mixture was then allowed to warm to room temperature and C_2Cl_6 (192 mg, 0.81 mmol) was used to oxidize all the reduced species. The volatile components were evaporated in vacuo, and the residue was washed several times with *n*-pentane and then redissolved in CH_2Cl_2. The organic phase was extracted three times with small amounts of water, and the combined extracts were treated with aqueous HPF_6 (5%) to precipitate the crude product, which was recrystallized from acetone/ethanol to yield 350 mg (42%) of pure **14**. Anal (%) calcd for $RhC_{20}H_{30}PF_6$: C 46.34, H 5.83; found: C 46.41, H 5.68. ^1H NMR (250 MHz, $CDCl_3$, TMS): $\delta = 1.84$ (s, CH_3); ^{13}C NMR (62.38 MHz): $\delta = 99.0$ (d, $^1J(Rh{\cdot}C) = 8.0$ Hz, C_5R_5), 8.0 (s, CH_3).

Synthesis of decaisopropylrhodicinium hexafluorophosphate (15): Complex **14** (518 mg, 1.00 mmol) was treated with a 100-fold excess of powdered KOH (5.60 g, 100 mmol) and CH_3I (14.2 g, 100 mmol) in DME. The procedure for this synthesis was carried out in the same way as described above for compounds **5** and **6**. After purification by recrystallization from acetone/ethanol, **15** was obtained in 55% yield. **15**: Anal (%) calcd for $RhC_{40}H_{70}PF_6$: C 60.14, H 8.59; found: C 60.21, H 8.83. ^1H NMR (200 MHz, $C_6D_5NO_2$, TMS): $\delta = 2.88$ (sept, 10H, $^3J(H,H) = 7.6$ Hz, CH). 1.34 and 1.17 (d, 2×30H, $^3J(H,H) = 7.6$ Hz, CH_3); ^{13}C NMR (50.3 MHz): $\delta = 114.8$ (d, $^1J(Rh{\cdot}C) = 8.0$ Hz, C_5R_5), 26.7 (CH), 26.2 and 24.4 (CH_3). Cyclic voltammetry (Hg, 5 °C, THF, 0.1 M nBu_4NBF_4, 400 mVs^{-1}) Rh^{III}/Rh^{II}: $E^\circ = -1.29$ V vs. SCE, $i_a/i_c = 0.96$; $E_{pa}-E_{pc} = 100$ mV, $n = 1$; Rh^{II}/Rh^{I}: $E^\circ = -2.52$ V vs. SCE, $i_a/i_c = 0$, $n = 1$.

Synthesis of 18 by reduction of 5: Complex **5** (405 mg, 0.75 mmol) in THF (5 mL) was stirred with 1% Na/Hg (17.0 g) for 3 h at room temperature. The solution immediately became brown. Then the solvent was removed in vacuo, and the neutral complex was extracted with anhydrous diethyl ether (100 mL). After filtration the solvent was also removed in vacuo, and the brownish residue was dissolved in THF (10 mL). A THF solution of naphthylpotassium (20 mL, 0.10 M, 2.0 mmol) was slowly added, and the resulting homogeneous solution, which gradually became red, was stirred at room temperature for 16 h before being concentrated to dryness by pumping. The resulting solid was dissolved in Et_2O (15 mL) at room temperature; this solution was filtered, and a solution of NH_4PF_6 (500 mg) in H_2O (25 mL) was added. The heterogeneous mixture was stirred at room temperature for 45 min, during which time the ether phase turned orange. This solution was dried, concentrated in vacuo to 5 mL, and transferred to a silica gel chromatography column (Kieselgeln 60, E. Merck, 70–238 mesh). Elution with CH_2Cl_2 gave a yellow-orange fraction, which contained **5** (130 mg). Further elution with MeOH yielded **18** as a yellow oil (80 mg, 27%). **18**: MS: *m/z* (relative intensity): 401 (M^+, 5.8), 400 ($M-H^+$, 28.3), 399 (M^+-2H, 100); ^1H NMR (250 MHz, $CDCl_3$, TMS): $\delta = 4.94$ (m, 2H, CH), 4.38 and 4.30 (m, 2H, CH), 3.00 (sept, 5H, CH), 2.90 (br m, 2H, CH_2), 1.51 (d, 15H, CH_3), 1.17 (d, 15H, CH_3); ^{13}C NMR (62.90 MHz): $\delta = 102.5$ (C_5R_5), 77.26, 74.58, 66.67 and 66.57 (CH); 29.74 (CH_2), 25.43 ($CHMe_2$), 23.77 and 22.29 (CH_3).

Synthesis of 18 from 5 by hydride addition: $LiAlH_4$ or $NaBH_4$ (1 mmol) was added to a solution of **5** (160 mg, 0.3 mmol) in THF (25 mL). A color change from yellow to red was observed in both cases. After stirring for 2 h at 20 °C, until no gas evolution was observed, evaporation of the solvent to dryness yielded **18** (respectively 65 mg (54%) and 40 mg (30%)), which was purified by filtration of a MeOH solution through a short silica-gel column.

Demetalation of 5: The compound **20** was synthesized by a variation of the method described above for the reduction of **5** to **18** by means of Na/Hg and naphthylpotassium. The red solution obtained by reduction with naphthylpotassium was filtered under argon into a Schlenk tube. The solvent was removed in vacuo and the reaction vessel was placed in an oil bath at high temperature (190 °C, 72 h). The resulting black solid was dissolved in a KOH solution (0.1 M, 2×10 mL) and washed with Et_2O (3×10 mL), before acidification with aqueous HCl (0.1 M). A pale yellow neutral compound was extracted with pentane. Filtration of the solution through a short column of silica gel and concentration in vacuo yielded 30 mg (13%) of crude **20** as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$, 303 K, TMS): $\delta = 3.04$ (m, 4H, $CHMe_2$), 2.83 (d, $J(H,H) = 2.3$ Hz, 1H, $CH(CHMe_2)$), 2.59 (m, 1H, $CH(CHMe_2)$), 1.27 (d, $J(H,H) = 7.2$ Hz, 2H, $CH(CH_3)_2$), 1.18 (d, $J(H,H) = 7.4$ Hz, $CH(CH_3)_2$), 1.00 (d, $J(H,H) = 7.1$ Hz, $CH(CH_3)_2$).

X-ray data collection and structure resolution for complex 5: Crystals suitable for an X-ray diffraction analysis were directly obtained by slow diffusion of an acetone/water system at 293 K. A colorless parallelepiped crystal with dimensions $0.20\times0.30\times0.60$ mm was selected for the data collection; 25 reflections with θ between 35 and 40° were used for crystal setting and least-squares refinement of cell parameters. The diffracted intensities were measured with a CAD-4 Enraf-Nonius diffractometer. The absorption was corrected with the SDP package [54]; minimum and maximum transmission factors are 78.5 and 89.1%, respectively. No significant decrease of reference reflections during data collection was observed. The crystal structure was solved by direct methods with the program Mithril [55]. Atomic parameters were refined with a full-square matrix by using Shelx 76 [56] with anisotropic scattering factors for non-hydrogen atoms. H atoms were positioned in their theoretical positions [57] and followed the C atoms to which they were attached. Scattering factors are from International Tables for X-ray Crystallography (1974, Vol. IV). The final reliability factors were $R = 0.068$, $Rw = 0.074$ with $s = 1.45$; $\Delta/\sigma_{max} = 0.15$, and the residual electron density is between −0.2 and 0.3 e Å^{-3}. A summary of crystal data is given in Table 1. For the fractional coordinates and B_{eq} (Å^2) factors, see ref. [58].

Acknowledgments: We thank Professor Joseph Vercauteren (Bordeaux) for the 500 MHz ^1H NMR spectra of **20** and Dr Jean-René Hamon and Paul Hamon (Rennes) for the 80 MHz ^1H NMR spectra of **5**. Financial support from the Centre National de la Recherche Scientifique, the Région Aquitaine, and the Université Bordeaux I, a PhD grant to B. G. from the Ministère de la Recherche et de la Technologie, and a post-doctoral fellowship to D. B. from the Deutsche Forschung Gemeinschaft are gratefully acknowledged.

Received: January 30, 1995 [F75]

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