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Synthesis and NMR study of the cations $C_5Me_5MC_5Me_4CHAr^+$ (M = Ru, Os). A comparison with Fe-containing analogues

M.I. Rybinskaya[*], **A.Z. Kreindlin, S.S. Fadeeva and P.V. Petrovskii**

Institute of Organoelement Compounds, Academy of Sciences of the USSR, 117813, Vavilov str. 28, Moscow (U.S.S.R.)

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Abstract

The novel secondary carbinols $C_5Me_5MC_5Me_4CH(OH)Ar$ have been prepared by reaction of $C_5Me_5MC_5Me_4CHO$ (M = Ru, Os) with an excess of ArLi. Protonation of the carbinols by the strong acids, CF_3COOH, HBF_4 and HPF_6 (HA), leads to the corresponding stable carbocations $C_5Me_5MC_5Me_4\overset{+}{C}HArA^-$, and the salts with A = BF_4 and PF_6 have been isolated as solids. Comparison of the behaviour of the various Fe-subgroup metal cations $C_5Me_5MC_5Me_4CHAr^+$ has shown that Ru and Os cations are more stable than the Fe derivatives and do not undergo the $C_5Me_5FeC_5Me_4\overset{+}{C}HAr \rightleftarrows C_5Me_5Fe^{\overset{+}{\cdot}}C_5Me_5\dot{C}HAr$ singlet–triplet transition. Comparison of the ruthenium and osmium cations $C_5Me_5MC_5Me_4CHAr^+$ of the ^1H and ^{13}C NMR data with the corresponding data for iron complexes [1] indicates that the shielding of ^1H and ^{13}C nuclei by the carbenium centre $-CH^+-$ increases on going from Fe to Ru and then to Os compounds. For the metal cations the shielding of the same nucleus (^1H and ^{13}C) increases in the series $Me_3C_6H_2 < Ph < C_6F_5$, i.e. with increasing electron withdrawing ability of the aryl substituent adjacent to the carbenium centre. A change in the properties of the Fe subgroup cations $C_5Me_5MC_5Me_4CHAr^+$ implies that direct participation by the metal atom in the stabilization of the carbenium centre increases from Fe to Os.

Introduction

Our systematic study of the Fe subgroup nonamethylmetallocenylcarbenium ions $Me_5C_5MC_5Me_4CH_2{}^+A^-$ (M = Fe, Ru, Os), obtained by protonation of the corresponding carbinols by strong acids, has shown that the behaviour of Fe-containing ions differed markedly from those of the ruthenium and osmium analogues [1–6]. The analogues are more stable and can thus be isolated as solids and were characterized by X-ray crystallography [4,5]. The Fe-containing analogues, however, exists only for a limited period of time in solution or as a solid and eventually yields the paramagnetic coupling product, bis(nonamethylferrocenio)ethane dication [3]. It should be noted that the initial concentration of paramagnetic particles (the triplet state population) is less than 1%. To prevent coupling, we obtained nonamethylferrocenylcarbinols with bulky aryl substituents in the α-position $Me_5C_5FeC_5Me_4CH(Ar)OH$). The treatment of the latter with protic acids results in an equilibrium mixture of isomeric diamagnetic and paramagnetic cations, i.e. the singlet–triplet transition $C_5Me_5FeC_5Me_4\overset{+}{C}HAr \rightleftharpoons C_5Me_5Fe^{+\cdot}C_5Me_4\dot{C}HAr$ is observed [1]. For the primary ion direct observation of the singlet–triplet transition is complicated by subsequent dimerisation (see above). The present investigation was undertaken to realise the possibility of the singlet–triplet transition in ruthenium and osmium arylsubstituted nonamethylmetallocenylcarbenium cations. We also wished to compare the behaviour of these carbenium ions with that of the Fe-triad.

Results and discussion

Carbenium ions of the type $C_5Me_5MC_5Me_4CHAr^+$ (M = Ru, Os) were obtained readily from the corresponding carbinols as described previously [4–6]. It should be noted that the method for the preparation of such carbinols is of special interest, since the number of functionally substituted permethylated metallocenes has been limited up to now. Arylnonamethylmetallocenylcarbinols of ruthenium and osmium (I, M = Ru; II, M = Os) were obtained by the interaction of the corresponding aldehydes $C_5Me_5MC_5Me_4CHO$ (III, M = Ru [4,5] and IV, M = Os [6]) with an excess of aryllithium compounds according to [1].

$$\begin{array}{lcl} C_5Me_5MC_5Me_4CHO + LiAr & \rightarrow & C_5Me_5MC_5Me_4CH(OH)Ar \\ \quad (III, M = Ru; & & (Ia\text{–}c, M = Ru; \\ \quad IV, M = Os) & & IIa\text{–}c, M = Os) \\ & & a, Ar = Ph;\ b, Ar = C_6H_2Me_3;\ c, Ar = C_6F_5) \end{array}$$

The carbinols Ia–c and IIa–c are all stable in air both in solution and in the solid state. Complexes containing the electron-withdrawing C_6F_5 substituent, Ic and IIc are especially noteworthy. (We have already pointed out the limited stability of the Fe analogue of Ic and IIc in solution).

Treatment of Ia–c and IIa–c with strong acids gives the corresponding cations Va–c and VIa–c.

$$\begin{array}{lcl} C_5Me_5MC_5Me_4CH(OH)Ar + HA & \rightarrow & C_5Me_5MC_5Me_4CHAr^+A^- \\ \quad (Ia\text{–}c, M = Ru; & & (Va\text{–}c, M = Ru; \\ \quad IIa\text{–}c, M = Os) & & VIa\text{–}c, M = Os) \\ & & HA = CF_3COOH, HBF_4, HPF_6 \end{array}$$

The cations Va–c and VIa–c, in addition to $C_5Me_5MC_5Me_4CH_2^+A^-$ (M = Ru, Os) isolated previously, are diamagnetic and are stable in air as solids. The structures of neutral Ia–c and IIa–c, and cationic Va–c and VIa–c have been confirmed by analytical, mass- and NMR (^{13}C and ^{1}H) spectral data (see Tables 1–4).

Table 1

Properties of the compounds obtained

Compound	Yield (%)	M.p. (°C)	Analysis (Found (calc)(%))				Empirical formula	Mass spectra (^{102}Ru, ^{192}Os)
			C	H	M	F		
Ia	56	109–110	67.30	7.38	–	–	$C_{26}H_{34}ORu$	464 M^+
			(67.35)	(7.39)				
Ib	51	157–158	68.41	7.92	–	–	$C_{29}H_{40}ORu$	506 M^+
			(68.88)	(7.97)				
Ic	38	129–131	56.50	5.19	–	–	$C_{26}H_{29}F_5ORu$	554 M^+
			(56.41)	(5.28)				
IIa	52	96–97	56.44	6.17	34.21	–	$C_{26}H_{34}OOs$	554 M^+
			(56.49)	(6.20)	(34.41)			
IIb	46	164–166	58.50	6.79	32.12	–	$C_{29}H_{40}OOs$	596 M^+
			(58.55)	(6.78)	(31.98)			
IIc	58	125–127	48.59	4.55	–	14.97	$C_{26}H_{29}F_5OOs$	644 M^+
			(48.59)	(4.54)	(29.59)	(14.78)		
Va	98	–	57.19	6.21	–	13.21	$C_{26}H_{33}BF_4Ru$	–
			(58.27)	(6.23)	–	(14.24)		
Vb	94	–	59.61	6.83	–	12.83	$C_{29}H_{39}BF_4Ru$	–
			(60.52)	(6.83)		(13.21)		
Vc	92	–	49.14	4.58	–	26.42	$C_{26}H_{28}BF_9Ru$	–
			(50.09)	(4.53)		(27.43)		
VIa	91	–	45.87	4.87	–	–	$C_{26}H_{33}F_6OsP$	–
			(45.87)	(4.89)				
VIb	59	–	47.98	5.44	–	–	$C_{29}H_{39}F_6OsP$	–
			(48.18)	(5.44)				
VIc	57	–	40.31	3.76	–	–	$C_{26}H_{28}F_{11}OsP$	–
			(40.52)	(3.66)				

A singlet–triplet transition of the type $C_5Me_5MC_5Me_4CHAr^+ \rightleftarrows C_5Me_5{}^+\dot{M}C_5$-$Me_4\dot{C}HAr$ was not observed for Ru and Os cations, nor for cations Vc and VIc which have the electron-withdrawing substituent C_6F_5. We have previously indicated that in the series of Fe-containing cations with different aryl groups ($C_6H_2Me_3$, α-$C_{10}H_7$, Ph, C_6F_5) [1] the population of the triplet state is greatest for $C_5Me_5FeC_5Me_4CHC_6F_5$ (~ 70%).

The high stability of the diamagnetic Ru and Os cations and their inability to transform into the paramagnetic species suggests that the carbenium centre is stabilized to a greater extent because of direct interaction between the metal atoms and the carbenium centre. This conclusion is supported by NMR data of the Ru- and Os-containing cations.

NMR Spectroscopy

The most complete NMR study of metallocenyl cations has been previously performed for ferrocene derivatives only, thus a systematic study of the NMR

Table 2

^{1}H NMR data for $C_5Me_5MC_5Me_4CH(OH)Ar$ (δ (ppm), J (Hz))

Compound	$C_5(CH_3)_4$	$C_5(CH_3)_5$	–CH–	OH	Arene ring	Methyl protons of the arene ring
FePh [a]	1.284(27H) [b]	[b]	2.11(1H)	5.16(1H)	7.1–7.5 [c]	
Ia	1.57(3H), 1.58(3H), 1.67(3H), 1.82(3H)	1.77(15H)	2.28(1H,d; J 0.5)	5.31(1H,d; J 0.5)	7.1–7.4 [c]	–
IIa	1.61(3H), 1.63(3H), 1.70(3H), 1.90(3H)	1.84(15H)	2.15(1H,d; J 1)	5.28(1H,d; J 1)	7.2–7.5 [c]	
FeMes [a]	1.14(3H), 1.59(3H), 1.64(3H), 2.02(3H)	1.74(15H)	1.49(1H,d; J 3.7)	6.17(1H,d; J 3.7)	6.73(2H)	2.21(3H; *p*), 2.23(6H; *o*)
Ib	1.49(3H), 1.52(3H), 1.56(3H), 1.61(3H)	1.72(15H)	1.88(1H,d; J 3.4)	5.62(1H,d; J 3.4)	6.74(2H)	2.21(3H; *p*), 2.23(6H; *o*)
IIb	1.43(3H), 1.63(3H), 1.65(3H0, 1.69(3H)	1.76(15H)	2.14(1H,d; J 1)	5.60(1H,d; J 3.8)	6.76(2H)	2.20(3H; *p*), 2.28(6H; *o*)
FePh^F [a]	1.43(3H), 1.54(3H), 1.55(3H), 1.88(3H)	1.63(15H)	2.36(1H)	5.78(1H)	–	–
Ic	1.60(3H), 1.64(3H), 1.70 [d](3H,t, J 0.9), 1.79 [d](3H,t, J 1.5)	1.75(15H)	2.26(1H;d; J 1.8)	5.60(1H;d; J 1.8)	–	–
IIc	1.64(3H), 1.68(3H), 1.80(3H)	1.82 [e](18H)	2.15(1H,d; J 1.5)	5.51(1H,d; J 1.5)	–	–

[a] FePh = $C_5Me_5FeC_5Me_4CH(OH)Ph$, FeMes = $C_5Me_5FeC_5Me_4CH(OH)C_6H_2Me_3$, FePh^F = $C_5Me_5FeC_5Me_4CH(OH)C_6F_5$. Data for Fe derivatives are from ref. 1. [b] One signal for all Me groups is observed. [c] The ^{1}H NMR spectra of all carbinols with Ph substituent contain a typical A_2B_2C multiplet for the aromatic protons. [d] Two signals for Me groups of the $C_5Me_4CH(OH)C_6F_5$ ring are seen as triplets owing to long-range coupling with ^{19}F nuclei. [e] A signal from one Me group of the $C_5Me_4CH(OH)C_6F_5$ ring overlaps with that of C_5Me_5 ring.

Table 3

^{1}H NMR data for $C_5Me_5MC_5Me_4\overset{+}{C}HAr$ [a] (δ (ppm), J (Hz))

Compound	C_5Me_4–$C_5\mathit{Me}_4$ ring protons	$C_5\mathit{Me}_5$	$-\overset{+}{C}H-$	Arene ring	Methyl protons of the arene ring
FePh [b]	1.88(6H)	1.28(21H)	[d]	7.2–7.8(5H) [c]	–
Va	1.62(3H), 1.78(3H), 1.91(3H), 1.93(3H)	1.70(15H)	6.51(1H)	7.27–7.54(5H) [c]	–
VIa	1.62(3H), 1.85(9H)	1.79(15H)	6.26(1H)	7.29–7.53(5H) [c]	–
FeMes [b]	1.15(3H), 1.74(3H), 1.83(3H)	1.31(15H)	9.31(1H)	6.68(2H)	1.90(3H, *p*-Me) 1.99(6H, *o*-Me)
Vb	1.44(3H), 1.80(3H), 1.91(3H), 2.01(3H)	1.76(15H)	7.84(1H)	6.96(2H)	2.25(3H, *p*-Me) 2.38(6H, *o*-Me)
VIb	1.52(3H), 1.80(3H), 1.87(3H), 1.92(3H)	1.94(15H)	7.98(1H)	6.91(2H)	2.13(3H, *p*-Me) 2.29(6H, *o*-Me)
FePh^F [b,e]	0.97(6H), 1.88(3H)	1.37(18H)	7.24(1H)	–	–
Vc	1.54(3H, t, J 2.6) [f], 1.70(3H), 1.94(3H), 2.00(3H)	1.82(15H)	6.21(1H)	–	–
VIc	1.62(3H, t, J 2.8) [f], 1.67(3H), 1.85(3H), 1.90(3H)	1.94(15H)	6.15(1H)	–	–

[a] FePh = $C_5Me_5FeC_5Me_4\overset{+}{C}HPh$, FeMes = $C_5Me_5FeC_5Me_4\overset{+}{C}HC_6H_2Me_3$, FePh^F = $C_5Me_5FeC_5Me_4\overset{+}{C}HC_6F_5$. Data for Fe derivatives are from ref. 1. [b] Cations Va–c and VIa–c are obtained on dissolution of Ia–c, IIa–c in $CDCl_3/CF_3COOH$ at 25 °C. [c] A typical A_2B_2C multiplet is observed for aromatic protons. [d] A signal from the $-CH^+$ proton, overlaps with aromatic proton. [e] Recorded at −60 °C. [f] In spectra of Vc and VIc a signal from one Me group of the $C_5Me_4\overset{+}{C}HC_6F_5$ ring is seen as a triplet due to long-range coupling with ^{19}F nuclei.

Table 4. ^{13}C NMR data for $C_5Me_5MC_5Me_4\overset{+}{C}HArBF_4^-$ (δ (ppm))

Compound	$C_5\mathit{Me}_4CHAr$	$C_5\mathit{Me}_5$	$C_5Me_4\overset{+}{C}HAr$	C_5Me_5	$-\overset{+}{C}H-$	Arene ring	Methyl carbons of arene ring
FePh [a,b]	7.86(1C), 9.14(1C) 9.31(1C), 11.33(1C)	8.69(5C)	81.55(1C), 89.97(1C), 105.13(1C), 106.72(1C), 109.42(1C)	99.63 (5C)	132.06 (1C)	129.59(2C-*m*) 131.75(3C-*o*,*p*) 134.47(1C-i)	
Va [c]	8.05(1C), 8.87(1C), 8.94(1C), 13.01(1C)	9.15(5C)	93.53(1C), 94.19(1C), 100.87 (1C), 107.20(1C), 107.40(1C)	96.47 (5C)	104.43 (1C)	128.68(2C-*m*) 130.62(1C-*p*) 131.94(2C-*o*) 132.02(1C-i)	
VIa [c]	7.46(1C), 12.55(1C), 12.75(1C)	9.09(6C)	89.89(1C), 91.73(1C), 93.09(2C), 100.2(1C)	84.57 (5C)	79.01 (1C)	128.77(2C-*m*) 129.33(1C-*p*) 131.63(1C-*o*) 133.15(1C-*i*)	
FeMes [a,b]		9.48(9C)	83.37(1C), 92.73(1C), 108.61 (1C), 111.51(1C), 117.09(1C)	94.02 (5C)	137.49 (1C)	134.77(1C-*p*) 138.02(1C-*o*) 139.48(1C-*o*) 142.43(1C-*i*)	22.00 (2C-*p*) 22.27 (1C-*p*)
Vb [c]	8.85(1C), 9.00(2C), 10.89(1C)	10.01(5C)	85.31(1C), 90.67(1C), 105.34 (1C), 105.89(1C), 110.31(1C)	95.28 (5C)	134.29 (1C)	130.27(2C-*m*) 131.05(1C-*p*) 139.48(2C-*o*) 142.46(1C-*i*)	21.43 (2C-*o*) 21.92 (1C-*p*)
VIb [c]	8.44(1C), 8.84(1C), 10.92(1C)	10.01(5C)	78.42(1C), 81.56(1C), 97.24(1C), 99.95(1C), 104.75(1C)	92.82(5C)	102.40(1C)	130.70(2C-*m*) 138.52(2C-*o*) 138.70(1C-*p*) 141.27(1C-*i*)	21.55(1C-*p*) 22.54(2C-*o*)
Vc [c]	8.19(1C), 8.80(1C), 10.68(1C)	9.32(5C)	90.94(1C), 94.13(1C), 106.29(1C), 108.22 (1C), 110.16(1C)	98.49(5C)	83.92(1C)	135.93 142.13 144.56 147.20	
VIc [c]	7.50(1C), 8.75(1C), 10.43(1C), 12.44(1C)	9.03(5C)	84.46(1C), 86.46(1C), 87.55(1C), 100.95(1C), 102.82(1C)	94.90(5C)	55.69(1C)	135.87 138.62 141.43 146.52	

[a] FePh = $C_5Me_5FeC_5Me_4\overset{+}{C}HPh$, FeMes = $C_5Me_5FeC_5Me_4\overset{+}{C}HC_6H_2Me_3$. Data for Fe derivatives from ref. 1. [b] Solutions of $C_5Me_5FeC_5Me_4CH(OH)Ar$ in $CH_2Cl_2/Et_2O \cdot HBF_4$ at −40 °C. [c] Solutions of $C_5Me_5MC_5Me_4\overset{+}{C}HArBF_4^-$ (M = Ru, Os) in CH_2Cl_2 at 25 °C.

spectra of the cations $CpMC_5H_4CHR^+$ (VIII, M = Ru, Os) was not carried out. There are only a few reports of such studies [7]. We have carried out previously a detailed investigation of the NMR spectra (^1H and ^{13}C) of permethyl metallocenylcarbenium ions of the type $C_5Me_5MC_5Me_4CH_2{}^+$ (IX, M = Fe, Ru, Os) and $C_5Me_5FeC_5Me_4CHR^+$ (R = Me, Fc, Ph, α-$C_{10}H_7$, $C_6H_2Me_3$, C_6F_5) [1–6]. Here we describe the NMR spectra (^1H and ^{13}C) of permethylated Ru- and Os-containing cations Va–c (M = Ru) and VIa–c (M = Os), in addition to the ^1H NMR spectra of their neutral precursors, i.e. carbinols Ia–c and IIa–c. The PMR spectral data of Ia–c, IIa–c and Va–c, VIa–c are listed in Tables 2, 3. The ^{13}C NMR spectral data of Va–c, VIa–c are listed in Table 4. The chemical shifts of the Fe analogues [1] are included in the Tables for comparison. Spectra of the compounds studied are typical of the spectra of planar chiral compounds containing an asymmetric carbon.

All ^1H and ^{13}C nuclei of the Me groups and ^{13}C nuclei of the C_5Me_4 ring of the $C_5Me_4CH(OH)Ar$ (or $C_5Me_4CHAr^+$) moiety are magnetically nonequivalent and there are four signals for every group of nuclei in the spectra of the molecules indicated. This was observed earlier for the nonmethylated compounds $CpMC_5H_4CHAr^+$.

A conversion of neutral compounds Ia–c, IIa–c into the cationic species Va–c and VIa–c results in the deshielding of the majority of protons (Tables 2 and 3). The differences between these shifts ($\Delta\delta$) for Me protons are in the range 0.02–0.20 ppm, whereas $\Delta\delta$ for the non-methylated analogues $CpMC_5H_4CH(OH)Ar$ $CpMC_5H_4CHAr^+$ (M = Fe) are in the range 0.6–2.2 ppm.

The NMR spectral data show that shielding of the $-CH^+-$ proton increases on going from ruthenium to osmium. The same situation is seen in the corresponding non-methylated cations VIII (M = Fe, Ru, Os) [7] and for the primary ion, $C_5Me_5MC_5Me_4CH_2{}^+$ (IX, M = Fe, Ru, Os) [6].

Consistent with the ^{13}C NMR data, shielding of the most arene carbon furthest from the metal atom does not change significantly on going from Va–c (M = Ru) to VIa–c (M = Os), with only small increases being observed in data for the Me groups of the arene ring.

The increase in shielding of the cyclopentadienyl carbons is 4–8 ppm. As expected, the strongest shielding is observed for the ^{13}C nuclei of the $-CH^+-$ group (see Table 6).

The values of $\Delta\delta$ (for ^{13}C nuclei of the $-CH^+-$ group) for every pair (Fe–Ru, Ru–Os) of cations with similar substituents are, as a rule, in the range 23–32 ppm (excluding the pair, $C_5Me_5FeC_5Me_4\overset{+}{C}HC_6H_2Me_3$ and Vb, with $\Delta\delta$ of 3.2 ppm). An increase in the shielding of ^{13}C nuclei was also observed in the case of the cations,

Table 5

Chemical shifts of the $-CH^+-$ protons

M	$C_6H_2Me_3$	Ph	C_6F_5	$C_5Me_5MC_5Me_4CH_2{}^+$ [3,5,6]
Fe	9.31	[a]	7.24	5.27
Ru	7.84	6.51	6.21	4.75
Os	7.98	6.26	6.15	4.42

[a] The value of the chemical shift of $-CH^+-$ is in the range of Ph protons (7.2–7.8 ppm) [1].

Table 6

Chemical shifts of ^{13}C nuclei of the $-CH^+-$ group

M	$C_6H_2Me_3$	Ph	C_6F_5	$C_5Me_5MC_5Me_4CH_2^+$ [3,5,6]
Fe	137.5 [1]	132.1 [1]	–	90.7
Ru	134.3	104.43	83.9	74.7
Os	102.4	79.0	55.7	55.4

$CpMC_5H_4\overset{+}{C}HC_5H_4FeCp$ (δ, ppm (CH^+): M = Fe, 147.2; M = Ru, 116.9) [8] and $C_7H_7M(CO)_3^+$ (δ, ppm ($C_7H_7^+$): M = Cr, 104.71; M = Mo, 100.0; M = W, 96.92) [9].

The effects due to the aryl substituents in the cations $C_5Me_5MC_5Me_4CH^+Ar$ can be elucidated from the ^1H and ^{13}C NMR spectral data. The shielding of the ^1H protons (and of the ^{13}C nuclei) of the $-CH^+-$ group increases with an increase in electron-withdrawing ability of the substituent: $Me_3C_6H_2 < Ph < C_6F_5$. Similar dependence was previously observed in the case of $C_5Me_5FeC_5Me_4CH^+Ar$ [1] and discussed for nonmethylated Fe analogues [10,11].

In the cations, $XC_6H_4\overset{+}{C}RMe$, the X of the arene ring brings about an opposite effect on the chemical shifts of the carbenium atom C^+ in [12]. The effect disappears, if account is taken of the fact that the stabilization of the α-metallocenylcarbenium ions occurs mainly by direct interaction of the metal with the carbocationic centre, the contribution of which increases in the order Fe < Ru < Os.

Other source of evidence (studies of solvolytic reactions, stereochemical data, pK_{R^+} measurements, NGR and NMR (^1H, ^{13}C, ^{19}F and ^{57}Fe) studies) suggest [7] that the interaction between a carbocationic centre and transition metal atom increases an going from Fe to Ru and then to Os derivatives. X-Ray diffraction studies were only carried out for the salts $C_5H_5FeC_5H_4\overset{+}{C}RR^1BF_4^-$ ($R = C_5H_4FeC_5H_5$, $R^1 = H$; $R = R^1 = Ph$) [13,14].

We have structurally characterized the cations $C_5Me_5RuC_5Me_4CH_2^+PF_6^-$ (VII) [5] and $C_5Me_5OsC_5Me_4CH_2^+BPh_4^- \cdot CH_2Cl_2$ * and have shown that the inclination of the CH_2^+ group towards the metal increases on going from Ru to Os compounds (the angle changes from 14 to 40°), whereas the $M \cdots C^+$ distance decreases from 2.603 (Ru compound) to 2.244 Å (Os compound), attaining the length of a covalent C–Os bond in the latter case. The conclusions drawn from the NMR data are thus consistent with those from the X-ray data. Unfortunately, there are no X-ray data for the Fe-containing analogues.

Their lower stability and participation in the singlet–triplet transition, suggest that the $C^+ \cdots Fe$ distance exceeds that of the covalent Fe–C bond length, and is in accord with diffraction studies on the nonmethylated compounds $(C_5H_5FeC_5H_4)_2CH^+BF_4^-$ [13] and $C_5H_5FeC_5H_4C^+Ph_2BF_4^-$ [14] carried out previously.

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Experimental

Mass spectra were measured with an AEI-MS spectrometer, NMR spectra were recorded with a Bruker WP-200, SY spectrometer (^1H 200, 13 MHz and ^{13}C 50.31 MHz) with TMS as internal standard. Compounds III [4,5] and IV [6] had been prepared previously by us. Preparation of Ia–c and IIa–c was performed under argon.

Synthesis of Ia. To a solution of III (0.6 g, 1.55 mmol) in dry ether (50 ml) was added dropwise 4 ml (2.6 mmol) of a 0.65 *M* ether solution of PhLi. After 15 min the solution was poured into an aqueous solution of NH_4Cl, and extracted with ether. The organic layer was dried over Na_2SO_4. An oil formed, and after evaporation of the solvent, the product was crystallized from C_2H_5OH, and cooled to $-20\,^\circ C$. The solvent was decanted. Recrystallization from acetone gave 0.41 g (0.88 mmol, 56%) of Ia.

Synthesis of Ib. To a solution of 2,4,6-$Me_3C_6H_2Br$ (1 g, 5 mmol) in dry ether (50 ml) was added dropwise 1.5 ml (5.25 mmol) of a 3.5 *M* hexane solution of n-BuLi. After 1.5 h a solution of III (0.4 g, 1.04 mmol) was added dropwise to the suspension to give 2,4,6-$Me_3C_6H_2Li$. The mixture was stirred for 1 h and then decomposed by addition of aqueous NH_4Cl. The product was extracted with ether, dried over Na_2SO_4, and the ether evaporated off. The oil that formed was crystallized by adding cold ($-20\,^\circ C$) C_2H_5OH, which was then decanted. The product was dissolved in refluxing pentane, and cooled to $-78\,^\circ C$. The yield of Ib was 0.27 g (0.53 mmol, 51%).

Synthesis of Ic. To a solution of C_6F_5Cl (0.5 ml, 0.8 g, 4 mmol) in dry ether during 1 min was added dropwise 1 ml (4 mmol) of 4 *M* hexane solution of n-BuLi. The solution was stirred for 0.5 h at the same temperature, then a solution of III (0.7 g, 1.8 mmol) in dry ether was added during 10 min. The solution was stirred for 20 min and then decomposed by addition of aqueous NH_4Cl. After extraction with ether, the organic layer was dried over Na_2SO_4 and evaporated. The crude product was treated with C_2H_5OH at $-20\,^\circ C$, and decanted. The residue was dissolved in pentane, cooled to $-78\,^\circ C$ and filtered. The yield of Ic was 0.39 g (0.7 mmol, 39%).

Synthesis of IIa was carried out as described for that of Ia; with IV (0.5 g, 1.05 mmol) and 3 ml (1.95 mmol) of a 0.65 *M* ether solution of PhLi. Crystallization from C_2H_5OH at $-20\,^\circ C$ and recrystallization from acetone gave 0.30 g (0.54 mmol, 52%) of IIa.

Synthesis of IIb was carried out similarly, starting from 2,4,6-$Me_3C_6H_2Br$ (1 g, 5 mmol), 1.5 ml (5.7 mmol) of a 3.8 *M* hexane solution of n-BuLi and IV (0.6 g, 1.27 mmol). Crystallization from methanol at $-20\,^\circ C$ and recrystallization from acetone gave 0.35 g (0.59 mmol, 46%) of IIb.

Synthesis of IIc was similar to that of Ic, starting from C_6F_5Cl (1 g, 5 mmol), 1.35 ml (5.15 mmol) of a 3.8 *M* hexane solution of n-BuLi and IV (0.5 g, 1.05 mmol). Crystallization from methanol at $-20\,^\circ C$ and recrystallization from pentane at $-78\,^\circ C$ gave 0.39 g (0.61 mmol, 58%) of IIc.

Synthesis of Va ($A = BF_4$). A solution of $HBF_4 \cdot Et_2O$ (0.5 ml) was added to an ether solution of Ia (220 mg, 0.41 mmol). The crystals that formed were washed with ether, dissolved in methylene chloride and precipitated with ether. The yield of Va was 252 mg (98%).

Synthesis of Vb ($A = BF_4$) was similar to that of the 203 mg (94%) of Vb was obtained from Ib (191 mg, 0.43 mmol) and $HBF_4 \cdot Et_2O$ (0.5 ml).

Synthesis of Vc ($A = BF_4$) was similar to that of Va, 213 mg (92%) of Vc was obtained from Ib (205 mg, 0.37 mmol) and $HBF_4 \cdot Et_2O$ (0.5 ml).

Synthesis of VIa ($A = BF_4$ or PF_6) was similar to that of Va, 68 mg (100%) of VIa ($A = BF_4$) was obtained from IIa (56 mg, 0.1 mmol) and $HBF_4 \cdot Et_2O$ (0.3 ml) or 143 mg (91%) of VIa ($A = PF_6$) was prepared from IIa (127 mg, 0.23 mmol) and 0.3 ml of 75% aqueous HPF_6.

Synthesis of VIb ($A = BF_4$ or PF_6) was similar to that of Va, 129 mg (100%) of VIb ($A = BF_4$) was obtained from IIb (112 mg, 0.19 mmol) and 0.5 ml $HBF_4 \cdot Et_2O$ or 123 mg (59%) * of VIb ($A = PF_6$) was prepared from IIb (173 mg, 0.3 mmol) and 0.3 ml of 75% aqueous HPF_6.

Synthesis of VIc ($A = BF_4$ or PF_6) was similar to that of Va, 128 mg (95%) of VIc ($A = BF_4$) was obtained from IIc (121 mg, 0.19 mmol) and 0.5 ml $HBF_4 \cdot Et_2O$ or 91 mg (57%) * of VIc ($A = PF_6$) was prepared from IIc (129 mg, 0.2 mmol) and 0.3 ml of 75% aqueous HPF_6.

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[*] Low yields of VIb,c ($A = PF_6$) are probably due to formation of highly dispersed, precipitates which are difficult to filter.