UV photolysis of protonated ruthenium and osmium decamethylmetallocenes as a new method for synthesis of the metallonium cations $[\mathrm{C_5Me_5}\overline{\mathrm{MC_5Me_4CH_2}}]^+$ (M = Ru, Os)

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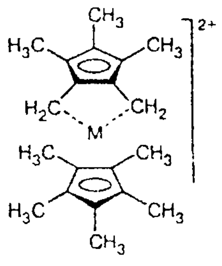
Decamethylmetallocenes Cp^*_2M (M = Ru, Os) in the presence of acids (CF_3CO_2H, CF_3SO_3H) give the protonation products $[Cp^*_2MH]^+An^-$. Broad-band UV photolysis of their solutions results in the formation of the salts of onium cations $[Cp^*\overline{MC_5Me_4CH_2}]^+An^-$. A preparative procedure for the synthesis of these salts has been developed. Hydrolysis of the salts gives the carbinol $Cp^*MC_5Me_4CH_2OH$.

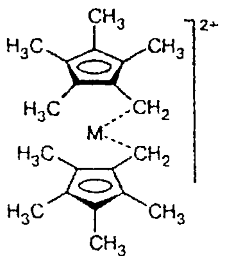
Key words: decamethylruthenocene, decamethylosmocene, protonation, UV photolysis, metallonium cations, hydrolysis, NMR spectra.

Many bis(cyclopentadienyl) complexes of transition metals Cp_2M, being Lewis bases, are readily protonated at the metal atom under the action of strong protic acids. The basicity of the metal atom in these complexes is due to unshared electron pairs, and the protonation products that formed are unique onium compounds. The protonation of permethylmetallocenes Cp^*_2M (Cp^* = C_5Me_5) (**1**) occurs especially easily. As shown for compounds of the iron subgroup (Fe, Ru, Os) with three unshared electron pairs, the metal atoms are readily protonated by such acids as CF_3CO_2H, CF_3SO_3H, and HPF_6[1–3] and capable of intramolecular donor-acceptor interaction with the α-carbocationic center preliminarily introduced into the cyclopentadienyl ring.[4,5] This results in the formation of salts of chelate metallonium cations $[Cp^*\overline{MC_5Me_4CH_2}]^+An^-$ (**2**, M = Ru (**a**), Os (**b**)). Using these compounds, we have shown for the first time that the $M-CH_2$ bond, according to the X-ray diffraction analysis data, has the standard σ-bond length,[6,7] and the MO calculation indicates that the positive charge is mainly localized on the metal atom.[8] Moreover, it is possible to generate metallonium dications **3a,b** and **4a,b** in which two carbocationic centers are bound to one metal atom,[9] *i.e.*, two unshared electron pairs of the metal atoms participate simultaneously in the donor-acceptor interaction.

Metallonium salts **2a,b** have been obtained by us for the first time from the corresponding carbinols $Cp^*MC_5Me_4CH_2OH$[10–11] synthesized in two stages from Cp^*_2M (**1a**, M = Ru; **1b**, M = Os). An alternative synthesis of **2a** from decamethylruthenocene (**1a**) by its oxidation with silver salts was reported.[12] We extended this method to decamethylosmocene (**1b**).[13]



3a,b



4a,b

In this work, we developed a new one-step method for the synthesis of salts **2a,b** by the UV irradiation of **1a,b** in the presence of strong protic acids. This method is very promising, because it not only gives monocations **2a,b**, but also, as the preliminary results showed, makes it possible to go from monocations **2a,b** to products of their subsequent transformation, onium dications **3a,b** and **4a,b**.

Results and Discussion

UV photolysis of protonation products has been studied[14] for the first time for cationic dihydride $[Cp^*_2ReH_2]^+BF_4^-$, whose irradiation resulted in the formation of the salt $[Cp^*Re(H)C_5Me_4CH_2]^+BF_4^-$.

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Based on these data, we studied the broad-band UV photolysis (irradiation with the light of a mercury lamp) of metallocenes **1a,b** in the presence of strong protic acids (CF_3CO_2H or CF_3SO_3H) and placed into sealed

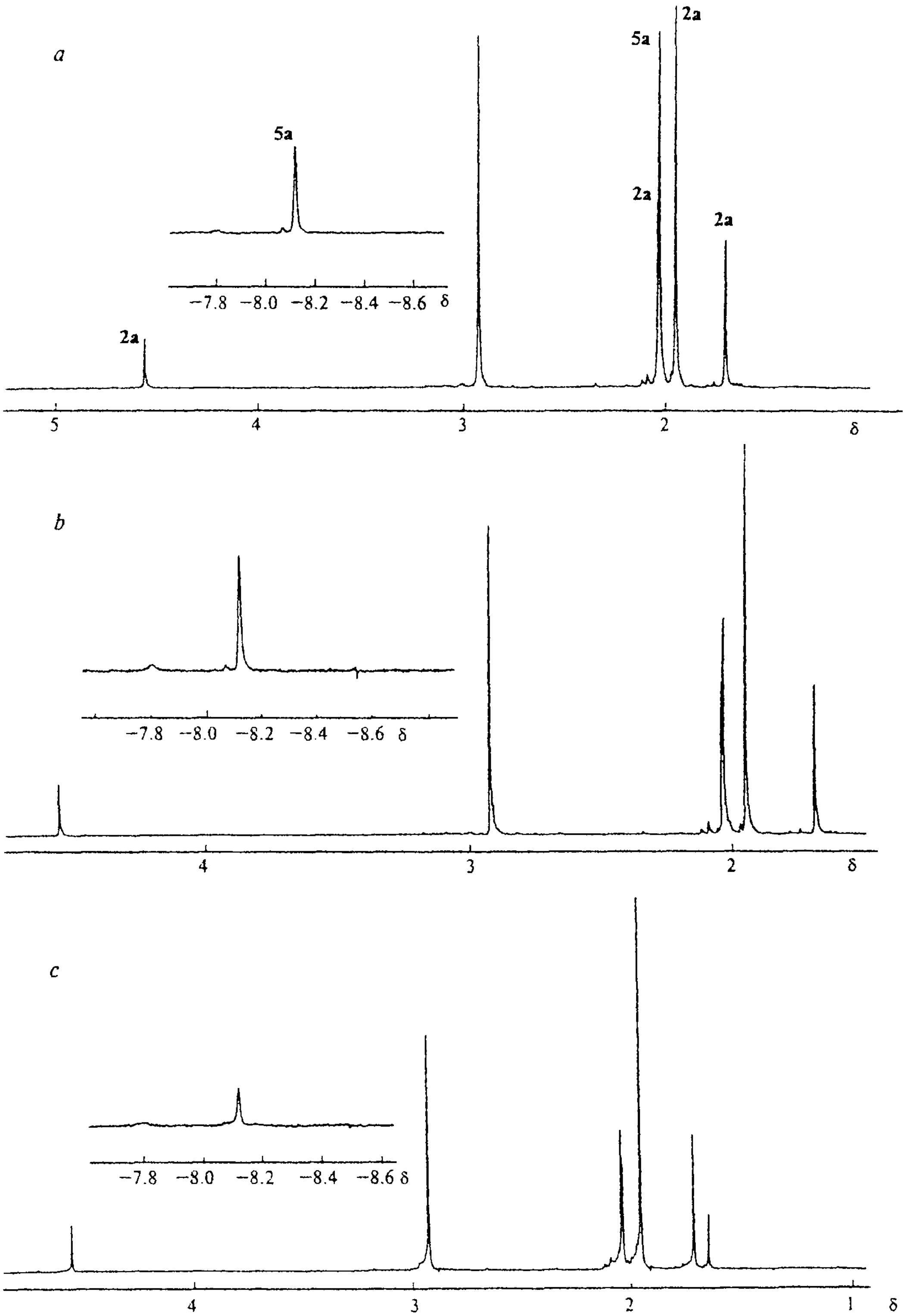


Fig. 1. ^{1}H NMR spectra for monitoring of irradiation of the $(C_5Me_5)_2Ru-CF_3SO_3H-KOAc$ reaction mixture, *hν*: 5 (*a*); 10 (*b*), and 15 h (*c*). Chemical shift (δ) of protons of the CH_3CO_2 group is 2.93 ppm.

Table 1. Data of ^1H NMR spectra of ruthenium and osmium complexes in various media

Entry	Complex	Medium	δ				
			C_5Me_5	$C_5Me_4CH_2$			RuH
				α-Me	β-Me	CH_2	
1	**2a**	CF_3CO_2H	2.25	2.00	2.35	4.84	
2	**2a**	CF_3SO_3H	1.97	1.72	2.05	4.58	
3	**2a**	CF_3SO_3H/oleum	1.92	1.67	2.01	4.53	
4	**2a**[a]	$CDCl_3$	1.77	1.54	1.86	4.46	
5	**2a**[b]	$CDCl_3$	1.78	1.55	1.86	4.51	
6	**2a**[c]	CD_2Cl_2	1.86	1.63	1.96	4.75	
7	**5a**	CF_3CO_2H	2.34				−7.83
8	**5a**	CF_3SO_3H	2.05				−8.11
9	**5a**	CF_3SO_3H/oleum	2.01				−8.15
10	**2b**	CF_3CO_2H	2.57	2.24	2.51	5.04	
11	**2b**	CF_3SO_3H/oleum	1.89	1.56	1.82	4.36	
12	**2b**[d]	CD_2Cl_2	1.90	1.59	1.83	4.40	
13	**2b**[d]	CD_3CN	1.92	1.61	1.86	3.78	
14	**5b**	CF_3CO_2H	2.51				−15.11
15	**5b**	CF_3SO_3H/oleum	2.13				−15.41[e]
16	**5b**[d]	CD_2Cl_2	1.99				−15.62
17	**5b**[d]	CD_3CN	2.02				−15.48

[a] An = $CF_3CO_2^-$. [b] An = $CF_3SO_3^-$. [c] Complex **2a** with An = PF_6^- was obtained by the method described in Ref. 10. [d] An = PF_6^-. [e] $\Delta\nu_{1/2}$ ~ 180 Hz.

glass tubes. The reaction course was monitored by periodical recording of the ^1H NMR spectra of these solutions. Upon dissolution in acids, metallocenes **1a,b** are immediately transformed into cationic hydrides $(Cp^*_2MH)^+An^-$ (**5a,b**). Since hydride **5b** is much more stable than hydride **5a** and can be isolated in the individual state,[3] we also studied the UV photolysis of hydride **5b** in neutral media. When acidic or neutral solutions are irradiated, salts **2a,b** are formed, and their characteristic resonance signals appear in the ^1H NMR spectra. As the reaction proceeds, the integral intensities of the signals of hydrides **5a,b** decrease and those of salts **2a,b** increase (Fig. 1). The data of the ^1H NMR spectra of the cationic Ru and Os complexes under study are presented in Table 1, and the changes in the ratios of **2a,b** and **5a,b** over time for Ru and Os are presented in Tables 2 and 3, respectively.

The differences in the behavior of solutions of **1a** and **1b** in the acids used are manifested in both the protonation stage and the rate of formation of reaction products **2a,b** during photolysis. For example, during dissolution in CF_3CO_2H, **1a,b** are completely transformed into hydrides **5a,b** (entry 1, Tables 2 and 3). At the same time, in the case of **1a**, monocation **2a** is formed along with hydride **5a** in a solution of CF_3SO_3H even without UV irradiation (Table 2, entry 5), and when the CF_3SO_3H/oleum mixture, with stronger oxidative properties is used, the amount of monocation **2a** increases substantially (Table 2, entry 10). By contrast, no transformation of **1b** into monocation **2b** was observed without irradiation in a similar system (Table 3, entry 3).

In the consideration of the specific features of the UV photolysis, it should be noted that the formation of monocation **2a** in CF_3SO_3H is retarded to a greater extent than that in a solution of CF_3CO_2H (Table 2, *cf.* entries 2 and 6, entries 3 and 7, and especially entries 4 and 7). The highest yield of **2a** (content in the mixture up to 90%) can be obtained by the addition of KOAc to a solution of CF_3SO_3H and irradiation of the mixture for 15 h (Table 2, entry 9, Fig. 1) or using the

Table 2. Protonation and UV photolysis of Cp^*_2Ru (0.1 mmol) (**1a**) in various media

Entry	Medium	τ[a]/h	Distribution of complexes (% of total sum)	
			5a	**2a**
1	CF_3CO_2H	—	100	—
2	CF_3CO_2H	15	33	67
3	CF_3CO_2H	30	10	90
4	CF_3CO_2H	45	6	94
5	CF_3SO_3H	—	78	22
6	CF_3SO_3H	15	44	56
7	CF_3SO_3H	35	19	81
8	CF_3SO_3H, KOAc[b]	5	31	69
9	CF_3SO_3H, KOAc	15	8	92
10	CF_3SO_3H[c] /oleum	—	21	79[d]
11	CF_3SO_3H /oleum	3	7	93[d]

[a] τ is irradiation time.
[b] KOAc, 0.16 mmol.
[c] CF_3SO_3H, 3.81 mmol; oleum, 0.024 g.
[d] Dications **3a** and **4a** are formed (6—9% with respect to **2a**).

Table 3. Protonation and UV photolysis of $Cp^*{}_2Os$ (0.1 mmol) (**1b**) or $[Cp^*{}_2OsH]^+PF_6^-$ (**5b**) in various media

Entry	Starting complex	Medium	τ^a/h	Distribution of complexes (% of total sum)		
				1b	**5b**	**2b**
1	**1b**	CF_3CO_2H	—		100	
2	**1b**	CF_3CO_2H	15	15^b	57	28^c
3^d	**1b**	CF_3SO_3H /oleum	—		100	
4	**1b**	CF_3SO_3H /oleum	15		18	82^c
5	**5b**	CD_2Cl_2	8	18	32	50
6	**5b**	CD_3CN	8	8	26	66
7	**5b**	CH_3CN	15	7	2	91

[a] τ is irradiation time.

[b] The amount of $[Cp^*{}_2Os]^{+\cdot}CF_3CO_2^-$ (**6b**) is indicated instead of **1b**.

[c] Dications **3b** and **4b** are formed along with the products indicated.

[d] $Cp^*{}_2Os$, 0.046 mmol; acid, 3.28 mmol; and oleum, 0.096 g.

CF_3SO_3H/oleum mixture and irradiation for 3 h (Table 2, entry 11). At the same time, for **1b**, the content of monocation **2b** in CF_3CO_2H was only 28% (Table 3, entry 2) and 82% for the CF_3SO_3H/oleum mixture (entry 4).

It is noteworthy that when oleum is used, dicationic products **3a,b** and **4a,b** are formed in minor amounts (which is indicated by the appearance of signals in the region of $\delta > 4.77$ in the ^1H NMR spectrum).[9]

The comparison of the behavior of Ru (**5a**) and Os hydrides (**5b**) during irradiation in CF_3CO_2H (Tables 2 and 3, entry 2) or in the CF_3SO_3H/oleum mixture (Table 2, entry 11 and Table 3, entry 4) shows that monocation **2a** is formed more easily than **2b**. This agrees with the data of theoretical calculations[15] indicating that the strength of the M—H bond for Ru is much lower than that for Os.

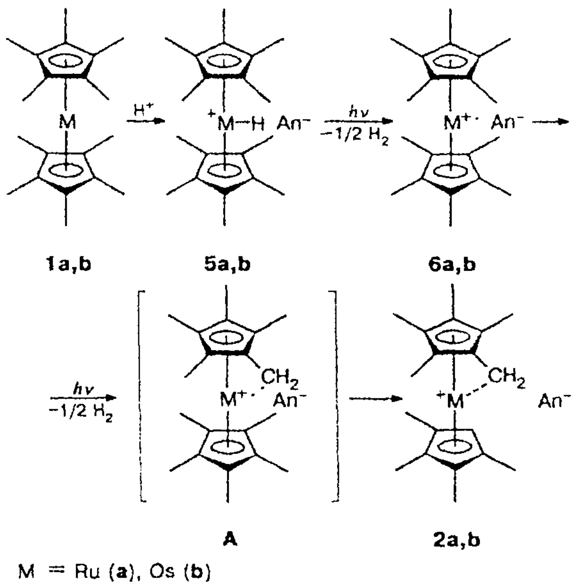
Using the stability of hydride **5b** and the possibility of obtaining it in the pure state,[3] we performed the photolysis of **5b** in neutral solvents (CD_2Cl_2, CH_3CN). In this case, monocation **2b** is also formed in a high yield (Table 3, entries 5—7). Thus, this experiment shows that cationic hydride **5b** is an intermediate product in the formation of monocation **2b** in both acidic and neutral media.

It is noteworthy that when the reaction of **1b** is carried out in CF_3CO_2H (Table 3, entry 2), the radical cation decamethylosmocenium $[Cp^*{}_2Os]^{+\cdot}$ (**6b**) is detected. The formation of **6b** is indicated by the signal at 23.54 ppm ($\Delta\nu_{1/2} \sim 667$ Hz) (*cf.* Ref. 16) in the ^1H NMR spectrum.

Thus, not only the stage of formation of cationic hydride **5a,b**, but also the stage of transformation of hydrides into metallocenium compounds **6a,b**, should be included in the possible mechanism of the reaction studied (Scheme 1). It is known that **6a** in a solution is rapidly transformed into monocation **2a**, whereas **6b** is sufficiently stable[16]; therefore, probably, **6b** can be detected in our experiments. It can be assumed that the transformation of metallocenium salts **6a,b** into monocations **2a,b** occurs through an intermediate species **A**, the possibility of which has been discussed previously.[4]

Based on the experimental ^1H NMR data obtained, we developed a preparative method for the synthesis of salts **2a** (An = $CF_3CO_2^-$, $CF_3SO_3^-$) in 79 and 78% yields, respectively. It is noteworthy that these salts are poorly soluble in water, and hence, they precipitate from acidic solutions upon partial neutralization of the acid by an aqueous solution of KOH. The salts isolated were characterized by ^1H (Table 1, entries 4 and 5) and ^{19}F NMR spectra (see Experimental). Because of a poor solubility of salts **2a** with the $CF_3CO_2^-$ and $CF_3SO_3^-$ anions in an aqueous medium, their hydrolysis to carbinol $Cp^*RuC_5Me_4CH_2OH$ (**7**) requires heating and a longer time as compared to the known procedure.[12] Carbinol **7** was obtained in 80% yield.

Scheme 1



The method developed by us for the preparation of salts **2a,b** provides new preparative possibilities for the synthesis of carbinols from permethylmetallocenes **1a,b**.

To identify carbinol **7**, we used the ^1H NMR spectra (Table 4) and the mass spectrum. It can be seen from the ^1H NMR spectrum that carbinol **7** in a solution of $CDCl_3$ exists as two conformers **7a** and **7b** with intramolecular (Ru...HO—) and intermolecular (—OH...OH) hydrogen bonds. As should be expected, the **7a** : **7b** ratio depends on the concentration of carbinol **7** in $CDCl_3$. The ratio of the conformers **7a** : **7b** increases (4.0—5.8—14.0) upon

Table 4. Data of ^1H NMR spectra of conformers $C_5Me_5RuC_5Me_4CH_2OH$ (7) in various media

Solvent	Conformer	δ					**7a** : **7b**
		C_5Me_5	α-Me	β-Me	CH_2	OH	
$CDCl_3$	**7a***	1.642	1.642	1.594	3.881	4.008	3.67
	7b	1.677	1.720	1.636	4.000	3.973	
$CDCl_3$ + + CD_3OD	**7a**	1.548	1.554	1.515	3.804	—	1.66
	7b	1.573	1.621	1.540	3.909	—	

* *Cf.* Refs. 4 and 12.

dilution of the solution (0.068—0.034—0.017 mol L^{-1}), and when a hydroxyl-containing solvent (CD_3OD) is added, this ratio decreases (Table 4). The amount of the conformer with intermolecular hydrogen bonds, *i.e.*, **7b**, should decrease upon dilution.

Thus, **7a** with the intramolecular hydrogen bond is the main conformer of carbinol in the solution. This result agrees with the data of the IR spectra of carbinol 7 in CCl_4, which show the strong Ru...HO— hydrogen bond.[17]

Experimental

^1H NMR spectra were recorded on Bruker WP-200SY (200.13 MHz) or Bruker AMX-400 (400.13 MHz) spectrometers in solutions of CD_2Cl_2 or $CDCl_3$ relative to Me_4Si. C_6D_6 (98% D) was used as the external standard for solutions of acids. ^{19}F NMR spectra were recorded on a Bruker WP-200SY spectrometer (188.31 MHz) using CF_3COOH as the external standard. Mass spectra (EI) were obtained on an MS-890 instrument (70 eV, 250 °C, direct injection of the sample) in a $CDCl_3$ solution.

Protonation and photolysis were carried out in NMR tubes filled with argon. A weighed sample of **1a,b** (~0.1 mmol) and acid (3—4 mmol) were placed in an tube, which was then sealed. An OKN-11 (850 W) mercury lamp was used for UV photolysis. The ratio of reaction products was calculated from the ^1H NMR spectra using the integral value per proton of each compound, and the total sum was taken as 100%. The amount of nonidentified substances was not higher than ~5%.

^1H NMR, δ, **1a** (CD_2Cl_2): 1.62; **1b** (CD_2Cl_2): 1.87; **1b** (CD_3CN): 1.87.

Oleum (60%) was used in the reaction.

Preparation of $[C_5Me_5\overline{RuC_5Me_4C}H_2]^+CF_3SO_3$ (2a). $Cp^*{}_2Ru$ (**1a**) (0.17 mmol), CF_3SO_3H (5.62 mmol), and KOAc (0.29 mmol) were placed in an ampoule. The mixture was irradiated for 20 h and neutralized with an aqueous solution of KOH during cooling to precipitation. The precipitate was separated, washed with ether, and dried. Compound **2a** (0.069 g, 0.133 mmol, 78%) was obtained. The solution was treated with alkali to the neutral reaction and extracted with ether. After evaporation of the ether and drying, compound **1a** was obtained (0.006 g, 0.016 mmol, 9%). ^{19}F NMR spectrum of the $CF_3SO_3^-$ anion ($CDCl_3$), δ: −1.07.

Preparation of $[C_5Me_5\overline{RuC_5Me_4C}H_2]^+CF_3CO_2$ (2a). Compounds **2a** (0.0156 g, 0.032 mmol, 79%) and **1a** (0.0011 g, 0.003 mmol, 7%) were obtained similarly from **1a** (0.041 mmol) and CF_3CO_2H (3.78 mmol) by irradiation for 45 h followed by neutralization with an aqueous solution of KOH. ^{19}F NMR spectrum of the $CF_3CO_2^-$ anion ($CDCl_3$), δ: 2.49.

Preparation of $C_5Me_5RuC_5Me_4CH_2OH$ (7). Similarly, a solution of **1a** (0.097 mmol), CF_3SO_3H (3.81 mmol), and oleum (0.024 g) was irradiated for 3 h. An aqueous solution of KOH was added to the mixture to the alkaline reaction, and the solution was heated (40—50 °C) for 8 h. Compound **7** (0.0302 g, 0.078 mmol, 80%) was isolated by filtration. MS, *m/z* (I_{rel} (%)): 388 $[M]^+$ (19), 386 $[M - 2H]^+$ (32), 371 $[M - OH]^+$ (73), 357 $[M - CH_2OH]^+$ (100), 233 $[Cp^*Ru^+ - 4H]$ (25) (*cf.* Ref. 12).

Preparation of $[C_5Me_5\overline{OsC_5Me_4C}H_2]^+PF_6$ (2b). A solution of $[Cp^*{}_2OsH]^+PF_6^-$ (**5b**) (0.22 g, 0.36 mmol) in CH_3CN (50 mL) was placed into a two-neck flask and irradiated with stirring on a magnetic stirrer for 15 h. After evaporation, the solid residue (0.20 g) was analyzed by ^1H NMR in CD_2Cl_2 (Table 3, entry 7). The yield of **2b** was 84%.

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