

CYCLOPENTADIENYLIDE COMPLEXES OF GROUP VII METALS

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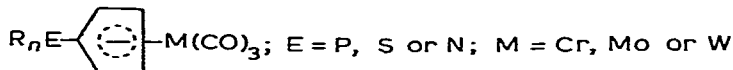
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Summary

$[(\text{CH}_3)_2\text{SC}_5\text{H}_4\text{Re}(\text{CO})_3]^+\text{PF}_6^-$ and $[\text{Ph}_3\text{PC}_5\text{H}_4\text{Re}(\text{CO})_3]^+\text{PF}_6^-$ were obtained by interaction of dimethylsulphonium- and triphenylphosphoniumcyclopentadienylides with $[(\text{CH}_3\text{CN})_3\text{Re}(\text{CO})_3]^+\text{PF}_6^-$. IR, mass, ^1H and ^{13}C NMR spectra of the complexes obtained and their manganese analogues are reported.

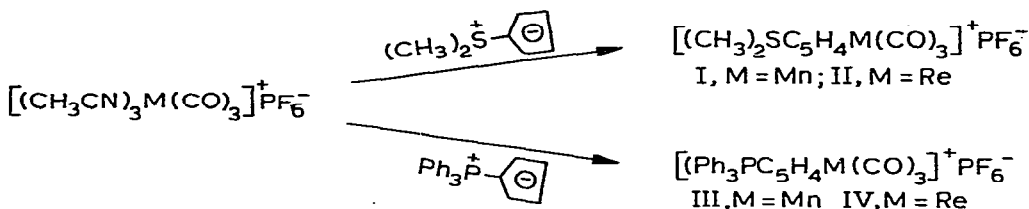
Cyclopentadienylides containing P, S and N onium atoms form complexes with carbonyls of Group VI metals or with their derivatives, in which the five-membered ylide ring is a donor of 6π -electrons [1–3].



Dimethylsulphonium- and triphenylphosphoniumcyclopentadienylides also interact with the acetonitrile derivative of manganese $[(\text{CH}_3\text{CN})_3\text{Mn}(\text{CO})_3]^+\text{PF}_6^-$ forming salt-like complexes [4]. The present study is concerned with the reaction of cyclopentadienylides with $[(\text{CH}_3\text{CN})_3\text{Re}(\text{CO})_3]^+\text{PF}_6^-$ and with comparison of the physico-chemical properties of Mn and Re cyclopentadienylide derivatives.

Synthesis of complexes was carried out according to Scheme 1:

SCHEME 1



It should be noted that, unlike the manganese analogue, $[(\text{CH}_3\text{CN})_3\text{Re}(\text{CO})_3]^+\text{PF}_6^-$ reacts with cyclopentadienylides only on boiling the reaction mixture in THF.

TABLE 1

MOLAR CONDUCTIVITY^a AND DISSOCIATION DEGREE^b OF Mn AND Re CYCLOPENTADIENYLIDE COMPLEXES

[Ph ₃ PC ₅ H ₄ M(CO) ₃] ⁺ PF ₆ ⁻				[(CH ₃) ₂ SC ₅ H ₄ M(CO) ₃] ⁺ PF ₆ ⁻			
M	C _M × 10 ³ (mol/l)	Λ _M (ohm ⁻¹ cm ² mol ⁻¹)	α	M	C _M × 10 ³ (mol/l)	Λ _M (ohm ⁻¹ cm ² mol ⁻¹)	α
Mn	1.1	144	0.49	Mn	1.0	140	0.37
Re	1.0	120	0.30	Re	0.7	140	0.20

^a In acetone. ^b In methyl ethyl ketone.

Complexes I–IV are crystalline substances that are readily soluble in acetone, THF, moderately in methanol and ethanol and insoluble in nonpolar solvents. In the solid state they are air stable, while in solution they gradually decompose. Acetone solutions of I–IV are conductive, the molar conductivity at 1 × 10⁻³ mole/l (Table 1) being close to the average value of Λ_M = 120 ohm⁻¹ cm² mol⁻¹ for binary electrolytes of coordination compounds [5].

The dissociation degrees of I–IV in methyl ethyl ketone* (Table 1) were calculated from the molecular weights determined ebullioscopically. Comparison of α values shows that rhenium cyclopentadienylide complexes are weaker electrolytes than similar manganese compounds and that triphenylphosphoniumcyclopentadienylide complexes are more dissociated in solution than dimethylsulphonium cyclopentadienylide complexes with the same central metal atom.

The IR, mass and NMR (¹H and ¹³C) spectra were studied to establish the structures of I–IV.

Since salts of organic compounds are usually non-volatile, mass spectrometric identification of such compounds is carried out by analysis of thermal decomposition products.

The most stable mass spectra were obtained at sample inlet temperatures of 135–175°C for I and II and of 180–200°C for III and IV.

The heaviest ions in the mass spectra of I and II are [CH₃SC₅H₄M(CO)₃]⁺ (A⁺) ions to which may be assigned the structure of thiomethyl derivatives of the corresponding cyclopentadienylmetal carbonyl complexes formed as a result of thermolysis of the initial compounds.

Ions A⁺, similar to derivatives of cyclopentadienyltricarbonylmanganese and -rhenium [6], successively lose three carbonyl groups forming [CH₃SC₅H₄M(CO)_n]⁺ (n = 0–2) ions. Degradation of the intensive [CH₃SC₅H₄M]⁺ ions proceeds with elimination of CH₃ and SCH₃ leading to [SC₅H₄M]⁺ and [C₅H₄M]⁺ respectively (see Schemes 2 and 3). In the mass spectrum of II, but not I, decarbonylation of A⁺ is accompanied by loss of a CH₃ group yielding [SC₅H₄Re(CO)_n]⁺ ions (n = 0–3).

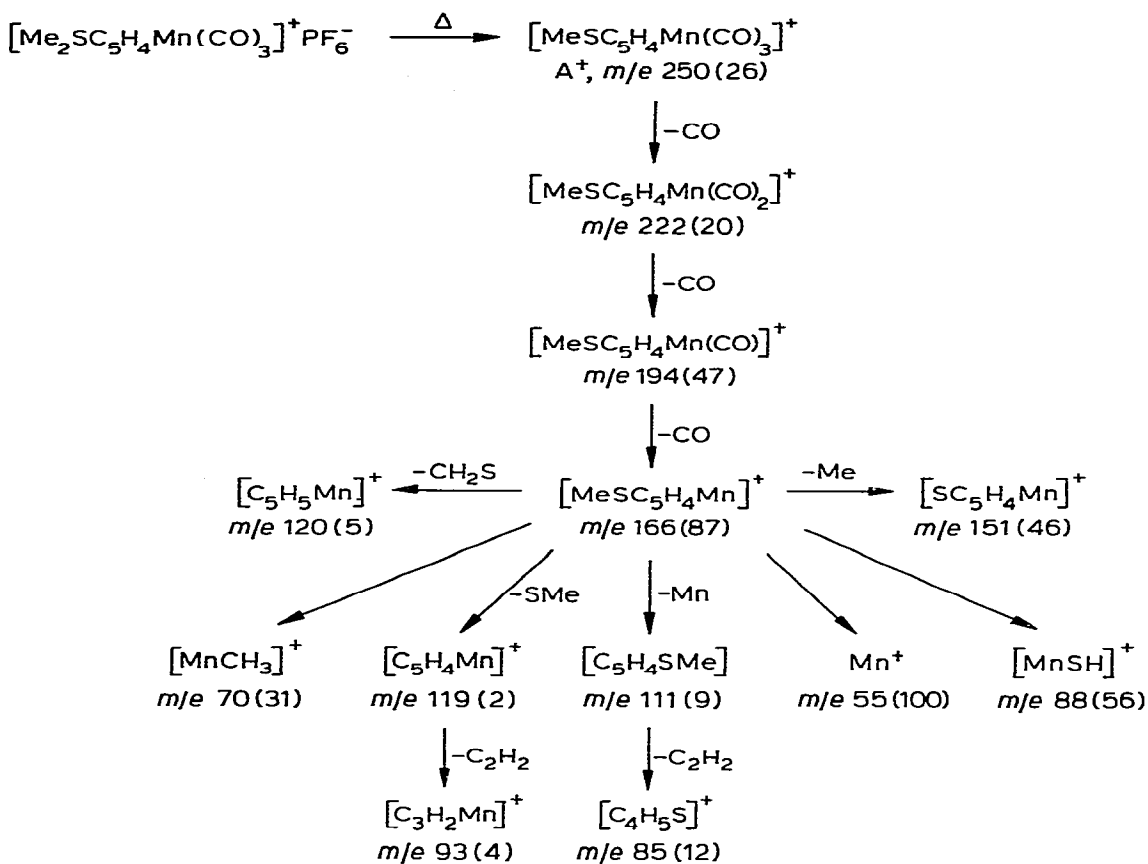
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* The dissociation degree was calculated as

$$\bar{M} = M_k \frac{\alpha}{1 + \alpha} + M_a \frac{\alpha}{1 + \alpha} + M_{ka} \frac{1 - \alpha}{1 + \alpha}$$

where α is the dissociation degree, \bar{M} is the experimental molecular weight, M_a and M_k are the calculated "molecular" weights of the cation and anion and M_{ka} is the calculated molecular weight of the salt.

SCHEME 2. (Relative intensities of the ions are given in parentheses.)



SCHEME 3. (Relative intensities of the ions are given in parentheses)

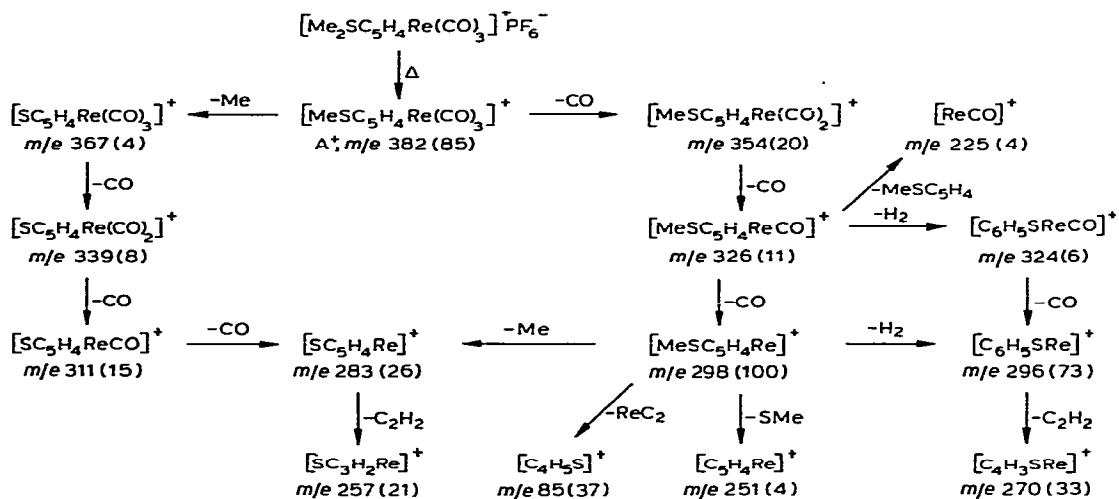

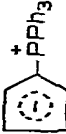


TABLE 2
PMR AND IR SPECTRA OF Mn AND Re CYCLOPENTADIENYLIDE COMPLEXES^a

Compound	Chemical shifts		$\nu(\text{CO})$ (cm^{-1})	Compound	Chemical shifts		$\nu(\text{CO})$ (cm^{-1})
	C ₅ H ₄	CH ₃			C ₅ H ₄	C ₆ H ₅	
	5.92 ^b 6.23	2.78			6.47 ^c	7.75	
$[(\text{CH}_3)_2\text{SC}_5\text{H}_4\text{Mn}(\text{CO})_3]^+\text{PF}_6^-$	5.47 6.23	3.55	1963 2042	$[\text{Ph}_3\text{PC}_5\text{H}_4\text{Mn}(\text{CO})_3]^+\text{PF}_6^-$	5.88	8.11	1963 2040
$[(\text{CH}_3)_2\text{SC}_5\text{H}_4\text{Re}(\text{CO})_3]^+\text{PF}_6^-$	6.15 6.90	3.57	1940 2022	$[\text{Ph}_3\text{PC}_5\text{H}_4\text{Re}(\text{CO})_3]^+\text{PF}_6^-$	6.27	7.92	1950 2038

^a PMR spectra were recorded in (CD₃)₂CO, IR spectra in (CH₃)₂CO. ^b in (CD₃)₂SO [9]. ^c in CDCl₃ [10].

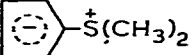
Additionally, the mass spectra of I and II exhibit sufficiently intensive $[\text{S}(\text{CH}_3)_2]^+$, PF_2^+ and PF_4^+ peaks which confirm the presence of $\text{S}(\text{CH}_3)_2$ and PF_6^- moieties in the original molecule.

More valuable information about the structure of the compounds studied is obtained from field desorption mass spectra (FDMS). The presence of $[(\text{CH}_3)_2\text{SC}_5\text{H}_4\text{Mn}(\text{CO})_3]^+$ (m/e 265) and associate ion $\{[(\text{CH}_3)_2\text{SC}_5\text{H}_4\text{Mn}(\text{CO})_3]_2\text{PF}_6\}^+$ (m/e 674) confirms the proposed structure. The relative intensity of $[\text{CH}_3\text{SC}_5\text{H}_4\text{Mn}(\text{CO})_3]^+$ ions increases with emitter current in FDMS, supporting our assumption that the presence of these ions in the electron impact mass spectrum is due to thermolysis of I.

In the mass spectra of III and IV the heaviest is the ligand ion $[\text{C}_5\text{H}_4\text{PPh}_3]^+$ (B^+) formed by thermal degradation of III and IV. Its fragmentation is identical to that of triphenylphosphoniumcyclopentadienylide and proceeds with formation of $\text{B}-\text{H}^+$ (m/e 325), PPh_3^+ (m/e 262), $\text{C}_{12}\text{H}_8\text{P}^+$ (m/e 183), $\text{C}_{12}\text{H}_8^+$ (m/e 152), $\text{C}_6\text{H}_5\text{P}^+$ (m/e 108) and C_6H_5^+ (m/e 77).

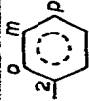
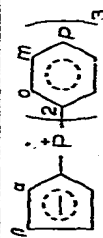
IR spectra of I–IV in solution exhibit two terminal CO stretching bands (Table 2) with frequencies close to $\nu(\text{C}=\text{O})$ for Mn and Re cyclopentadienyltricarbonyl derivatives. IR spectra of I–IV recorded in KBr pellets also show strong absorption at 830 cm^{-1} that is characteristic of the PF_6^- anion. PMR spectra of Mn and Re dimethylsulphoniumcyclopentadienylide complexes in deuterioacetone reveal two signals of α - and β -protons of the cyclopentadienyl ring, both being shifted upfield in the Mn complexes and downfield in the Re complexes in relation to the original ylide (Table 2). In the PMR spectra of triphenylphosphoniumcyclopentadienylide complexes of Group VII metals proton signals of the cyclopentadienyl ring are observed in the form of multiplets the centres of which are slightly shifted upfield (by 0.2–0.6 ppm) as compared with the initial ylide (Table 2). The most important information concerning the change of electron density in π -ligands of these complexes was obtained while studying ^{13}C NMR spectra. It has been shown previously that coordination of cyclopentadienylides with Group VI metals leads to appreciable levelling of the electron density on the ylide cyclopentadienyl ring along with a general increase of shielding of carbon nuclei of this fragment [7]. Unlike cyclopentadienylide complexes of Group VI metals, similar carbonyl derivatives of Group VII metals are salt-like

TABLE 3
 ^{13}C $\{^1\text{H}\}$ NMR SPECTRA OF DIMETHYLSULPHONIUMCYCLOPENTADIENYLIDE COMPLEXES WITH Mn AND Re CARBONYLS (IN ACETONE)

Compound	$\pi\text{-C}_5\text{H}_4$		CH_3		δ CO (ppm)		
	δ C_1 (ppm)	$\Delta\delta$ C_1^b (ppm)	δ C_α and C_β (ppm)	$\Delta\delta^b$ C_α and C_β (ppm)			
	85.4 ^a		111.4 109.3		34.2		
$[(\text{CH}_3)_2\text{SC}_5\text{H}_4\text{Mn}(\text{CO})_3]^+\text{PF}_6^-$	84.4	1.0	85.5 89.3	25.9–20.0	30.3	3.9	222.5
$[(\text{CH}_3)_2\text{SC}_4\text{H}_5\text{Re}(\text{CO})_3]^+\text{PF}_6^-$	85.8	–0.4	87.7 92.1	23.7–17.2	32.1	2.1	191.5

^a In $(\text{CH}_3)_2\text{SO}$ [7]. ^b $\Delta\delta = \delta_{\text{ylide}} - \delta_{\text{complex}}$.

TABLE 4
 ^{13}C $\{^1\text{H}\}$ NMR SPECTRA OF TRIPHENYLPHOSPHONIUMCYCLOPENTADIENYLIDE COMPLEXES
 WITH Mn AND Re CARBONYLS

Compound	$\pi\text{-C}_5\text{H}_4$		$\Delta\delta$		δ C_α and C_β (ppm)	$\Delta\delta$ C_α and C_β^c (ppm)				δ CO (ppm)
	δ C_1^c (ppm)	$\Delta\delta$ C_1 (ppm)	δ C_1 (ppm)	$\Delta\delta$ C_1 (ppm)			δ C_2 (ppm)	δ $\text{C}_\alpha, \text{C}_\gamma$ (ppm)	δ C_β (ppm)	
 $[\text{Ph}_3\text{PC}_5\text{H}_4\text{Mn}(\text{CO})_3]^+\text{PF}_6^-$	78.0 ^a (112) ^b		116.8(16) 114.5(16)				126.7 (93)	129.0(13) 133.7(12)	132.0	
	75.6 (101)	2.4	88.4(10) 93.3(10)	28.4-21.2	119.0 (88)	131.2(13) 134.9(12)	136.6		222.4	
$[\text{Ph}_3\text{PC}_5\text{H}_4\text{Re}(\text{CO})_3]^+\text{PF}_6^-$	82.1 (99)	-4.1	90.7(9) 95.8(10)	26.1-18.9	119.0 (81)	131.3(13) 134.9(10)	136.6		191.2	

^aIn CH_2Cl_2 [7]. ^b $J(^{13}\text{C}-^31\text{P})$ values (Hz) are given in parentheses. ^c $\Delta\delta = \delta_{\text{ylide}} - \delta_{\text{complex}}$.

compounds. Consequently, shielding the π -ligand carbons in these complexes affects not only coordination with the metal but also the positive charge. It follows from the data of Tables 3 and 4 that cyclopentadienyl α - and β -carbon nuclei are noticeably more shielded in I–IV than in the corresponding uncomplexed ylides. It should be noted that the difference in shielding, in manganese

$$\Delta\delta_{\alpha,\beta} = \delta_{\text{ylide}} - \delta_{\text{complex}}$$

and rhenium derivatives practically coincides with that of similar Group VI metal compounds. Thus, for dimethylsulphoniumcyclopentadienylide complexes of Mn and Re $\Delta\delta_{\alpha,\beta} = 17.2\text{--}25.9$ ppm and for complexes of the same ylide with Cr, Mo and W carbonyls $\Delta\delta_{\alpha,\beta} = 17.9\text{--}25.8$ ppm [7]. In the case of triphenylphosphoniumcyclopentadienylide derivatives of Group VII metals $\Delta\delta_{\alpha,\beta} = 18.9\text{--}28.4$ ppm and for Group VI metals $\Delta\delta_{\alpha,\beta} = 19.6\text{--}29.5$ ppm [7]. Under the effect of complexation signals of key cyclopentadienyl carbons (C_1) are shifted to a considerably lesser extent in complexes I–IV: by 1.0–2.0 ppm upfield in manganese complexes and by 0.4–4.1 ppm downfield in rhenium complexes. As a result shielding of all cyclopentadienyl carbon nuclei is equalized in ylide complexes of Group VII metals, as is the case with similar compounds of Group VI metals. The values of spin-spin coupling constants $J(^{13}\text{C}_1\text{--}^{31}\text{P})$ for Mn and Re triphenylphosphoniumcyclopentadienylide complexes, 101 and 99 Hz, are close to the constants of the same complexes of Group VI metals (109–112 Hz). Presumably, the order of $C_1\text{--P}$ bonds in III and IV is approximately the same as in similar Cr, Mo and W complexes.

Therefore, it may be assumed on the basis of ^{13}C NMR spectra of Mn and Re cyclopentadienylide complexes that the π -ligand resembles in structure the π -ligands in corresponding derivatives of Group VI metals and that the effect of charge is insignificant.

Experimental

IR spectra were obtained on UR-20 instrument, PMR spectra on an R-12 Perkin–Elmer spectrometer (60 MHz) with HMDS as internal reference. ^{13}C $\{^1\text{H}\}$ NMR spectra were recorded on an HX-90 Bruker instrument (22.63 MHz) with Fourier transform, proton decoupling and noise modulation. Ampoules for NMR spectrometry were filled under argon. Electron impact mass spectra were obtained on an AEI MS-30 instrument using a system of direct sample inlet, at an ionization chamber temperature of 250°C and an ionization voltage of 70 eV. DS-50 data processing system was used.

Field desorption mass spectra were recorded with a CH5 instrument, using acetone as solvent. Emitter current was 10–18 mA.

The following values of experimental molecular weight were obtained ebullioscopically in methyl ethyl ketone solution: 300 for I, 450 for II, 410 for III and 570 for IV. In conductivity and ^{13}C NMR measurements, spectroscopy grade acetone was used without further purification.

Dimethylsulphoniumcyclopentadienylide [11], triphenylphosphoniumcyclopentadienylide [12], manganese complexes I and II [4] and $\text{BrRe}(\text{CO})_5$ [13] were synthesized by the published procedures. NH_4PF_6 was prepared as described in [14]. All reactions and distillation of solvents were carried out under argon.

Acetonitrile was purified by multiple boiling over P_2O_5 and then by distillation over K_2CO_3 . Prior to reactions THF was distilled over $LiAlH_4$.

$[(CH_3CN)_3Re(CO)_3]^+PF_6^- *$

0.41 g (1.0 mmol) of $BrRe(CO)_5$ was boiled in 25 ml of acetonitrile for 4 h. 0.25 g (1.5 mmol) of NH_4PF_6 was dissolved in a mixture containing 2 ml of ethanol and 2 ml of water, then 0.25 g (1.5 mmol) of $AgNO_3$ was added and the suspension obtained was added to the reaction mixture. A white precipitate was formed immediately. The reaction mixture was stored overnight at $20^\circ C$. The precipitate was then filtered off and the solution was evaporated to dryness. The white solid substance obtained was boiled three times in CH_2Cl_2 each time filtering the solution. The solution in methylene chloride was evaporated to small volume and hexane was added. Cooling yielded white crystals of $[(CH_3CN)_3Re(CO)_3]^+PF_6^-$ (0.48 g, 90%); IR (acetone): 1955s, 2055s cm^{-1} ($\nu(C\equiv O)$) and 2300w, 2335w cm^{-1} ($\nu(C\equiv N)$). Lit. [15]: $\nu(C\equiv O)$ 1956, 2045 cm^{-1} (in $CHCl_3$).

$[(CH_3)_2SC_5H_4Re(CO)_3]^+PF_6^-$

A solution of 0.34 g (0.6 mmol) of $[(CH_3CN)_3Re(CO)_3]^+PF_6^-$ and 0.08 g (0.6 mmol) of $(CH_3)_2SC_5H_4$ in 60 ml of THF was boiled for 5 h. The reaction mixture turned turbid and dark. The dark precipitate was filtered off and the solution evaporated to dryness. The dark oil with crystals obtained was boiled in 96% ethanol. The solution was then filtered, evaporated to small volume and cooled, yielding 0.06 g (18%) of II, m.p. $141-142^\circ C$ (with dec.) (twice recrystallized from ethanol). Found: C, 23.05, 23.22 **; H, 2.15; 2.00; S, 5.89; F, 21.12, 21.28; P, 5.98, 6.14. $C_{10}H_{10}F_6O_3PReS$ calcd.: C, 22.18; H, 1.85; S, 5.91; F, 21.07; P, 5.73%.

$[Ph_3PC_5H_4Re(CO)_3]^+PF_6^-$

A solution of 0.20 g (0.37 mmol) of $[(CH_3CN)_3Re(CO)_3]^+PF_6^-$ and 0.13 g (0.35 mmol) of $Ph_3PC_5H_4$ in 65 ml of THF was stored for 48 h at $\sim 20^\circ C$. After filtering off a small dark precipitate the reaction mixture was boiled for 5 h, evaporated to dryness and the dark crystals obtained boiled with methanol. The solution was then filtered, evaporated to small volume and cooled yielding 0.14 g (50%) of IV (violet crystals). Found: C, 41.82, 41.89; H, 2.49, 2.56; F, 15.78, 15.74. $C_{26}H_{19}F_6O_3P_2Re$ calcd.: C, 42.10; H, 2.56; F, 15.38%.

Acknowledgments

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* The compound was published in [15] but its synthesis was not described.

** The high values for carbon are apparently due to a small admixture of $CH_3SC_5H_4Re(CO)_3$.

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