Iron- and Ruthenium-Containing Triple-Decker Complexes with a Central Pentaphospholyl Ligand − X-ray Structures of $[(\eta\text{-}C_5H_5)Fe(\mu\text{-}\eta{:}\eta\text{-}P_5)Ru(\eta\text{-}C_5Me_5)]PF_6$ and $[(\eta\text{-}C_5Me_5)Ru(\mu\text{-}\eta{:}\eta\text{-}P_5)Ru(\eta\text{-}C_5Me_5)]PF_6$

Alexander R. Kudinov,*[a] **Dmitry A. Loginov,**[a] **Zoya A. Starikova,**[a] **Pavel V. Petrovskii,**[a]
Maddalena Corsini,[b] **and Piero Zanello**[b]

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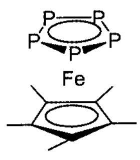
Triple-decker cationic complexes with a central pentaphospholyl (pentaphosphacyclopentadienyl) ligand $[Cp^{*}M(\mu\text{-}\eta{:}\eta\text{-}P_5)M'(\eta\text{-}C_5R_5)]^+$ (**3b**: M = M′ = Fe, R = Me; **4a**: M = Ru, M′ = Fe, R = H; **4b**: M = Fe, M′ = Ru, R = H; **4c**: M = Fe, M′ = Ru, R = Me; **5a**: M = M′ = Ru, R = H; **5b**: M = M′ = Ru, R = Me) were synthesized by exploitation of the stacking reactions of pentaphosphametallocenes $Cp^{*}M(\eta\text{-}P_5)$ (**1**: M = Fe; **2**: M = Ru) with half-sandwich fragments $[(\eta\text{-}C_5R_5)M']^+$. They were isolated as salts with BF_4^- or PF_6^- anions, and the structures of **4a**PF_6 and **5b**PF_6 were determined by X-ray diffraction. Triple-decker complexes with a central pentaphospholyl ligand are less reactive in nucleophilic degradation reactions than analogous complexes with C_4Me_4P and Cp^{*} ligands in the bridging position. Only **4a** and the previously known analogue **3a** (M = M′ = Fe, R = H), containing the CpFe fragment, are nucleophilically destroyed by MeCN and NaI. The electrochemical properties of **2**, **3a**, **3b**, **4a**–**c**, **5a** and **5b** and the related cobalt-containing complexes $[(\eta\text{-}C_4Me_4)Co(\mu\text{-}\eta{:}\eta\text{-}P_5)MCp^{*}]^+$ (**6**: M = Fe; **7**: M = Ru) were investigated.

Introduction

Several examples of triple-decker complexes with a central pentaphospholyl (pentaphosphacyclopentadienyl) ligand (*cyclo*-P_5) are known.[1] The first complexes of this type, $(\eta\text{-}C_5R_5)Cr(\mu\text{-}\eta{:}\eta\text{-}P_5)Cr(\eta\text{-}C_5R_5)$ (R = H, Me), were synthesized by Scherer[2] and other authors[3] by treatment of $[(\eta\text{-}C_5R_5)Cr(CO)_x]_2$ (x = 2, 3) with P_4. Scheer has prepared the similar complex $(\eta\text{-}C_5H_4tBu)Cr(\mu\text{-}\eta{:}\eta\text{-}P_5)Cr(\eta\text{-}C_5H_4tBu)$ by treatment of $K[(\eta\text{-}C_5H_4tBu)Cr(CO)_3]$ with $Cr(CO)_5PCl_3$.[4]

A straightforward approach to the synthesis of triple-decker complexes is based on the use of stacking reactions of coordinatively unsaturated metal complex fragments with sandwich compounds.[5] In particular, this approach has proved to be very useful for the preparation of triple-decker complexes with a central *cyclo*-P_5 ligand. By using stacking reactions of pentaphosphaferrocene $Cp^*Fe(\eta\text{-}P_5)$ (**1**) with the fragments $[CpFe]^+$ and $(CO)_3M$ (M = Cr, Mo) Scherer has prepared the triple-decker complexes $[CpFe(\mu\text{-}\eta{:}\eta\text{-}P_5)FeCp^*]^+$ (**3a**) and $(CO)_3M(\mu\text{-}\eta{:}\eta\text{-}P_5)FeCp^*$.[6] We have described the synthesis of complex $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}\eta{:}\eta\text{-}P_5)FeCp^*]^+$ by treatment of **1** with the fragment $[(\eta\text{-}C_7H_7)Mo]^+$.[7]



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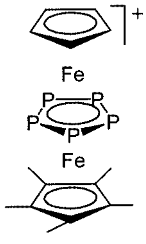

3a

We report here the results obtained in an extension of this approach to the preparation of new iron- and ruthenium-containing triple-decker complexes with a central pentaphospholyl ligand $[Cp^*M(\mu\text{-}\eta{:}\eta\text{-}P_5)M'(\eta\text{-}C_5R_5)]^+$ (M, M′ = Fe, Ru; R = H, Me),[8] together with their electrochemical and structural properties.

Results and Discussion

Synthesis of Triple-Decker Complexes

In 1987 we described the synthesis of the first 30 VE (valence electron) triple-decker complexes with a central cyclopentadienyl ligand $[Cp^*M(\mu\text{-}\eta{:}\eta\text{-}Cp^*)M'(\eta\text{-}C_5R_5)]^+$ (M = Fe, Ru, Os; M′ = Fe, Ru).[9] These compounds were synthe-

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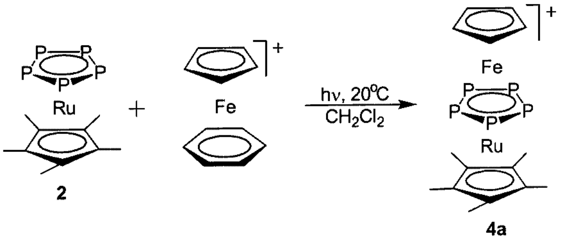
[a] A. N. Nesmeyanov Institute of Organoelement Compounds,
28 ul. Vavilova, 119991 Moscow, GSP-1, Russian Federation
Fax: (internat.) + 7-095/1355085
E-mail: arkudinov@ineos.ac.ru

[b] Dipartimento di Chimica, University of Siena,
Via Aldo Moro, 53100 Siena, Italy

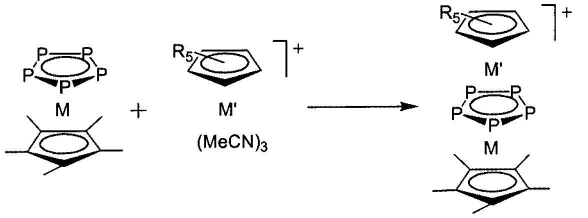
sized by exploitation of the stacking reactions of decamethylmetallocenes MCp^*_2 with the coordinatively unsaturated 12 VE half-sandwich fragments $[(\eta\text{-}C_5R_5)M']^+$. In particular, the iron-containing triple-decker complexes $[CpFe(\mu\text{-}\eta{:}\eta\text{-}Cp^*)MCp^*]^+$ were prepared by use of the $[CpFe]^+$ fragment, generated in situ by visible light irradiation of the benzene complex $[CpFe(\eta\text{-}C_6H_6)]^+$. The same method was used later by Scherer for the preparation of complex **3a**.[6a]

Analogously, the iron-ruthenium triple-decker complex **4a** was prepared by us through the use of the stacking reaction of the fragment $[CpFe]^+$ with pentaphospharuthenocene $Cp^*Ru(\eta\text{-}P_5)$ (**2**) (Scheme 1).[10]



Scheme 1. Formation of complex **4a**

Since the methylated fragment $[Cp^*Fe]^+$ cannot be generated from the corresponding benzene complex $[Cp^*Fe(\eta\text{-}C_6H_6)]^+$, due to its rather high stability,[11] we used the labile acetonitrile complex $[Cp^*Fe(MeCN)_3]^+$ as the source of this fragment. The complex $[Cp^*Fe(MeCN)_3]^+$ was successfully used earlier by Herberich for the synthesis of the μ-boratabenzene triple-decker complex $[Cp^*Fe(\mu\text{-}\eta{:}\eta\text{-}C_5H_5BMe)FeCp^*]^+$.[12] Treatment of $[Cp^*Fe(MeCN)_3]^+$ with **1** at 20 °C affords the permethylated diiron triple-decker complex **3b** (Scheme 2). However, treatment of $[Cp^*Fe(MeCN)_3]^+$ with **2** under the same conditions failed to give the iron-ruthenium triple-decker complex $[Cp^*Fe(\mu\text{-}\eta{:}\eta\text{-}P_5)RuCp^*]^+$. Nevertheless, we were able to synthesize it through the stacking reaction of the fragment $[Cp^*Ru]^+$ with **1** (see below).



3b: M = M' = Fe, R = Me
4b: M = Fe, M' = Ru, R = H
4c: M = Fe, M' = Ru, R = Me
5a: M = M' = Ru, R = H
5b: M = M' = Ru, R = Me

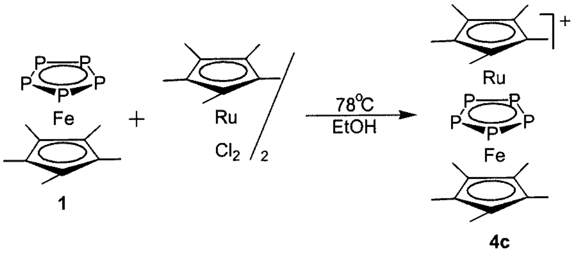
Scheme 2. Formation of complexes **3b**, **4b**, **4c**, **5a** and **5b**

The ruthenium-containing triple-decker complexes $[(\eta\text{-}C_5R_5)Ru(\mu\text{-}\eta{:}\eta\text{-}Cp^*)MCp^*]^+$ (M = Ru, Os) had been prepared by us earlier, by use of stacking reactions of decamethylmetallocenes MCp^*_2 with the fragments $[(\eta\text{-}C_5R_5)Ru]^+$ generated by heating the acetonitrile complexes $[(\eta\text{-}C_5R_5)Ru(MeCN)_3]^+$ in $MeNO_2$.[9] We used the same method for the preparation of μ-pentaphospholyl triple-decker complexes containing the unsubstituted Cp ring at the ruthenium atom. It was shown that stacking reactions of the $[CpRu]^+$ fragment, generated from $[CpRu(MeCN)_3]^+$, with compounds **1** and **2** yield the iron-ruthenium and diruthenium triple-decker complexes **4b** and **5a**, respectively (Scheme 2). Heating was essential for successful preparation of these complexes. Under mild conditions (20 °C, CH_2Cl_2) a mixture of products was formed. In the ^{31}P NMR spectra of these mixtures, the signals of the triple-decker complex **4b** or **5a** ($\delta = -37.2$ and -54.9 ppm, respectively) were accompanied by complicated multiplets in the range between $\delta = 250$ and 20 ppm. Such multiplets are characteristic of an AA′MM′X spin system. Probably, the formation of **4b** and **5a** is complicated by side-formation of phosphane-type complexes, due to coordination of ruthenium atoms of the species $[CpRu(MeCN)_x]^+$ ($x \leq 2$) with lone pairs of phosphorus atoms of pentaphosphametallocenes.[13] It was shown by ^{31}P NMR spectroscopy that phosphane-type complexes are unstable and very slowly turn into triple-decker complexes at room temperature. This process becomes faster with increasing temperature, and complexes **4b** and **5a** were isolated in high yields when the reactions were carried out in $MeNO_2$ at 100 °C. It is noteworthy that the formation of the triple-decker complex **4a** mentioned above is also complicated by side-formation of phosphane-type complexes. In order to obtain pure complex **4a**, the crude product was heated under reflux in $MeNO_2$.

μ-Pentaphospholyl triple-decker complexes **4c** and **5b**, containing the Cp* ring at the ruthenium atom, were prepared through stacking reactions of the $[Cp^*Ru]^+$ fragment with **1** and **2** (Scheme 2). It was shown in this case that the methylated fragment $[Cp^*Ru]^+$ can also be generated from the corresponding acetonitrile complex $[Cp^*Ru(MeCN)_3]^+$ in $MeNO_2$ at 100 °C. However, it is more convenient to use labile solvent complexes $[Cp^*Ru(S)_3]^+$ (S = Me_2CO, THF) as the source of the $[Cp^*Ru]^+$ fragment. These solvates were generated in solution by treatment of $[Cp^*RuCl_2]_2$ with Zn dust and $TlBF_4$ in Me_2CO or THF at room temperature.[14] Alternatively, they could also be generated by treatment of $[Cp^*Ru(OMe)]_2$ with CF_3SO_3H.[15] The further stacking reaction of $[Cp^*Ru(S)_3]^+$ with **1** is selective at room temperature, and the iron-ruthenium triple-decker complex **4c** was isolated in 84% yield. However, similar treatment of **2** primarily yields phosphane-type complexes, which turn into the diruthenium triple-decker complex **5b** (82%) in refluxing THF or Me_2CO. Some differences in the conditions of the stacking reactions for **1** and **2** may be connected with the greater stability of phosphane-type complexes formed by **2**.

Complex **4c** was also obtained (80%) by direct treatment of **1** with $[Cp^*RuCl_2]_2$ in refluxing alcohol (Scheme 3). This method had previously been developed by us for the preparation of the arene complexes $[Cp^*Ru(arene)]^+$.[16] Unfortunately, it proved to be useless for the preparation of

5b, probably due to the rather high stability of phosphane-type complexes (formed by reaction between **2** and [Cp*RuCl$_2$]$_2$), which do not turn into **5b** even after prolonged heating under reflux in alcohol.



Scheme 3. Formation of complex **4c** by treatment of complex **1** with [Cp*RuCl$_2$]$_2$

NMR Spectroscopy

The ^{1}H, ^{13}C and ^{31}P NMR spectroscopic data for triple-decker complexes **3b**, **4a−c**, **5a** and **5b** are given in Table 1. In the ^{31}P NMR spectra, the signals of the phosphorus atoms of the pentaphospholyl ligand are observed as singlets in the δ = −58.0 to −23.0 ppm range. These signals are strongly shifted upfield from the corresponding signals for sandwich compounds **1** and **2** (δ = 153.0 and 83.8 ppm, respectively); this makes ^{31}P NMR spectroscopy very informative for the establishment of the triple-decker structure. Substitution of the ruthenium atoms for iron and introduction of methyl groups also cause upfield shifts of the signal.

In the ^{1}H NMR spectra, the signals of Cp ring protons and of Cp* methyl groups are observed in the ranges δ = 4.0−4.6 and 1.2−1.5 ppm, respectively. In the ^{13}C NMR spectra, the signals of the C_5R_5 ring carbon atoms and of the Cp* methyl groups are observed in the ranges δ = 74.9−97.1 and 7.8−9.2 ppm, respectively. These spectroscopic data are also in accordance with the triple-decker structure.

X-ray Diffraction Study

The structures of complexes **4a**PF$_6$ and **5b**PF$_6$ were investigated by single-crystal X-ray diffraction. They contain separated **4a** or **5b** cations and PF_6^- anions. The cations have triple-decker structures formed by three cyclic frames, between which two metal atoms are located (Figures 1 and 2). Selected bond lengths and angles are given in Tables 2 and 3. In both cases the planes of the cyclic ligands are coplanar [for **4a** the dihedral angles Cp/P$_5$ and Cp*/P$_5$ are equal to 1.3 and 3.5°; for **5b** the dihedral angles Cp*(1)/P$_5$ and Cp*(2)/P$_5$ are equal to 0.2 and 1.7°, respectively]. The carbon atoms of the Cp* methyl groups in **4a** and **5b** deviate somewhat from the ring planes in direction from the ruthenium atoms, these deviations amounting to 0.06−0.11 Å. The cross-orientation of all five-membered rings is perfectly eclipsed in **4a** and close to eclipsed in **5b**, the corresponding torsion angles for the latter being: P(1−5)CtCt′C(1−5) 12.4−12.8° (average 12.6°) and P(1−5)CtCt″C(11−15) 5.1−5.2° (average 5.2°).[17] The metal atoms are located over the centres of all the rings; the metal-to-ring distances (Δ) are as follows: Fe···Cp 1.687(3), Ru···Cp* 1.837(1), Fe···P$_5$ 1.527(1), and Ru···P$_5$ 1.669(1) Å for **4a**; Ru(1)···Cp*(1) 1.831(1), Ru(2)···Cp*(2) 1.830(1), Ru(1)···P$_5$ 1.675(1), and Ru(2)···P$_5$ 1.678(1) Å for **5b**. The Fe···Ru [3.196(1) Å] and Ru(1)···Ru(2) [3.352(1) Å] distances are longer than the corresponding sums of the covalent radii for Fe−Ru (average 2.83 Å) and Ru−Ru (average 2.98 Å),[18] suggesting the absence of direct metal−metal bonds in both cases. It is noteworthy that Δ(Ru···P$_5$) for **4a** and **5b** are longer than the corresponding value in the sandwich compound (η-C$_5$Me$_4$Et)Ru(η-P$_5$) (1.652 Å).[19] The P−P bonds in **4a** (2.155−2.159 Å, average 2.157 Å) and **5b** (2.152−2.161 Å, average 2.156 Å) are longer than the corresponding bonds in (η-C$_5$Me$_4$Et)Ru(η-P$_5$)

Table 1. ^{1}H, ^{13}C and ^{31}P NMR spectroscopic data for compounds **3b**, **4a−c**, **5a** and **5b**

Compound[a]	^{1}H	^{13}C{^{1}H}	^{31}P{^{1}H}
3bBF$_4$ [b]	1.22 (Me)	8.14 (Me), 88.47 (C_5Me$_5$)	−23.0
4aPF$_6$ [b]	1.33 (15 H, Me), 4.00 (5 H, C$_5$H$_5$)	7.81 (Me), 74.92 (C$_5$H$_5$), 97.00 (C_5Me$_5$)	−35.0 (P$_5$), −142.7 [sept., PF$_6$, J(PF) = 708]
4bBF$_4$ [b]	1.32 (15 H, Me), 4.35 (5 H, C$_5$H$_5$)	8.20 (Me), 81.37 (C$_5$H$_5$), 88.26 (C_5Me$_5$)	−37.2
4cBF$_4$ [c]	1.27 (15 H, FeC$_5$Me$_5$ or RuC$_5$Me$_5$), 1.30 (15 H, RuC$_5$Me$_5$ or FeC$_5$Me$_5$)	8.77 (FeC$_5$$Me_5$), 9.14 (RuC$_5$$Me_5$), 87.98 (Fe$C_5Me_5$), 96.91 (Ru$C_5Me_5$)	−39.2
5aPF$_6$ [b]	1.48 (15 H, Me), 4.58 (5 H, C$_5$H$_5$)	8.17 (Me), 81.24 (C$_5$H$_5$), 97.11 (C_5Me$_5$)	−54.9 (P$_5$), −142.7 [sept.,PF$_6$, J(PF) = 708]
5bPF$_6$ [b]	1.51(Me)	8.48 (Me), 96.99 (C_5Me$_5$)	−58.0 (P$_5$), −142.7 [sept., PF$_6$, J(PF) = 708]

[a] Chemical shifts in ppm, coupling constants in Hz. The signals are singlets, unless otherwise stated. [b] In (CD$_3$)$_2$CO. [c] In CD$_2$Cl$_2$.

(2.082−2.118 Å, average 2.101 Å). The elongation of the Ru−P and P−P bonds is apparently connected with loosening of bonds upon bifacial coordination of the P_5 ring with two metal atoms as compared with its monofacial coordination with only one metal atom. The values of Δ(Ru···Cp*) for **4a** and **5b**, however, are shorter than the corresponding value in the sandwich compound (η-C_5Me_4Et)Ru(η-P_5) (1.850 Å). Probably, loosening of the Ru−P_5 bond in the triple-decker complexes causes increased occupancy of the Ru−Cp* bond. The values of Δ(Fe···P_5) and Δ(Fe···Cp) in **4a** are close to the corresponding values in the related triple-decker cation [CpFe(μ-η:η-P_5)Fe(η-C_5Me_4Et)]$^+$ [Δ(Fe···P_5) 1.534 Å and Δ(Fe···Cp) 1.679 Å].[6a] However, the P−P bonds in **4a** (average 2.157 Å) are somewhat longer than the corresponding bonds in [CpFe(μ-η:η-P_5)Fe(η-C_5Me_4Et)]$^+$ (average 2.125 Å), which suggests a greater π bond-loosening effect by the Cp*Ru fragment than by (C_5Me_4Et)Fe.

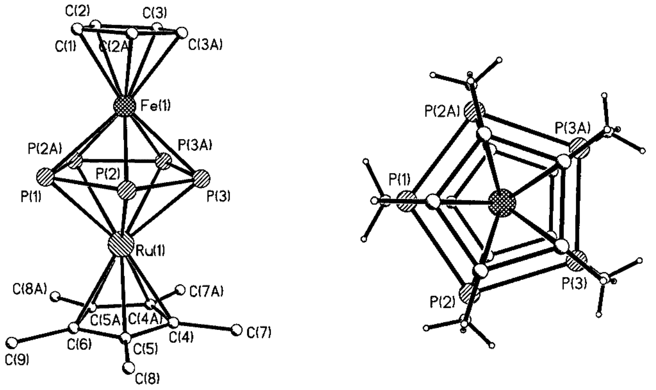


Figure 1. Structure of cation **4a**

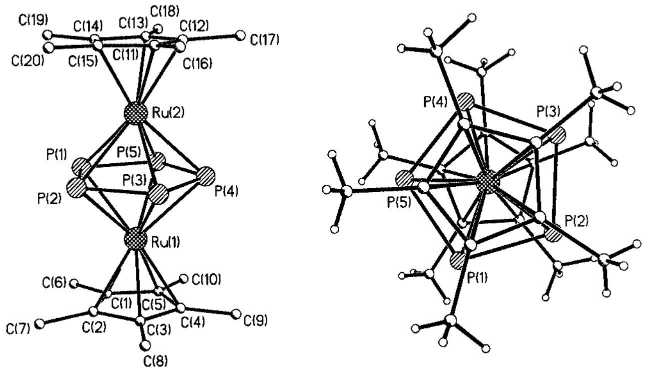


Figure 2. Structure of cation **5b**

Table 2. Selected bond lengths [Å] and angles [°] for cation **4a**

Ru(1)−P(1)	2.4960(9)	Ru(1)−C(5)	2.205(2)
Ru(1)−P(2)	2.4819(6)	Ru(1)−C(6)	2.219(3)
Ru(1)−P(3)	2.4705(6)	Fe(1)−C(1)	2.072(3)
Fe(1)−P(1)	2.3935(9)	Fe(1)−C(2)	2.074(2)
Fe(1)−P(2)	2.3931(7)	Fe(1)−C(3)	2.078(2)
Fe(1)−P(3)	2.3776(7)	P(1)−P(2)	2.1545(8)
Ru(1)−C(4)	2.200(2)	P(2)−P(3)	2.1590(9)
P(1)−P(2)−P(3)	107.96(4)	Fe(1)−P(2)−Ru(1)	81.90(2)
Fe(1)−P(1)−Ru(1)	81.60(3)	Fe(1)−P(3)−Ru(1)	82.45(2)

Table 3. Selected bond lengths [Å] and angles [°] for cation **5b**

Ru(1)−P(1)	2.4869(6)	Ru(1)−C(4)	2.209(2)
Ru(1)−P(2)	2.4835(7)	Ru(1)−C(5)	2.199(2)
Ru(1)−P(3)	2.4819(6)	Ru(2)−C(11)	2.211(2)
Ru(1)−P(4)	2.4828(7)	Ru(2)−C(12)	2.199(2)
Ru(1)−P(5)	2.4856(7)	Ru(2)−C(13)	2.193(2)
Ru(2)−P(1)	2.4778(7)	Ru(2)−C(14)	2.199(2)
Ru(2)−P(2)	2.4880(7)	Ru(2)−C(15)	2.201(2)
Ru(2)−P(3)	2.4887(6)	P(1)−P(2)	2.1613(11)
Ru(2)−P(4)	2.4813(6)	P(2)−P(3)	2.1519(11)
Ru(2)−P(5)	2.4930(7)	P(3)−P(4)	2.1562(10)
Ru(1)−C(1)	2.198(2)	P(4)−P(5)	2.1565(11)
Ru(1)−C(2)	2.204(2)	P(5)−P(1)	2.1563(11)
Ru(1)−C(3)	2.198(2)		
P(1)−P(2)−P(3)	107.87(4)	Ru(1)−P(1)−Ru(2)	84.95(2)
P(2)−P(3)−P(4)	107.99(4)	Ru(1)−P(2)−Ru(2)	84.81(2)
P(3)−P(4)−P(5)	108.29(4)	Ru(1)−P(3)−Ru(2)	84.83(2)
P(4)−P(5)−P(1)	107.64(4)	Ru(1)−P(4)−Ru(2)	84.97(2)
P(5)−P(1)−P(2)	108.21(4)	Ru(1)−P(5)−Ru(2)	84.66(2)

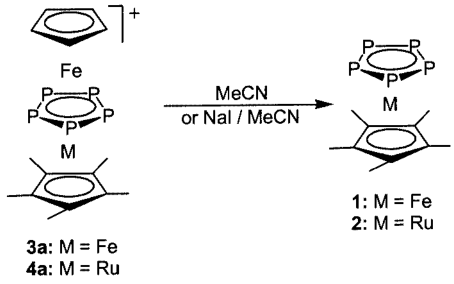
Nucleophilic Degradation

The μ-pentaphospholyl triple-decker complexes described here have 30 VEs, which explains their stability in accordance with Hoffmann's rule for triple-decker complexes.[20] They are indefinitely stable under inert gas. However, they are stable in air only for short periods of time and lose solubility after prolonged storage. This is apparently connected with the interaction between lone electron pairs of the phosphorus atoms and oxygen.

The properties of triple-decker complexes are insufficiently studied. The most studied reaction is nucleophilic degradation. Examples of such reactions have been described for the complexes with bifacially bonded cyclopentadienyl,[9,15d,21] borole,[22] thiadiborolene,[23] boratabenzene,[12,24] and phospholyl[25] ligands.

We studied the reactions of triple-decker complexes **3a**, **3b**, **4a−c**, **5a** and **5b** with MeCN and NaI. Only the CpFe-containing complexes **3a** and **4a** proved to be reactive. The reactions proceed with elimination of the [CpFe]$^+$ fragment and formation of the corresponding pentaphosphametallocenes **1** and **2** (Scheme 4). The selectivity of elimination of this fragment in the case of **3a** is apparently connected with hindrance of nucleophilic attack at the metal atom coordinated with the Cp* ring as a consequence of electronic and steric effects.

It is noteworthy that the iron-ruthenium complex **4a** is more reactive than the diiron analogue **3a** towards MeCN. From the ^{31}P NMR spectroscopic data, the degree of conversion in the case of **4a** was ca. 70% after 10 h at 80 °C, while in the case of **3a** at the same temperature it was only ca. 10% after 38 h. Addition of NaI accelerates degradation of **3a**, the degree of conversion being ca. 80% after 10 h. Unlike **3a** and **4a**, the diruthenium complex **5a**, with the same number of methyl groups, proved to be inert to nucleophilic degradation even by NaI in MeCN. This is obvi-



Scheme 4. Nucleophilic degradation of complexes **3a** and **4a**

ously connected with stronger bonding of *cyclo*-P_5 with the ruthenium atom than with iron. The obtained results suggest that the reactivity of μ-pentaphospholyl triple-decker complexes in nucleophilic degradation reactions decreases in the order FeRu > Fe_2 > Ru_2. It should be emphasized that the heterometallic compounds are more reactive than homometallic analogues.

The permethylated complexes **3b** and **4c** proved to be much less reactive than the pentamethylated analogues **3a** and **4a**; in fact, they are not destroyed by NaI in MeCN at 80 °C. Unfortunately, attempts to use other nucleophilic reagents (Me_2SO, $EtNH_2$, KOH, KCN, *t*BuOK and CpTl) resulted only in the formation of unidentified product mixtures.

The reactivity of the diiron triple-decker complex **3a** was compared with that of the related complexes [CpFe(μ-η:η-Cp*)FeCp*]$^+$ and [CpFe(μ-η:η-C_4Me_4P)FeCp*]$^+$, with Cp* and C_4Me_4P ligands in their bridging positions. Unlike diiron complex **3a**, which is destroyed by MeCN or NaI at 80 °C, complexes [CpFe(μ-η:η-Cp*)FeCp*]$^+$ and [CpFe(μ-η:η-C_4Me_4P)FeCp*]$^+$ are destroyed even by Me_2CO at room temperature,[9,25b] the complex with a central Cp* ring being destroyed most rapidly. Thus, the reactivity of the triple-decker complexes of the type [CpFe(ring)-FeCp*]$^+$ in nucleophilic degradation reactions greatly depends upon the central ligand and decreases in the order Cp* > C_4Me_4P > P_5.

Electrochemistry

In agreement with a previous report,[26] the iron building block **1** undergoes either a one-electron reduction or a one-electron oxidation, both showing features of chemical irreversibility. In the case of ruthenium analogue **2** we found clear evidence only of the presence of an irreversible oxidation. A possible reduction is probably localized very close to the solvent discharge. The relevant electrode potentials are compiled in Table 4, together with those for the complexes studied here.

Let us start the examination of the redox behaviour of the current triple-decker complexes with the diiron complexes **3a** and **3b**. Figure 3 shows the cyclic voltammetric response given by the permethylated complex **3b** in dichloromethane solution. It exhibits one oxidation and two separate reduction processes. Both the anodic and the first cathodic steps possess features of chemical reversibility on the cyclic voltammetric timescale [$i_{p(reverse)}/i_{p(forward)} \approx 1$], whereas the second reduction appears partially chemically reversible [$i_{p(reverse)}/i_{p(forward)} = 0.7$ at 0.2 Vs^{-1}]. A further irreversible oxidation, not shown in Figure 3, almost completely overlaps the solvent discharge.

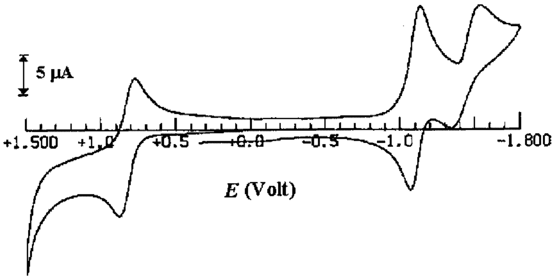


Figure 3. Cyclic voltammogram recorded at a platinum electrode on a CH_2Cl_2 solution containing **3b** (1.2×10^{-3} mol dm^{-3}); supporting electrolyte $[Bu_4N][PF_6]$ (0.2 mol dm^{-3}); scan rate 0.2 Vs^{-1}

Consistent with the behaviour of the related complexes $[(triphos)MP_3M(triphos)]^{n+}$ (M = Ni, Co),[27] Cp*MP_6MCp* (M = V, Mo, W),[28] Cp*Fe(As_2Se_2)FeCp*,[29]

Table 4. Formal electrode potentials (V, vs. SCE) and peak-to-peak separations (mV) for the redox changes exhibited by complexes **1**, **2**, **3a**, **3b**, **4a−c**, **5a**, **5b**, **6**, and **7** in dichloromethane solution; supporting electrolyte $[Bu_4N]PF_6$ (0.2 mol dm^{-3})

Complex	$E_{p(3+/2+)}$[a][b]	$E^{\circ\prime}_{(2+/+)}$	i_{pc}/i_{pa} [a]	ΔE_p [a]	$E^{\circ\prime}_{(+/0)}$	i_{pa}/i_{pc} [a]	ΔE_p [a]	$E^{\circ\prime}_{(0/-)}$	i_{pa}/i_{pc} [a]	ΔE_p [a]
1		+0.92[a,b]	–	–	−1.63[a,b]	–	–			
2		+1.18[a,b]	–	–	−1.95[c]	–	–			
3a	> 1.6	+0.99	0.92	100	−0.90	1.0	120	−1.30	0.56	220
3b	+1.54	+0.84	0.87	94	−1.10	1.0	78	−1.41	0.70	150
4a	+1.5	+1.5	–	–	−0.90	0.80	160	−1.39[b]	–	–
4b	+1.30	+0.87[d]	0.6[d]	260[d]	−1.24	[e]	[e]	−1.35	[e]	[e]
4c	+1.35	+0.91	0.80	96	−1.15	1.0	76	−1.40	0.40	144
5a	+1.2[b] [f]	+1.2[b,f]	–	–	−1.10[g]	0.25	180[g]	−1.10[g]	0.25	180[g]
5b	+1.5[b,c]	+1.2[b,c]	–	–	−1.27	0.45	68	−1.27	0.45	68
6	–	+1.02	0.85	96	−1.05	1.0	88	−1.32	0.54	120
7	+1.57[f]	+1.11	0.5[e]	102	−1.22	0.90	86	−1.22	0.90	86
FcH					+0.39	1.0	88			

[a] Measured at 0.2 Vs^{-1}. [b] Peak-potential value. [c] Ill-defined. [d] Measured at 2.0 Vs^{-1}. [e] Difficult to evaluate. [f] Multielectron process. [g] Measured at 5.1 Vs^{-1}.

and in particular $Cp^*CrP_5CrCp^*$,[2] controlled potential coulometry performed in correspondence to the first cathodic step ($E_w = -1.2$ V) consumed one electron per molecule, thus supporting the involvement of one-electron transfers in all the redox processes. This means that the oxidation processes should correspond to the $Fe^{II}Fe^{II}/Fe^{II}Fe^{III}/Fe^{III}Fe^{III}$ sequence, whereas the reduction steps should correspond to the $Fe^{II}Fe^{II}/Fe^{II}Fe^{I}/Fe^{I}Fe^{I}$ sequence. In this context, it should be noted that the Fe^{I} oxidation state is not completely unusual in organometallic chemistry,[30] and the present unexpected processes could be due to cooperative electronic effects inside the triple-decker assembly.

It is interesting to note that, if allowance is made to evaluate the separation between the sequential redox changes $Fe^{II}Fe^{II}/Fe^{II}Fe^{III}/Fe^{III}Fe^{III}$ as roughly about 0.7 V, a K_{com} value of about 7×10^{11} is obtained.[31] This may well indicate that the mixed-valent $Fe^{II}Fe^{III}$ dication electrogenerated in the first oxidation process belongs to the delocalized (in the electrochemical timescale) Robin-Day class III. Analogously, the separation of 0.31 V evaluated for the $Fe^{II}Fe^{II}/Fe^{II}Fe^{I}/Fe^{I}Fe^{I}$ sequence should afford a K_{com} value of 2×10^5, which suggests that the neutral, mixed-valent $Fe^{II}Fe^{I}$ species electrogenerated in the first reduction process should be at the border of the slightly and the completely delocalized classes II and III. In this connection, a $K_{com} = 4 \times 10^{17}$ has been calculated for $Cp^*CrP_5CrCp^*$, which, also supported by EPR spectroscopic measurements, was classified as a delocalized $Cr^{II}Cr^{I}$ system.[2] It should be noted finally that, in spite of the chemical reversibility of the $Fe^{II}Fe^{II}/Fe^{II}Fe^{III}$ and $Fe^{II}Fe^{II}/Fe^{II}Fe^{I}$ redox changes on the cyclic voltammetric timescale, cyclic voltammetric tests performed after the exhaustive $Fe^{II}Fe^{II}/Fe^{II}Fe^{I}$ reduction show that the mixed-valent neutral species undergoes slow decomposition over the long timescales of macroelectrolysis.

The cyclic voltammetric profile of the pentamethylated analogue **3a** is quite similar to that of **3b**, exept for a general shift of all the redox processes towards more positive, or less negative, potential values. Indeed, as far as the anodic region is concerned, no further anodic step (which should correspond to the $Fe^{II}Fe^{III}/Fe^{III}Fe^{III}$ redox change) could be detected within the potential window of the solvent (about +1.7 V), probably because of this general anodic shift. As expected, the decrease in the number of methyl groups makes the $Fe^{II}Fe^{II}/Fe^{II}Fe^{III}$ oxidation somewhat more difficult (by 0.15 V), while favouring the $Fe^{II}Fe^{II}/Fe^{II}Fe^{I}$ reduction step (by 0.2 V) with respect to **3b**. Controlled potential coulometry at the first reduction process consumes one electron per molecule. The resulting solution no longer displays the original peak system, thus indicating that, as happens for **3b**, the neutral species is not indefinitely stable.

Let us now continue to the mixed-metal iron-ruthenium complexes **4a−c**. The cyclic voltammetric pattern of permethylated **4c** is very similar to that of the diiron analogue **3b**. An irreversible oxidation is also present at very positive potential values in this case, which in addition is complicated by electrode adsorption phenomena.

As illustrated in Figure 4, complex **4a**, which contains the Cp* ring at the ruthenium atom, undergoes either two discrete reductions, the first of which possesses features of partial chemical reversibility (the current ratio i_{pa}/i_{pc} is equal to 0.8 at 0.2 Vs^{-1}) whereas the second is substantially irreversible, or an irreversible oxidation, probably involving two electrons. From the redox potential of the related complex **3a**, it might be speculated that the first reduction process is centred on the iron fragment.

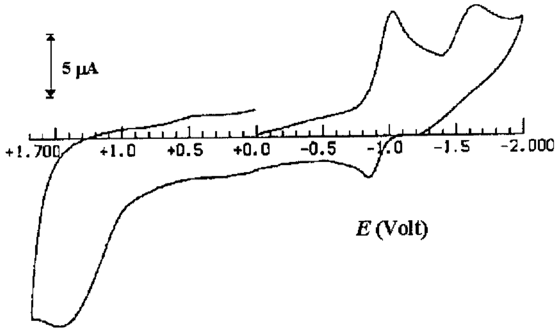


Figure 4. Cyclic voltammogram recorded at a platinum electrode of a CH_2Cl_2 solution containing **4a** (1.1×10^{-3} mol dm^{-3}) and $[Bu_4N][PF_6]$ (0.2 mol dm^{-3}); scan rate 0.2 Vs^{-1}

As illustrated in Figure 5, complex **4b**, which contains the Cp* ring at the iron atom, undergoes two separate oxidations and two apparently closely spaced reductions. In spite of the apparent irreversibility of both oxidation processes, cyclic voltammetry limited to the first oxidation step shows that a directly associated return peak can be detected at a high scan rate (see bottom inset). As far as the appearance of two slightly separated reduction processes is concerned, it must be taken into account that, as illustrated in the top inset, the second process is almost absent at low scan rates, indicating that the first step primarily involves a single two-electron reduction complicated by following chemical reactions.

Let us now examine the diruthenium complexes **5a** and **5b**. As illustrated in Figure 6, permethylated **5b** exhibits a single, partially chemically reversible, reduction process (the current ratio i_{pa}/i_{pc} is equal to 0.4 at 0.2 Vs^{-1} and 0.6 at 2.0 Vs^{-1}). Ill-defined oxidation processes are also present. Comparison with the one-electron oxidation of an equimolar amount of *N*,*N*-dimethyl-1-[1′,2-bis(diphenylphosphanyl)ferrocenyl]ethylamine ($M = 625.5$; $E_p = +0.53$ V) indicates that the cathodic process involves a two-electron addition. On the naive assumption that this process might correspond to the $Ru^{II}Ru^{II}/Ru^{I}Ru^{I}$ transition, its proceeding through a single step should suggest the absence of communication between the two ruthenium centres.

The partially methylated complex **5a** also undergoes a single two-electron reduction, as well as an ill-defined and unsplit multielectron oxidation. Analysis of the cathodic process with scan rate indicates that only at scan rates higher than 1.0 Vs^{-1} does a directly associated reoxidation peak clearly appear in the backscan. This means that the decomposition rate of the electrogenerated monoanion is

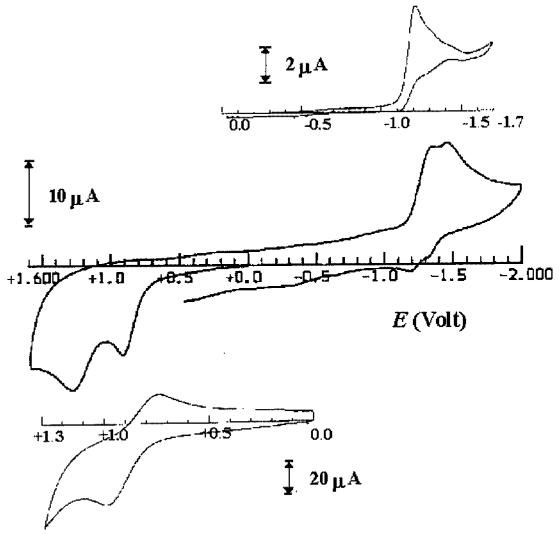


Figure 5. Cyclic voltammograms recorded at a platinum electrode of a CH_2Cl_2 solution containing **4b** (1.3×10^{-3} mol dm^{-3}) and $[Bu_4N][PF_6]$ (0.2 mol dm^{-3}); scan rate 0.2 Vs^{-1}; top inset: scan rate 0.05 Vs^{-1}; bottom inset: 2.0 Vs^{-1}

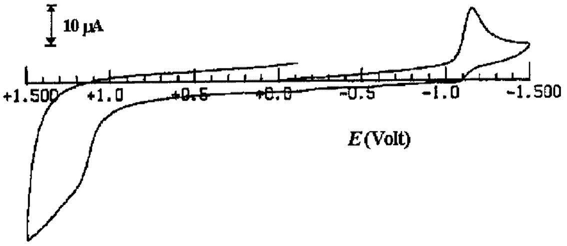


Figure 6. Cyclic voltammogram recorded at a platinum electrode of a CH_2Cl_2 solution containing **5b** (1.3×10^{-3} mol dm^{-3}) and $[Bu_4N][PF_6]$ (0.2 mol dm^{-3}); scan rate 0.2 Vs^{-1}

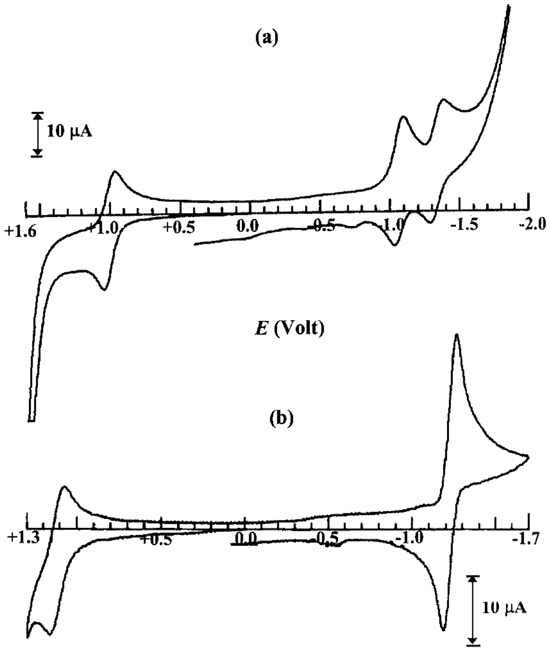


Figure 7. Cyclic voltammograms recorded at a platinum electrode of a CH_2Cl_2 solution containing $[Bu_4N][PF_6]$ (0.2 mol dm^{-3}) and: (a) **6** (1.6×10^{-3} mol dm^{-3}); (b) **7** (1.5×10^{-3} mol dm^{-3}); scan rate 0.2 Vs^{-1}

notably faster than that of **5b**. For **5b**, for instance, a current ratio i_{pa}/i_{pc} of 0.4 is reached at a scan rate of 0.2 Vs^{-1}, whereas for **5a** the same current ratio value is reached at 10.2 Vs^{-1}. Finally, and consistently with the partial demethylation, the reduction process occurs earlier (by 0.17 V) than that of **5b**.

Lastly, let us discuss the related cobalt-containing complexes $[(\eta\text{-}C_4Me_4)Co(\mu\text{-}\eta{:}\eta\text{-}P_5)MCp^*]^+$ (**6**: M = Fe; **7**: M = Ru).[32] Figure 7 immediately shows the different role played by a sandwiched iron against a ruthenium centre.

Similarly to the permethylated diiron complex **3b**, the iron-cobalt complex **6** undergoes either an oxidation or two reductions, all showing features of chemical reversibility [Figure 7, (a)]. Controlled potential coulometric experiments performed in correspondence to the first reduction process consume one electron per molecule. The exhaustively reduced solution maintains the red colour of the original species, but displays a cyclic voltammetric profile quite complementary to that shown in Figure 7. At variance with **3b**, this result testifies to the chemical reversibility of the one-electron reduction also on the long timescales of macroelectrolysis. On this basis we assign a one-electron nature to all the redox processes. As far as the assignment of such redox steps is concerned, it is at the moment difficult to assign the oxidation process to the $Fe^{II}Co^{I}/Fe^{III}Co^{I}$ or to $Fe^{II}Co^{I}/Fe^{II}Co^{II}$ electron transfers, or the Co^{I} or Fe^{II} nature of the reduction processes.

The cyclic voltammetric profile exhibited by the cobalt-ruthenium complex **7** [Figure 7, (b)] is reminiscent of that of the iron-ruthenium complex **4b** and the diruthenium complex **5b**. It is evident that both the oxidation and the reduction have features of chemical reversibility. As can be seen, the height of the reduction step is about twice that of the oxidation step. Comparison of the peak heights with that of an equimolar amount of *N*,*N*-dimethyl-1-[1′,2-bis(diphenylphosphanyl)ferrocenyl]ethylamine reliably allows the cited redox changes to be assigned as two-electron and one-electron processes, respectively. It must be noted that the two-electron reduction in cyclic voltammetry at low scan rates displays a current ratio slightly lower than 1 (i_{pa}/i_{pc} is equal to 0.8 at 0.02 Vs^{-1}), thus suggesting that the electrogenerable monoanion undergoes slow decomposition. As in the case of **6**, it is difficult at the moment to assign the oxidation process as Ru^{II}- or Co^{I}-centred, whereas in this case, probably because of the reduction of the Cp*Ru system being generally more difficult than that of the Cp*Fe system (see **3b** and **5b**), the reduction process seems to involve the simultaneous reduction of both the Ru^{II} and Co^{I} centres.

In conclusion, it has been demonstrated that the presence of a ruthenium atom inside these triple-decker complexes tends to make the corresponding redox changes unstable.

Only if the ruthenium atom is bonded to the Cp* ring do the redox congeners partially increase their stability.

Conclusion

The stacking reactions of pentaphosphametallocenes **1** and **2** with half-sandwich fragments $[(\eta\text{-}\mathrm{C_5R_5})\mathrm{M'}]^+$ (M′ = Fe, Ru) were used to prepare triple-decker complexes **3b**, **4a−c**, **5a** and **5b**, in which the pentaphospholyl ligand is bifacially bonded with two metal atoms. These reactions are often complicated by side-formation of phosphane-type complexes, due to coordination of metal atoms with lone pairs of phosphorus atoms. Such complexes usually turn into triple-decker complexes on heating; the greater stability of phosphane-type complexes formed by **2** results in considerable differences in the conditions for the stacking reactions for **1** and **2**. The main structural feature of μ-pentaphospholyl triple-decker complexes is the elongation of bonds in the triple-decker fragment $\mathrm{M}(\mu\text{-}\eta{:}\eta\text{-}\mathrm{P_5})\mathrm{M'}$ as compared with the corresponding bonds in mononuclear sandwich compounds. Study of nucleophilic degradation reactions has shown that heterometallic (FeRu) triple-decker complexes are more reactive than their homometallic ($\mathrm{Fe_2}$, $\mathrm{Ru_2}$) analogues. Electrochemical data allow assignment of the diiron dication $\mathbf{3b}^{2+}$ as a class III (delocalized) mixed-valent species.

Experimental Section

General: All reactions were carried out under argon in anhydrous solvents. The isolation of products was conducted in air. Starting materials $[\mathrm{Cp^*Fe(CO)_2}]_2$,[11] **2**,[33] $[\mathrm{CpFe}(\eta\text{-}\mathrm{C_6H_6})]\mathrm{PF_6}$,[34] $[\mathrm{Cp^*Fe(MeCN)_3}]\mathrm{BF_4}$,[11] $[\mathrm{CpRu(MeCN)_3}]\mathrm{X}$ (X = $\mathrm{BF_4}$, $\mathrm{PF_6}$),[35] $[\mathrm{Cp^*Ru(MeCN)_3}]\mathrm{PF_6}$ [36] and $[\mathrm{Cp^*RuCl_2}]_2$ [37] were prepared as described in the literature. Complex **1** was prepared by Scherer's method,[38] with the use of the simplified isolation procedure given below. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded with a Bruker AMX 400 spectrometer operating at 400.13, 100.61 and 161.98 MHz, respectively. Materials and the apparatus for electrochemistry have been described elsewhere.[39] *N*,*N*-Dimethyl-1-[1′,2-bis(diphenylphosphanyl)ferrocenyl]ethylamine was an Aldrich product. Potential values are referenced to the saturated calomel electrode (SCE).

$(\eta\text{-}\mathrm{P_5})\mathrm{FeCp^*}$ (1): A mixture of $[\mathrm{Cp^*Fe(CO)_2}]_2$ (4.5 g, 9.1 mmol) and $\mathrm{P_4}$ (5 g, 40.3 mmol) in decalin (300 mL) was stirred under reflux for 3 h. The reaction solvents were evaporated to a small volume (ca. 30 mL) under atmospheric pressure and the remaining solvent was then removed at 100 °C under water-pump vacuum. Admixed $\mathrm{P_4}$ was sublimed at 100 °C at ca. 0.1 Torr. The solid residue was recrystallized from petroleum ether to give dark green crystals. Yield 3.4 g (59%). ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$): $\delta = 152.7$ ppm.

$[\mathrm{CpFe}(\mu\text{-}\eta{:}\eta\text{-}\mathrm{P_5})\mathrm{RuCp^*}]\mathrm{PF_6}$ (4aPF$_6$): Dichloromethane (10 mL) was added to a mixture of **2** (60 mg, 0.15 mmol) and $[\mathrm{CpFe}(\eta\text{-}\mathrm{C_6H_6})]\mathrm{PF_6}$ (52 mg, 0.15 mmol) in a Schlenk tube ($d = 15$ mm). The reaction mixture was irradiated for 10 h with a 400-W high-pressure discharge lamp (sodium lamp or mercury luminescent lamp). Both the Schlenk tube and the lamp were contained in a suitable vessel covered inside with aluminium foil; cooling was accomplished with running water. The solvent was removed in vacuo. The residue was dissolved in $\mathrm{MeNO_2}$ (ca. 4 mL) and the solution was heated under reflux for ca. 2 h in order to destroy phosphane-type by-products. After removal of the solvent, unchanged **2** (15 mg) was extracted with ether. The residue was reprecipitated twice from $\mathrm{CH_2Cl_2}$ with ether to give a red-brown solid. Yield 70 mg (71%). $\mathrm{C_{15}H_{20}F_6FeP_6Ru}$ (657.06): calcd. C 27.42, H 3.07; found C 27.76, H 3.08.

$[\mathrm{Cp^*Fe}(\mu\text{-}\eta{:}\eta\text{-}\mathrm{P_5})\mathrm{FeCp^*}]\mathrm{BF_4}$ (3bBF$_4$): A mixture of **1** (115 mg, 0.33 mmol) and $[\mathrm{Cp^*Fe(MeCN)_3}]\mathrm{BF_4}$ (129 mg, 0.32 mmol) in $\mathrm{CH_2Cl_2}$ or $\mathrm{Me_2CO}$ (10 mL) was stirred for 2.5 h at room temperature. The solvent was removed in vacuo and the residue was reprecipitated twice from $\mathrm{CH_2Cl_2}$ with ether to give a green solid. Yield 120 mg (60%). $\mathrm{C_{21}H_{32}BCl_2F_4Fe_2P_5}$ (**3b**$\mathrm{BF_4\cdot CH_2Cl_2}$; 708.75): calcd. C 35.59, H 4.55; found C 36.22, H 4.70.

$[\mathrm{Cp^*M}(\mu\text{-}\eta{:}\eta\text{-}\mathrm{P_5})\mathrm{RuCp}]\mathrm{X}$ (4bBF$_4$: M = Fe; 5aPF$_6$: M = Ru): A mixture of **1** (or **2**) (0.2 mmol) and $[\mathrm{CpRu(MeCN)_3}]\mathrm{X}$ (0.21 mmol) in $\mathrm{MeNO_2}$ (5 mL) was heated under reflux for 5 h. The solvent was removed in vacuo and the residue was reprecipitated twice from $\mathrm{CH_2Cl_2}$ with ether to give a red-brown solid. Compound **4b**$\mathrm{BF_4}$: Yield 75 mg (63%). $\mathrm{C_{15}H_{20}BF_4FeP_5Ru}$ (598.91): calcd. C 30.08, H 3.37; found C 29.46, H 3.36. Compound **5a**$\mathrm{PF_6}$: Yield 58 mg (41%). $\mathrm{C_{15}H_{20}F_6P_6Ru_2}$ (702.28): calcd. C 25.65, H 2.87; found C 26.45, H 2.89.

$[\mathrm{Cp^*Fe}(\mu\text{-}\eta{:}\eta\text{-}\mathrm{P_5})\mathrm{RuCp^*}]\mathrm{BF_4}$ (4cBF$_4$). A: A mixture of **1** (80 mg, 0.23 mmol), $[\mathrm{Cp^*RuCl_2}]_2$ (57 mg, 0.09 mmol), $\mathrm{TlBF_4}$ (125 mg, 0.43 mmol) and Zn dust (100 mg, excess) in $\mathrm{Me_2CO}$ (5 mL) was stirred for 2 h at room temperature. The solvent was removed in vacuo and the residue was reprecipitated twice from $\mathrm{CH_2Cl_2}$ with ether to give a red-brown solid. Yield 104 mg (84%). $\mathrm{C_{20}H_{30}BF_4FeP_5Ru}$ (669.04): calcd. C 35.90, H 4.52; found C 35.23, H 4.39. **B:** A solution of **1** (87 mg, 0.25 mmol) and $[\mathrm{Cp^*RuCl_2}]_2$ (77 mg, 0.125 mmol) in ethanol (5 mL) was heated under reflux for 1 h. The solvent was removed in vacuo and the residue was dissolved in water (5−10 mL). The solution was filtered, and the filtrate was treated with 0.2 mL (excess) of aqueous $\mathrm{HBF_4}$ (48%). The precipitate formed was filtered off, washed with water, dried in vacuo and reprecipitated from $\mathrm{CH_2Cl_2}$ with ether to give a red-brown solid. Yield 134 mg (80%).

$[\mathrm{Cp^*Ru}(\mu\text{-}\eta{:}\eta\text{-}\mathrm{P_5})\mathrm{RuCp^*}]\mathrm{X}$ (5bBF$_4$, 5bPF$_6$). A: A mixture of $[\mathrm{Cp^*RuCl_2}]_2$ (32 mg, 0.05 mmol), $\mathrm{TlBF_4}$ (70 mg, 0.24 mmol) and Zn dust (100 mg, excess) in THF (5 mL) was stirred for 0.5 h at 0 °C. The solution of the thus formed solvate $[\mathrm{Cp^*Ru(THF)_3}]\mathrm{BF_4}$ was treated with **2** (41 mg, 0.11 mmol) and the mixture was heated under reflux for 8 h. The solvent was removed in vacuo and the residue was reprecipitated twice from $\mathrm{CH_2Cl_2}$ with ether to give complex **5b**$\mathrm{BF_4}$ as a red-brown solid. Yield 61 mg (82%). $\mathrm{C_{20}H_{30}BF_4P_5Ru_2}$ (714.26): calcd. C 33.63, H 4.23; found C 33.45, H 4.18. **B:** A mixture of **2** (30 mg, 0.08 mmol) and $[\mathrm{Cp^*Ru(MeCN)_3}]\mathrm{PF_6}$ (42 mg, 0.08 mmol) in $\mathrm{MeNO_2}$ (5 mL) was heated under reflux for 7 h. The solvent was removed in vacuo and the residue was reprecipitated twice from $\mathrm{CH_2Cl_2}$ with ether to give complex **5b**$\mathrm{PF_6}$ as a red-brown solid. Yield 34 mg (57%). $\mathrm{C_{20}H_{30}F_6P_6Ru_2}$ (772.41): calcd. C 31.10, H 3.92; found C 31.28, H 3.72.

Nucleophilic Degradation of 4a by MeCN: A solution of **4a** (26 mg, 0.04 mmol) in MeCN (4 mL) was heated under reflux for 10 h. The solvent was removed in vacuo and the solid residue was extracted with ether. After removal of ether in vacuo, complex **2** was obtained as an orange solid. Yield 8 mg (ca. 50%). The residue, after extrac-

Table 5. Crystal data and structure refinement parameters for **4a**PF_6 and **5b**PF_6

Compound	**4a**PF_6	**5b**PF_6
Empirical formula	$C_{15}H_{20}F_6FeP_6Ru$	$C_{20}H_{30}F_6P_6Ru_2$
Formula mass	657.05	772.40
Crystal colour, habit	Yellow plate	Dark red needle
Crystal size [mm]	0.40 × 0.20 × 0.05	0.45 × 0.30 × 0.25
Crystal system	orthorhombic	orthorhombic
Space group	*Ibam*	*Fddd*
a [Å]	15.2363(7)	21.192(1)
b [Å]	20.0508(9)	29.148(1)
c [Å]	14.9157(7)	35.561(2)
V [$Å^3$]	4556.7(4)	21966(2)
Z	8	32
D(calcd.) [g cm^{-3}]	1.916	1.869
Diffractometer	Bruker SMART 1000 CCD	Bruker SMART 1000 CCD
Temperature [K]	110	110
Radiation	Mo-K_α ($\lambda = 0.71073$)	Mo-K_α ($\lambda = 0.71073$)
Scan mode	φ and ω	φ and ω
θ range [°]	1.68−31.47	1.32−30.03
Abs.coeff. μ(Mo-K_α) [cm^{-3}]	17.70	15.00
Absorption correction	SADABS	SADABS
$T_{max.}$ and $T_{min.}$	0.928 and 0.471	1.000 and 0.692
Collected reflections	24940	58712
Independent reflections	3702 ($R_{int} = 0.0604$)	8041 ($R_{int} = 0.0322$)
Reflections used in refinement	3676	7998
Observed reflections [$I > 2\sigma(I)$]	2944	6875
Parameters	203	428
R_1 (on F for obs. refls.)[a]	0.0376	0.0292
wR_2 (on F^2 for all refls.)[b]	0.1069	0.0839
F(000)	2592	12224
GOF	0.779	1.055
Largest diff. peak and hole [e $Å^{-3}$]	3.333 and −1.017	1.518 and −0.914

[a] $R1 = \Sigma||F_o| - |F_c||/\ \Sigma(F_o)$ for observed reflections. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{0.5}$ for all reflections.

tion with ether, was extracted with CH_2Cl_2. Addition of ether to the solution regenerated starting material **4a** (8 mg, 30%).

Nucleophilic Degradation of 3a by NaI in MeCN: A solution of **3a** (31 mg, 0.05 mmol) and $NaI{\cdot}2H_2O$ (100 mg, 0.54 mmol) in MeCN (4 mL) was heated under reflux for 10 h. The solvent was removed in vacuo and the solid residue was extracted with ether. After removal of ether in vacuo, complex **1** was obtained as a green solid. Yield 12 mg (ca. 70%).

X-ray Crystal Structure Determinations: Crystals of **4a**PF_6 and **5b**PF_6 were obtained by slow diffusion of petroleum ether into CH_2Cl_2 solutions of the complexes. Data collection was carried out with a Bruker SMART 1000 diffractometer with a CCD detector by a combination of four sets of ω scans (each scan 0.3° in 20 s), each set at different φ ($2\theta = -28°$). Low crystal temperatures were maintained with a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. Unit cell parameters were determined with SMART software[40] and refined with SAINT[41] on all observed reflections. Data reduction was performed with SAINT, absorption corrections were applied with the SADABS program.[42] The detailed crystal data and structure refinement parameters are listed in Table 5. The structures were solved by direct methods and refined by full-matrix, least-squares against F^2 of all data, with SHELXTL software.[43] All non-hydrogen and hydrogen atomic positions were located in difference Fourier maps and refined in anisotropic and isotropic approximations, respectively. CCDC-177284 (**4a**PF_6) and -177285 (**5b**PF_6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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