Facile [N]C−H Activation by a (*P*,*N*)-Chelate [3]Ferrocenophane−Ruthenium System

Patrick Liptau,[a] Daniel Carmona,*[b] Luis A. Oro,*[b] Fernando J. Lahoz,[b] Gerald Kehr,[a] and Gerhard Erker*[a]

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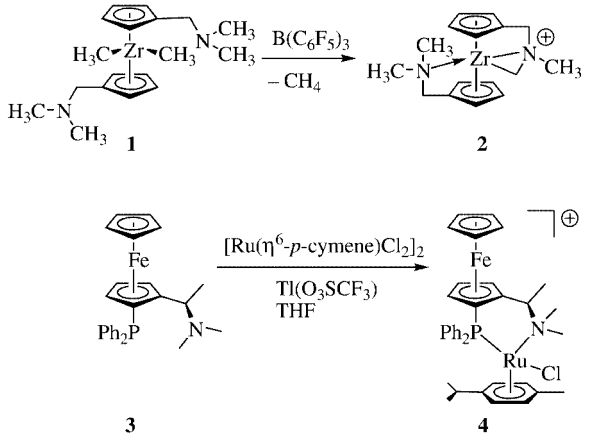
The chelate ligand **5** was prepared from the corresponding (dimethylamino)[3]ferrocenophane by directed *ortho*-lithiation with *n*-butyllithium followed by treatment with $ClPPh_2$. The rigid (*P*,*N*)-chelate ligand reacts with [Ru(η^6-*p*-cymene)Cl_2] dimer in the presence of KPF_6 in methanol to afford two products in an almost equimolar ratio. Instead of the simple addition product of the [Ru(*p*-cymene)Cl]$^+$ cation reagent to the chelate, selective C–H abstraction at an N–CH_3 moiety occurs with the formation of the "metallaaziridinium"-type product **8** (isolated as its PF_6^- salt). The liberated equivalent of HCl is trapped by the putative (*P*,*N*)-chelate [RuCl]$^+$ complex intermediate to form the corresponding internal hydrochloride complex **7**. The starting material **5** and the products **8** and **7** were characterised by single-crystal X-ray diffraction studies.

Introduction

The activation of aliphatic C−H bonds by transition metal complexes in a homogeneous phase has continued to attract considerable attention.[1] C−H activation in a position α to a nitrogen atom is of interest for carbon−carbon coupling reactions as well as because of its participation in hydrodenitrogenation of petroleum feedstocks.[2,3] This is commonly observed with early transition metals[4] (see Scheme 1). In the case of late transition metals, only a few examples have been reported.[5] Here, C−H activation mostly takes place next to a phosphorus atom,[6] but a much smaller number of examples of [N]C−H activation has been reported. Weissensteiner et al. have recently described the formation of the stable cationic chelate complex **4** which was obtained by treatment of the ferrocene-derived (*P*,*N*)-chelate ligand **3** with [Ru(η^6-cymene)Cl_2] dimer and a chloride abstractor.[7] We have now employed a related, more rigid [3]ferrocenophane (*P*,*N*)-ligand in a similar reaction and observed markedly different behaviour which is characterised by rapid C−H activation adjacent to nitrogen.



Scheme 1

Results and Discussion

The [3]ferrocenophane-based (*P*,*N*)-chelate ligand system **5** was prepared as described previously by us.[8] Treatment of 1,1′-diacetylferrocene with dimethylamine/$TiCl_4$ resulted in an intramolecular Mannich-type condensation reaction to generate the C_3 bridge. Subsequent catalytic hydrogenation (Pd/C) then gave an approximately 1:7 mixture of the corresponding saturated *cis*- and *trans*-disubstituted [3]ferrocenophane derivatives. The major *trans* isomer **5** was then treated with *n*-butyllithium to bring about directed *o*-lithiation at the Cp ring. Treatment with $ClPPh_2$ then gave the [3]ferrocenophane (*P*,*N*)-chelate ligand **5** in good yield.

Single crystals of the racemate (*rac*-**5**) were obtained from pentane at −18 °C. In the crystal, the enantiomers (*R*)-**5** (6*R*,8*R*,R_{pl}) and (*S*)-**5** (6*S*,8*S*,S_{pl}, see Scheme 2) were found as crystallographically independent molecules. The molecu-

[a] Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, 48149 Münster, Germany
Fax: (internat.) + 49-251-8336503
[b] Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, C.S.I.C., 50009 Zaragoza, Spain
Fax: (internat.) + 34-976-761143

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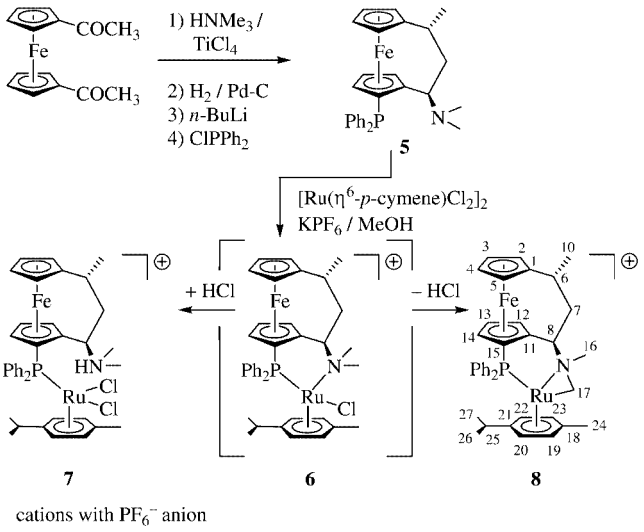
lar structure of the (*R*)-**5** enantiomer is depicted in Figure 1. The structure features an almost undistorted central ferrocene unit. The C_3 bridge that spans between the pair of almost parallel Cp ring systems attains a typically folded



Scheme 2

conformation. At this [3]ferrocenophane framework, the methyl substituent is found in a pseudoaxial orientation whereas the apparently more bulky NMe_2 group is attached pseudo-equatorially. This results in a strong deviation of the P1−C23−C27−C36−N1 chelate pincer from planarity. Inside this framework, the C23−P1 and C36−N1 vectors are found close to a *gauche* arrangement.

Ligand **5** was treated with $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ (*p*-cymene = 4-isopropyl-1-methylbenzene) and KPF_6 as a chloride abstractor in methanol at room temperature. The ^{31}P NMR spectra of the crude reaction mixture indicated the formation of two main products. Instead of the expected cationic (*P*,*N*)-chelate compound **6** the hydrochloride **7** and the cyclometallated species **8** were obtained (Scheme 2).

In the solid state, both **7** and **8** show the ruthenium centre as formally hexacoordinate with similar three-legged pianostool environments. Both cationic complexes exhibit an η^6-coordination of the *p*-cymene ring and the *P*-bonded metallo-ligand. In **7**, two chloride ligands with similar but statistically different Ru−Cl bond lengths [2.4102(8) and 2.3942(8) Å] complete the Ru coordination sphere. The molecular structure of complex **8** can be related to that of **7** if we assume the formal substitution of the two halogen atoms by an η^2-bonded CH_2N moiety (Figures 2 and 3).

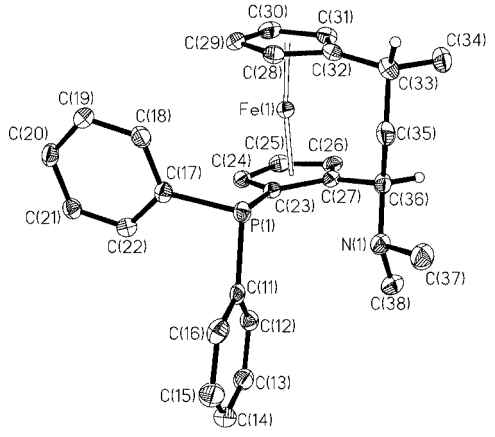


Figure 1. Molecular structure of *rac*-**5** [only the structure of the (*R*)-**5** enantiomer is depicted]; selected bond lengths [Å] and bond and torsional angles [°] [values of the (*S*)-**5** enantiomer in brackets]: Fe−G(2) 1.6307(10) [1.6278(9)], Fe−G(3) 1.6342(10) [1.6314(10)], P−C(11) 1.840(2) [1.836(2)], P−C(17) 1.847(2) [1.841(2)], P−C(23) 1.824(2) [1.820(2)], N−C(36) 1.478(3) [1.482(2)], N−C(37) 1.454(3) [1.453(3)], N−C(38) 1.464(3) [1.454(3)], C(27)−C(36) 1.511(3) [1.515(3)], C(32)−C(33) 1.504(3) [1.510(3)], C(33)−C(35) 1.551(3) [1.547(3)], C(35)−C(36) 1.546(3) [1.538(3)], G(2)−Fe−G(3) 172.47(5) [172.94(5)], C(11)−P−C(17) 99.56(9) [103.00(9)], C(11)−P−C(23) 102.46(9) [100.13(9)], C(17)−P−C(23) 99.03(9) [99.59(9)], C(36)−N−C(37) 115.14(18) [114.62(17)], C(36)−N−C(38) 109.43(17) [110.31(17)], C(37)−N−C(38) 109.17(18) [108.36(17)], C(32)−C(33)−C(35) 112.65(18) [113.32(17)], C(33)−C(35)−C(36) 116.59(19) [116.30(17)], N−C(36)−C(27) 106.20(17) [106.56(16)], N−C(36)−C(35) 111.62(18) [111.67(16)], C(27)−C(36)−C(35) 113.56(17) [113.30(17)], C(23)−C(27)−C(36)−C(35) −69.9(3) [69.8(2)], C(28)−C(32)−C(33)−C(35) 52.3(3) [−50.0(3)], C(32)−C(33)−C(35)−C(36) 69.1(3) [−70.2(2)], C(33)−C(35)−C(36)−C(27) −60.2(2) [60.0(2)], C(33)−C(35)−C(36)−N 179.81(18) [−179.68(16)], C(35)−C(36)−N−C(37) −42.5(2) [47.4(2)], C(35)−C(36)−N−C(38) −165.86(18) [170.01(17)]; G(2) and G(3) represent the centroids of the substituted Cp ligands

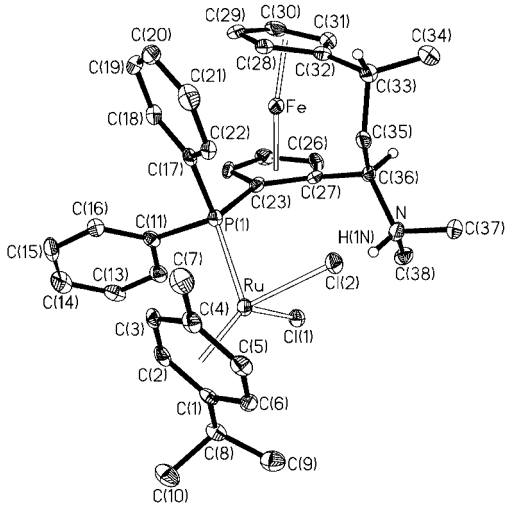


Figure 2. Molecular structure of complex **7** (only the cation is depicted); selected bond lengths [Å] and bond and torsional angles [°]: Ru−Cl(2) 2.4102(8), Ru−Cl(1) 2.3942(8), Ru−P 2.4011(9), Ru−G(1) 1.6964(13), Fe−G(2) 1.6352(14), Fe−G(3) 1.6552(15), P−C(11) 1.834(3), P−C(17) 1.819(3), P−C(23) 1.865(3), N−C(36) 1.527(4), N−C(37) 1.497(4), N−C(38) 1.489(3), C(27)−C(36) 1.520(4), C(32)−C(33) 1.522(4), C(33)−C(35) 1.551(4), C(35)−C(36) 1.521(4), Cl(2)−Ru−P 93.09(3), Cl(1)−Ru−P 83.61(3), Cl(2)/Ru−Cl(1) 87.96(3), G(2)−Fe−G(3) 172.54(8), Ru−P−C(11) 103.31(10), Ru−P−C(17) 117.25(11), Ru−P−C(23) 123.63(10), C(11)−P−C(17) 103.39(15), C(11)−P−C(23) 101.79(14), C(17)−P−C(23) 104.50(13), C(36)−N−C(37) 111.9(2), C(36)−N−C(38) 111.6(2), C(37)−N−C(38) 108.6(3), C(32)−C(33)−C(35) 111.3(3), C(33)−C(35)−C(36) 113.7(3), N−C(36)−C(27) 111.5(2), N−C(36)−C(35) 114.3(2), C(27)−C(36)−C(35) 113.5(3), C(23)−C(27)−C(36)−C(35) −39.0(4), C(28)−C(32)−C(33)−C(35) 75.2(4), C(32)−C(33)−C(35)−C(36) 59.4(3), C(33)−C(35)−C(36)−C(27) −82.8(3), C(33)−C(35)−C(36)−N 147.7(3), C(35)−C(36)−N−C(37) −52.7(3), C(35)−C(36)−N−C(38) −174.7(2); G(1) denotes the centroid of the *p*-cymene ring

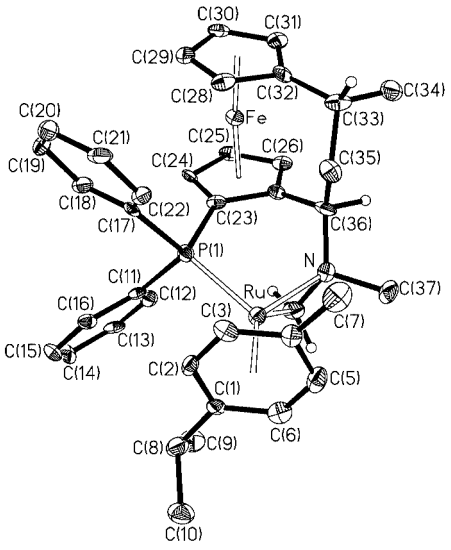


Figure 3. View of the molecular geometry of complex **8** (only the cation is depicted); selected bond lengths [Å] and bond and torsional angles [°]: Ru−N 2.120(4), Ru−C(38) 2.068(5), Ru−P 2.3133(15), Ru−G(1) 1.738(2), Fe−G(2) 1.624(2), Fe−G(3) 1.630(2), P−C(11) 1.827(5), P−C(17) 1.836(5), P−C(23) 1.806(5), N−C(36) 1.481(6), N−C(37) 1.488(6), N−C(38) 1.417(6), C(27)−C(36) 1.468(7), C(32)−C(33) 1.489(7), C(33)−C(35) 1.544(6), C(35)−C(36) 1.567(6), N−Ru−P 93.03(13), C(38)−Ru−P 85.11(16), N−Ru−C(38) 39.55(15), G(2)−Fe−G(3) 173.78(13), Ru−P−C(11) 111.47(16), Ru−P−C(17) 121.60(18), Ru−P−C(23) 112.94(18), C(11)−P−C(17) 101.7(2), C(11)−P−C(23) 101.6(2), C(17)−P−C(23) 105.2(2), C(36)−N−Ru 122.6(3), C(37)−N−Ru 116.4(3), C(38)−N−Ru 68.3(2), C(36)−N−C(37) 109.7(4), C(36)−N−C(38) 120.2(5), C(37)−N−C(38) 114.3(4), C(32)−C(33)−C(35) 113.0(4), C(33)−C(35)−C(36) 115.3(4), N−C(36)−C(27) 113.2(4), N−C(36)−C(35) 108.8(4), C(27)−C(36)−C(35) 113.5(4), C(23)−C(27)−C(36)−C(35) −71.4(7), C(28)−C(32)−C(33)−C(35) 46.2(6), C(32)−C(33)−C(35)−C(36) 72.0(5), C(33)−C(35)−C(36)−C(27) −60.1(6), C(33)−C(35)−C(36)−N 172.8(4), C(35)−C(36)−N−C(37) −78.7(4), C(35)−C(36)−N−C(38) 145.8(4)

The bond lengths within this three-membered metallacycle being Ru−N 2.120(4), Ru−C(38) 2.068(5) and N−C(38) 1.417(6) Å. From these structural parameters an intermediate situation, slightly closer to $(sp^3)C-NR_2$ between a methylene ammonium salt [the $(sp^2)C=N^+R_2$ mean distance in CSD is 1.334 Å] and an aza-metallacyclopropane system [$(sp^3)C-NR_2$ mean distance 1.469 Å] seems to be present. A relevant structural feature of **7** seems to be the presence of a bifurcated asymmetric hydrogen bond between the dimethylammonium group and the two chloride ligands [N···Cl(1) 3.143(3) and N···Cl(2) 3.203(3) Å, see Figure 2]. This may account for the conformational modification observed for the bridging C_3 chain in **7** from the free ligand **5** [torsion angles C(28)−C(32)−C(33)−C(35) 52.3(3)° (in **5**) and 75.2(4)° (in **7**); C(23)−C(27)−C(36)−C(35) −69.9(3)° (**5**) and −39.0(4)° (**7**)]. Interestingly, the strain of this presumably enforced conformation is released when **8** is formed, as confirmed by the values detected for its torsion angles [46.2(6)° and −71.4(7)°] which are very similar to those observed in **5**. Both compounds crystallise in centrosymmetric space groups with only one independent molecule in the unit cell. This feature implies the presence of racemic mixtures of **7** and **8** in the crystals.

As mentioned above, the Ru/N/C ring in **8** can be described as an iminium salt coordinated to the metal atom or as an aza-metallacyclopropane system. We measured direct NMR coupling constants ^1J(C,H) as a method of estimating the s-character of the corresponding C−H bond. For the CH_2 group of the ring, the obtained values of 167 and 176 Hz fall in the range of aziridine (168 Hz) and oxirane (176 Hz). For an iminium salt, larger values would be expected. These data, together with the determined structural parameters, seem to indicate a more accurate description of the metallacycle as an aza-metallacyclopropane ring.[4]

To explain the formation of **7** and **8** it is reasonable to assume that an intermediate (*P*,*N*)-chelate complex [Ru(*p*-cymene)(Cl)(**5**)]·[PF_6] (**6**, Scheme 2) is initially formed. Subsequent cleavage of a C−H methyl bond and cyclometallation lead to **8**, liberating 1 equiv. of HCl. This HCl then may react with a second equivalent of the (*P*,*N*)-chelate complex to yield the hydrochloride **7** (see Scheme 2).

Complex **8** was obtained as a single diastereoisomer. It is likely that this results from a diastereoselective formation of the intermediate **6** which may be efficiently controlled by the rigid framework of this special (*P*,*N*)-chelate ligand. An inspection of molecular models revealed that the (pro-*S*)-*N*-methyl group may be oriented almost coplanar with the Ru−Cl vector. This may possibly have favoured the selective C−H activation[9] at this $N-CH_3$ group to form the observed product **8**. It is likely that such conformational features may have caused the observed differences in the behaviour of the systems described here from the open, more flexible system **4** which was described previously in the literature (see Scheme 1).[7,10]

Experimental Section

General Remarks: All reactions were carried out under dry argon in Schlenk-type glassware or in a glove-box. Solvents were dried and distilled prior to use. NMR spectra were recorded with a Bruker AC 200 P (^{31}P, 81.0 MHz), Varian UNITY 300 (^{31}P, 121.5 MHz) or Varian UNITYplus 600 (^{1}H, 599.9 MHz; ^{13}C, 150.8 MHz; ^{31}P, 242.5 MHz) spectrometer. Most assignments were confirmed using 2D spectra.[11] Exact masses were determined with a Micromass Quattro LC-Z electrospray mass spectrometer. The following instruments were used for additional physical characterisation: IR spectroscopy: Nicolet 5DXC FT-IR spectrometer; melting points: DSC 2010 (TA instruments); elemental analyses: Foss Heraeus CHN-O-Rapid. Compound *rac*-**5** was prepared in an analogous manner previously described by us for the (*R*)-**5** and (*S*)-**5** enantiomers.[8]

X-ray Structure Determinations: Data for **5**, **7** and **8** were collected at low temperature (100 K) with a Bruker SMART APEX diffractometer equipped with a CCD area detector using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data were measured through the use of CCD recording of ω-rotation frames

(0.3° each). Data were integrated with the Bruker SAINT program (*SAINT*+, version 6.01; Bruker AXS, Inc., Madison, WI, **2001** and SAINT, version 6.02) and corrected for Lorentz and polarisation effects. Absorption corrections were applied using the SADABS routine (SADABS: Area-Detector Absorption Correction, **1996**; Bruker-AXS within SAINT+ package, v. 6.01). Structures were solved by direct methods and completed by subsequent difference Fourier techniques. Refinement on F^2 was carried out by full-matrix least squares (SHELXL-97) (G. M. Sheldrick, *SHELXL-97 Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997**). All non-hydrogen atoms were refined with anisotropic displacement parameters. In **5** and **7**, hydrogen atoms were found from difference Fourier maps and refined with positional parameters riding on carbon atoms and free thermal parameters. Hydrogen atoms in **8** were analogously refined except a terminal methyl group for which hydrogen atoms were included in calculated positions.

Preparation of 5: To a solution of the corresponding amino[3]ferrocenophane (714 mg, 2.52 mmol) in Et_2O (10 mL) at 4 °C was added *n*-butyllithium (1.9 mL, 1.6 M, 3.02 mmol, 1.2 equiv.). The cooling bath was removed and the solution stirred for 3 h, during which the colour changed from light orange to dark orange. Afterwards, the mixture was cooled to 4 °C and chlorodiphenylphosphane (0.54 mL, 3.02 mmol, 1.2 equiv.) was added dropwise. The cooling bath was removed and the resultant suspension stirred at room temperature for 12 h. The reaction was quenched with saturated $NaHCO_3$ solution (10 mL) and the aqueous phase extracted with pentane (3 × 10 mL). The combined organic phases were washed with water and brine and dried with $MgSO_4$. Column chromatography on silica (SiO_2; pentane/ethanol, 6:1) yielded **5** as a yellow solid (0.547 g, 1.17 mmol, 46%), m.p. 156.1 °C (DSC). IR (KBr): $\tilde{\nu}$ = 3104 (w), 3072 (w), 2993 (m), 2953 (m), 2854 (m), 2808 (m), 2751 (s), 1643 (m), 1617 (m), 1466 (m), 1446 (s), 1308 (m), 1143 (m), 1038 (s), 755 (s), 702 (s), 531 (m) cm^{-1}. ^1H NMR (599.9 MHz, $CDCl_3$, 25 °C): δ = 1.22 [d, $^3J_{H,H}$ = 7.3 Hz, 3 H, C(10)−H], 1.79 [s, 6 H, C(16), C(17)−H], 2.31 [m, 1 H, C(7)−H_{trans}], 2.68 [pd, 1 H, C(8)−H], 2.84 [m, 1 H, C(6)−H], 3.16 [m, 1 H, C(7)−H_{cis}], 3.68 [m, 2 H, C(2−5)−H, C(12−14)−H], 3.85 [m, 1 H, C(2−5)−H], 4.11 [m, 1 H, C(2−5)−H], 4.14 [m, 2 H, C(12−14)−H], 4.41 [m, 1 H, C(2−5)−H], 7.22−7.47 (m, 10 H, phenyl−H) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, $CDCl_3$, 25 °C): δ = 16.7 [C(10)], 27.7 [C(6)], 44.2 [C(16), C(17)], 45.3 [C(7)], 59.1 [C(8)], 67.5 [C(2−5)], 68.6 [C(2−5)], 68.9 [C(12−14)], 70.2 [C(2−5)], 72.2 [C(2−5)], 73.9 [C(12−14)], 74.1 [C(12−14)], 75.2 [d, $^1J_{C,P}$ = 12.0 Hz, C(15)], 91.4 [br., C(11)], 93.3 [C(1)], 127.5, 127.7, 128.1, 133.1, 133.4 (d, $J_{C,P}$ = 19.0 Hz), 134.2, (d, $J_{C,P}$ = 19.0 Hz), 138.9, 139.4 (all broad, phenyl−C) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = −21.6 ppm. $C_{28}H_{30}FeNP$ (467.375): calcd. C 71.96, H 6.47, N 3.00; found C 71.74, H 6.07, N 2.96.

Crystal Data for *rac*-5: Crystals suitable for the X-ray structure analysis were grown from a pentane solution at −18 °C. $C_{28}H_{30}FeNP$ (467.35), triclinic, $P\bar{1}$ (no.2), a = 8.8320(5), b = 14.6260(8), c = 18.0284(10) Å, α = 98.110(1), β = 93.210(1), γ = 96.919(1)°, V = 2282.4(2) Å^3, Z = 4, $\rho_{calcd.}$ = 1.360 Mg·m^{-3}, μ = 0.747 mm^{-1}, F(000) = 984, crystal size 0.30 × 0.27 × 0.15 mm. θ range for data collection 1.42 to 28.58° (−11 ≤ h ≤ 11, −19 ≤ k ≤ 19, −22 ≤ l ≤ 23), reflections collected/unique 26891/10615 [R(int) = 0.0361], max. and min. transmission 0.876172 and 0.667727, data/parameters 10615/619, S (on F^2) = 0.924, final R_{int} [$I > 2\sigma(I)$]: $R1$ = 0.0397, $wR2$ = 0.0799, R_{int} (all data): $R1$ = 0.0543, $wR2$ = 0.0847, largest diff. peak and hole 0.513 and −0.387 e·Å^{-3}.

Preparation of the Complexes 7 and 8: A solution of **5** (762 mg, 1.63 mmol), [Ru(η^6-*p*-cymene)Cl_2]$_2$ (500 mg, 0.81 mmol) and KPF_6 (300 mg, 1.63 mmol) in MeOH (48 mL) was stirred at room temperature for 12 h. The hydrochloride **7** which precipitated was collected by filtration and washed with MeOH to yield an orange solid (520 mg, 0.56 mmol, 34%), m.p. 207 °C (dec., DSC). The combined filtrates were concentrated in vacuo to yield **8** in two crops as an orange solid (286 mg, 0.33 mmol, 20%), m.p. 261 °C (DSC). **Metallacycle 8:** Crystals suitable for the X-ray structure analysis were grown by slow diffusion of Et_2O into an MeOH solution. IR (KBr): $\tilde{\nu}$ = 3058 (w), 2966 (m), 2920 (m), 2868 (w), 1630 (w), 1492 (m), 1446 (m), 1097 (m), 1018 (m), 841 (s), 755 (m), 702 (m), 564 (m) cm^{-1}. ^1H NMR (599.9 MHz, $CDCl_3$, 25 °C): δ = 1.00 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, C(10)−H], 1.11 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, C(26)/C(27)−H], 1.14 [d, $^3J_{H,H}$ = 7.2 Hz, 3 H, C(26)/C(27)−H], 1.90 [m, 1 H, C(5)−H], 2.01 [m, 1 H, C(25)−H], 2.04 [m, 1 H, C(7)−H], 2.15 [s, 3 H, C(24)−H], 2.42 [m, 1 H, C(7)−H], 2.54 [m, 1 H, C(6)−H], 2.77 [d, $^3J_{H,H}$ = 11.8 Hz, 1 H, C(17)−H], 3.05 [s, 3 H, C(16)−H], 3.40 [dd, $^3J_{H,H}$ = 2.1, 11.6 Hz, 1 H, C(8)−H], 3.45 [m, 1 H, C(17)−H], 3.47 [m, 1 H, C(2−4)−H], 3.77 [m, 1 H, C(2−4)−H], 4.00 [m, 1 H, C(2−4)−H], 4.09 [m, 1 H, C(12−14)−H], 4.26 [m, 2 H, C(12−14)−H], 4.41 [d, $^3J_{H,H}$ = 5.1 Hz, 1 H, C(19)/C(20)/C(22)/C(23)−H], 4.72 [d, $^3J_{H,H}$ = 5.8 Hz, 1 H, C(19)/C(20)/C(22)/C(23)−H], 5.58 [d, $^3J_{H,H}$ = 5.6 Hz, 1 H, C(19)/C(20)/C(22)/C(23)−H], 5.74 [d, $^3J_{H,H}$ = 5.8 Hz, 1 H, C(19)/C(20)/C(22)/C(23)−H], 6.98 (m, 2 H, phenyl−H), 7.27 (m, 3 H, phenyl−H), 7.68 (m, 3 H, phenyl−H), 8.22 (m, 2 H, phenyl−H) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, $CDCl_3$, 25 °C): δ = 16.4 [C(26)/C(27)], 18.9 [C(24)], 23.4 [C(26)/C(27)], 23.8 [C(10)], 27.0 [C(6)], 31.3 [C(25)], 46.3 [d, $J_{C,P}$ = 9.5 Hz, C(17)], 50.7 [C(7)], 57.6 [C(16)], 60.7 [C(8)], 67.8 [d, $J_{C,P}$ = 42.2 Hz, C(15)], 68.4 [C(2−4)], 68.9 [C(2−4)], 69.3 [d, $J_{C,P}$ = 5.2 Hz, C(12−14), 71.1 [C(2−4)], 71.4 [d, $J_{C,P}$ = 8.3 Hz, C(12−14)], 72.6 [C(5)], 74.2 [C(12−14)], 83.4 [d, $J_{C,P}$ = 18.8 Hz, C(11)], 84.9 [C(19)/C(20)/C(22)/C(23)], 88.2 [d, $J_{C,P}$ = 4.4 Hz, C(19)/C(20)/C(22)/C(23)], 89.5 [d, $J_{C,P}$ = 3.6 Hz, C(19)/C(20)/C(22)/C(23)], 92.7 [d, $J_{C,P}$ = 2.0 Hz, C(19)/C(20)/C(22)/C(23)], 92.8 [C(1)], 128.2 (d, $J_{C,P}$ = 9.9 Hz, *ortho*/*meta*-phenyl C), 128.4 (d, $J_{C,P}$ = 10.3 Hz, *ortho*/*meta*-phenyl C), 129.4 (*para*-phenyl C), 130.3 (d, $J_{C,P}$ = 9.5 Hz, *ortho*/*meta*-phenyl C), 131.6 (*para*-phenyl C), 134.9 (d, $J_{C,P}$ = 12.9 Hz, *ortho*/*meta*-phenyl C), 135.8 (d, $^1J_{C,P}$ = 49.1 Hz, *ipso*-phenyl C), 141.4 (d, $^1J_{C,P}$ = 53.6 Hz, *ipso*-phenyl C) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = −145.1 (sept, $^1J_{F,P}$ = 716.6 Hz, PF_6), 37.1 ppm. Exact mass ($C_{38}H_{43}FeNPRu$): calcd. 702.1519, found 702.1511. **Hydrochloride 7:** Crystals suitable for the X-ray structure analysis were grown by slow concentration of an acetone solution. IR (KBr): $\tilde{\nu}$ = 3651 (m), 3045 (s), 2973 (m), 2874 (m), 1630 (w), 1485 (s), 1439 (s), 1393 (m), 1328 (m), 913 (s), 854 (s), 702 (s), 564 (s) cm^{-1}. ^1H NMR (599.9 MHz, $CDCl_3$, 25 °C): δ = 1.01 [d, $^3J_{H,H}$ = 6.9 Hz, 3 H, C(26)/C(27)−H], 1.13 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, C(26)/C(27)−H, C(10)−H], 1.83 [s, 3 H, C(24)−H], 1.85 [m, 1 H, C(5)−H], 2.26 [m, 1 H, C(7)−H], 2.37 [sept, $^3J_{H,H}$ = 6.8 Hz, 1 H, C(25)−H], 2.45 [m, 1 H, C(6)−H], 2.51 [m, 1 H, C(7)−H], 2.92 [s, 6 H, C(16), C(17)−H], 3.72 [m, 1 H, C(8)−H], 3.74 [m, 2 H, C(2−4)−H], 4.16 [m, 2 H, C(12−14)−H, C(19)/C(20)/C(22)/C(23)−H], 4.25 [m, 1 H, C(2−4)−H], 4.28 [m, 1 H, C(12−14)−H], 4.48 [bm, 1 H, C(19)/C(20)/C(22)/C(23)−H], 4.74 [m, 1 H, C(12−14)−H], 5.08 [bm, 1 H, C(19)/C(20)/C(22)/C(23)−H], 5.31 [d, $^3J_{H,H}$ = 5.3 Hz, 1 H, C(19)/C(20)/C(22)/C(23)−H], 7.42 (m, 6 H, phenyl H), 7.64 (m, 4 H, phenyl H), 8.12 (br., 1 H, N−H) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, $CDCl_3$, 25 °C): δ = 15.6 [C(10)], 17.9 [C(24)], 21.3 [C(26)/C(27)],

23.1 [C(26)/C(27)], 28.3 [C(6)], 30.5 [C(25)], 42.6 [C(16)/C(17)], 44.9 [C(7)], 45.3 [C(16)/C(17)], 66.3 [C(8)], 68.9 [C(2−4)], 69.7 [C(2−4)], 70.1 [C(12−14)], 71.5 [C(2−4)], 75.0 [C(5)], 77.0 [d, $^1J_{C,P}$ = 14.8 Hz, C(15)], 78.3 [d, $J_{C,P}$ = 16.3 Hz, C(12−14)], 82.0 [C(12−14)], 83.3 [d, $J_{C,P}$ = 25.0 Hz, C(11)], 84.6, 86.9, 87.0, 93.4 [C(19)/C(20)/C(22)/C(23)], 94.6 [C(1)], 97.4 [C(18)], 109.4 [C(21)], 128.1 (d, $J_{C,P}$ = 8.7 Hz, *ortho*/*meta*-phenyl C), 128.4 (br., *ortho*/*meta*-phenyl C), 128.5 (br., *ortho*/*meta*-phenyl C), 130.1 (*para*-phenyl C), 131.9 (br., *ortho*/*meta*-phenyl C), 132.3 (*para*-phenyl C), 136.7 (d, $^1J_{C,P}$ = 41.4 Hz, *ipso*-phenyl C), 142.2 (d, $^1J_{C,P}$ = 47.5 Hz, *ipso*-phenyl C) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = −145.1 (sept, $^1J_{F,P}$ = 716.6 Hz, PF_6), 13.3 ppm. $C_{38}H_{45}Cl_2F_6FeNP_2Ru$ (919.544): calcd. C 49.64, H 4.93, N 1.52; found C 49.61, H 4.73, N 1.31.

Crystal Data for 7: $C_{41}H_{51}Cl_2F_6FeNOP_2Ru$ (977.59), monoclinic, $P2_1/c$ (no. 14), a = 14.5842(12), b = 15.6498(13), c = 17.5933(14) Å, β = 95.272(2)°, V = 3998.5(6) Å^3, Z = 4, $\rho_{calcd.}$ = 1.624 Mg·m^{-3}, μ = 1.017 mm^{-1}, F(000) = 2000, crystal size 0.22 × 0.16 × 0.13 mm. θ range for data collection 1.74 to 28.52° (−15 ≤ h ≤ 19, −20 ≤ k ≤ 20, −22 ≤ l ≤ 23) reflections collected/unique 25996/9345 [R_{int} = 0.0486], max. and min. transmission 0.887895 and 0.735866, data/parameters 9345/547, S (on F^2) = 0.916, R_{int} [$I > 2\sigma(I)$]: $R1$ = 0.0420, wR^2 = 0.0622, R_{int} (all data): $R1$ = 0.0637, wR^2 = 0.0656, largest diff. peak and hole 1.170 and −0.823 e·Å^{-3}.

Crystal Structure of 8: $C_{38}H_{43}F_6FeNP_2Ru$ (846.59), orthorhombic, *Pbca* (no. 61), a = 16.7411(15), b = 18.9689(17), c = 21.6800(18) Å, V = 6884.7(10) Å^3, Z = 8, $\rho_{calcd.}$ = 1.634 Mg·m^{-3}, μ = 1.016 mm^{-1}, F(000) = 3456, crystal size 0.14 × 0.13 × 0.96 mm. θ range for data collection 1.87 to 26.00° (−20 ≤ h ≤ 20, −23 ≤ k ≤ 19, −23 ≤ l ≤ 26), reflections collected/unique 39041/6769 [R(int) = 0.1310], max. and min. transmission 0.916497 and 0.806607, data/parameters 6769/484, S (on F^2) 0.733, final R_{int} [$I > 2\sigma(I)$]: $R1$ = 0.0464, wR^2 = 0.0601, R_{int} (all data): $R1$ = 0.1061, wR^2 = 0.0686, largest diff. peak and hole 1.004 and −0.640 e·Å^{-3}.

CCDC-237957 to -237959 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 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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