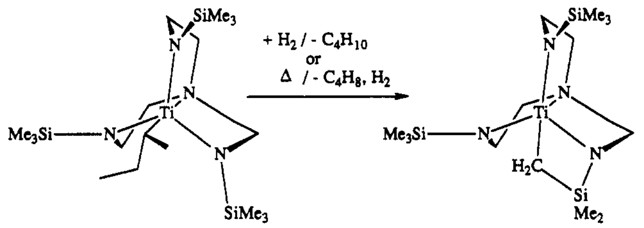
passed through a short alumina (activity 1) column before the complexes are recovered by crystallization. NMR spectra of the *n*-Bu derivative are similar to those for the chloro precursor, while the methylene protons in the $(Me_3SiNCH_2CH_2)_3N$ ligand are rendered diastereotopic in the *s*-Bu case.[37] Stable butyl derivatives of the early transition metals are rare, but known examples frequently contain electronegative, π-donating ancillary ligands in the coordination sphere.[31-36] Paramagnetic, crystalline brown $PhSCH_2V[(Me_3SiNCH_2CH_2)_3N]$[37] is formed cleanly using $[Li{\cdot}TMED]CH_2SPh$[38] (TMED = $Me_2NCH_2CH_2NMe_2$); the methyl analogue[37] was generated similarly but did not crystallize. Alkyls such as CH_2SPh may be of interest with respect to generation of a metal–carbon double bond.[39] A volatile, waxy aquamarine complex tentatively formulated as $V[(Me_3SiNCH_2CH_2)_3N]$ is obtained upon reducing $ClV[(Me_3SiNCH_2CH_2)_3N]$ with sodium amalgam in pentane; characterization of this paramagnetic species is underway.

The titanium *s*-Bu complex is cleanly converted to a metallacycle[37] either upon heating (k_{obs} = [2.0 (3)] × 10^{-4} at 66 °C) or upon treating the complex with H_2 (25 °C, 12 h, 3 atm) as in eq 4. Thermal conversion gives rise to butenes and H_2, while butane is produced in the dihydrogen reaction. A resonance at δ 8.29 observed in the proton NMR spectrum during the reaction with dihydrogen in a sealed NMR tube is tentatively assigned to a titanium(IV) monohydride intermediate. A related metallacycle is known for titanium,[40] and the proposition of a hydride intermediate in our case mirrors the loss of dihydrogen from $HM[N(SiMe_3)_2]_3$ (M = Th, U) with cyclization.[41] It would be one of the very few observable Ti(IV) hydride complexes[42,43] and therefore warrants further study.



(4)

We are continuing to investigate the chemistry of titanium and vanadium complexes containing the $(Me_3SiNCH_2CH_2)_3N$ ligand and will be attempting to prepare related complexes that contain metals in the chromium or manganese triads.

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Supplementary Material Available: Tables of final positional parameters and final thermal parameters (4 pages). Ordering information is given on any current masthead page.

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(38) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1966**, *31*, 4097.

(39) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

(40) Simpson, S. J.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3627.

(41) Simpson, S. J.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991.

(42) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059.

(43) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087.

Decamethylbimetallocenes

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Summary: Decamethylbimetallocenes have been synthesized for Fe, Co, and Rh, and the crystal structures of the 36-electron iron and rhodium complexes show a fully transoid conformation; electron-transfer studies indicate the 35-electron mixed-valence PF_6^- diiron salt is localized and suggest the neutral dicobalt and dirhodium bis-sandwich species have respectively 38 and 36 valence electrons.

The originality of transition-metal fulvalene chemistry is related to the large electronic delocalization of this bridging ligand, which results in considerable mutual influence of the two transition-metal centers.[1-7] For in-

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(1) (a) Review: McGovern, P. A.; Vollhardt, K. P. C. *Synlett* **1990**, 493. (b) Dragé, J. S.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 280. (c) Weidman, T. W.; Vollhardt, K. P. C. *Organometallics* **1984**, *3*, 82. (d) Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1983**, *105*, 1676. (e) Kahn, A. P.; Newman, D. A.; Vollhardt, K. P. C. *Synlett* **1990**, 141.

(2) (a) Wielstra, Y.; Gambarotta, S.; Spek, A. L.; Smeets, W. J. J. *Organometallics* **1990**, *9*, 2142. (b) Gambarotta, S.; Chiang, M. Y. N. *Organometallics* **1987**, *6*, 897.

(3) (a) Rausch, M. D. *J. Org. Chem.* **1961**, *26*, 1802. (b) Rausch, M. D. *J. Am. Chem. Soc.* **1960**, *82*, 2080. (c) Rausch, M. D.; Kovar, R. F.; Kraihemzel, C. S. *J. Am. Chem. Soc.* **1972**, *94*, 1271. (d) Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888. (e) Rausch, M. D.; Spink, W. C.; Conway, B. G.; et al. *J. Organomet. Chem.* **1990**, *383*, 227.

(4) (a) Smart, J. C.; Curtis, C. J. *J. Am. Chem. Soc.* **1977**, *99*, 3518. (b) Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 1009. (c) Smart, J. C.; Curtis, C. J. *Inorg. Chem.* **1977**, *16*, 1788; **1978**, *17*, 3290.

0276-7333/92/2311-1454$03.00/0

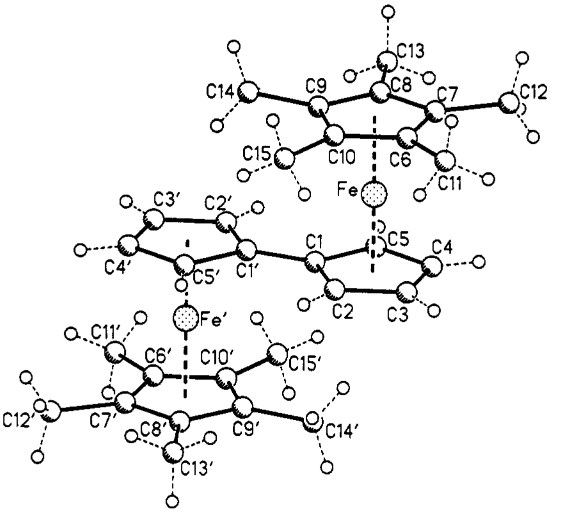


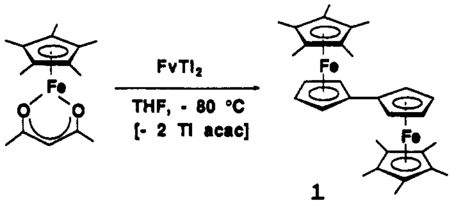
Figure 1. Molecular structure of the centrosymmetric molecule of 1. Atomic distances (Å) and angles (deg): Fe–C(1-5), mean value 2.052 (6); Fe–C(6-10), mean value 2.043 (4); C_{ring}–C_{ring} in Cp* and Fv, 1.428 (7) and 1.436 (7), respectively; Fe–cent(Cp*) and Fe–cent(Fv), 1.637 and 1.654, respectively; cent(Cp*)–Fe–cent(Fv), 178.8.

Table I. $E°$ Values (V vs SCE) for 1 and Other Ferrocene Derivatives

	$Fe_2FvCp^*_2$ (1)[a]	Fe_2FvCp_2[b]	FeCpCp* (2)	$FeCp_2$[c]	$FeCp_2^*$[d]
$E°_1$	0.27	0.48	0.35	0.58	–0.03
$E°_2$	0.51	0.81			

[a] Conditions: THF, 0.1 M n-Bu_4NBF_4, 20 °C. The same conditions were used for 3^{2+} and 4^{2+} (see text). All the literature values are given here with a slight solvent correction. For recent reviews on the electrochemistry of metallocenes, see: Geiger, W. E. *J. Organomet. Chem. Libr.* **1990**, *22*, 142. Strelets, V. V. *Russ. Chem. Rev.* (*Engl. Transl.*) **1989**, *48*, 297. [b] See: Matsumoto, T.; Sato, M.; Ichimura, A. *Bull. Soc. Chim. Jpn.* **1971**, *44*, 1720. Morrison, W. H.; Krogsrud, S.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 1998. [c] Kuwana, T.; Bublitz, D. E.; Hoh, G. *J. Am. Chem. Soc.* **1960**, *82*, 5811. [d] Koelle, U.; Khouzami, F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 640; *Chem. Ber.* **1981**, *114*, 2929.

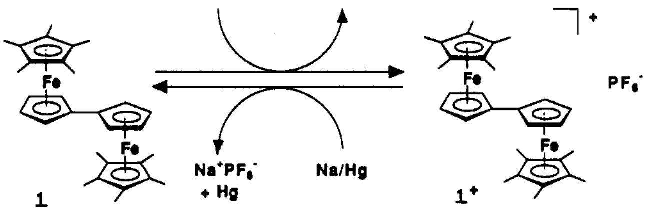
stance, the *permethylation* of the ancillary rings in bis-sandwich complexes provides the opportunity to *isolate and study a number of oxidation states of redox cascades*[7] as in rigid clusters. The systematic and rational synthesis of fulvalene complexes has been addressed by the Vollhardt group,[1] but most other fulvalene transition-metal chemistry is specific to each transition metal[2-7] (the coupling of paramagnetic states of monometallic compounds could become a promising generalized synthetic approach,[2,3] however). For example, there is no general synthetic route to decamethylbimetallocenes and there is not even any example of this family in the literature. Therefore, we addressed this problem, whose solution should much enrich the list of electron-reservoir complexes,[7] namely *robust redox reagents* able to transfer a variable number of electrons in stoichiometric and catalytic electron-transfer processes. Adding to the potential interest are the ferromagnetic properties of several odd-electron decamethylmetallocenes.[8] The synthetic strategy combines the use of the recently available fulvalene dianion[1,9] and [MCp*(acac)].[10a] The reaction of $[Tl_2Fv]$[1c,3e,9] (Fv = μ_2-η^{10}-fulvalene) with [FeCp*(acac)][10a] (Cp* = η^5-C_5Me_5) in THF at –80 °C for 2 h gives a 25% yield of 1 and (eq 1) as yellow-orange crystals after sublimation (0.01 Torr, 160 °C).



(1)

The ORTEP plot of the X-ray crystal structure of 1[11] is shown in Figure 1; 1 melts at 215 °C and is air-sensitive in solution and unstable in halogenated solvents. TLC analysis on SiO_2 plates leads to instantaneous oxidation to give blue 1^+ upon aerobic exposure. The cyclic voltammogram of 1 shows two chemically and electrochemically reversible one-electron oxidation waves: 1 (36e) $\rightleftharpoons$ 1^+ (35e) $\rightleftharpoons$ 1^{2+} (34e) (ΔE = 60 mV; $i_a/i_c = 1 \pm 0.1$ for scan rates between 20 and 800 mV s^{-1}). $E°$ values are compared in Table I.

The salt $1^+PF_6^-$ was synthesized by the instantaneous reaction of 1 with 1 equiv of $[FeCp_2]^+PF_6^-$ (Cp = η^5-C_5H_5) in THF. Workup gave blue microcrystals (76.5% yield) of $1^+PF_6^-$, which can be reduced back to 1 using Na/Hg in THF at 20 °C (eq 2). $1^+PF_6^-$ was characterized as a d^5–d^6 complex[15] by its ESR spectrum at 8 K, giving two g values ($g_1 = 3.66$, $g_2 = 1.73$), by elemental analysis, and by UV–visible and IR spectra.



(2)

The green pentamethylferrocinium complex $2^+PF_6^-$ was similarly synthesized and characterized (Table I; 2^{10a} is much less air-sensitive than 1). The Mössbauer spectra

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(5) (a) Herrmann, W. A.; Andrejewski, D.; Herdtweck, E. *J. Organomet. Chem.* **1987**, *319*, 183. (b) Ashworth, T. V.; Cuenca, A.; Herdtweck, E.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 289.

(6) (a) Köhler, F. H.; Doll, K. H.; Prössdorf, W.; Müller, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 151. (b) Note added in proof: A note by P. Hudeczek and F. H. Köhler on paramagnetic metallocenes has recently been submitted for publication in *Organometallics*.

(7) (a) Astruc, D. *Acc. Chem. Res.* **1986**, *19*, 377. (b) Lacoste, M.; Astruc, D.; Garland, M. T.; Varret, F. *Organometallics* **1988**, *7*, 2253. (c) Desbois, M.-H.; Astruc, D.; Guillin, J.; Varret, F. *J. Am. Chem. Soc.* **1985**, *111*, 5800. (d) Desbois, M.-H.; Astruc, D.; Guillin, J.; Varret, F. *Organometallics* **1989**, *8*, 1848. (e) Desbois, M.-H.; Astruc, D. *Organometallics* **1989**, *8*, 1841. (f) Desbois, M.-H.; Astruc, D.; Guillin, J.; Varret, F.; Trautwein, A. X.; Villeneuve, G. *J. Am. Chem. Soc.* **1989**, *111*, 5800.

(8) (a) Miller, J. S.; Epstein, A.-J.; Reiff, W.-H. *Chem. Rev.* **1988**, *88*, 201. (b) Kollmar, C.; Conty, M.; Kahn, O. *J. Am. Chem. Soc.* **1991**, *113*, 7994. (c) Broderick, W. E.; Thompson, J. A.; Godfrey, M. R.; Sabat, M.; Hoffman, B. M.; Day, E. P. *J. Am. Chem. Soc.* **1989**, *111*, 7656. (d) Broderick, W. E.; Thomson, J. A.; Day, E. P.; Hoffman, B. M. *Science* **1990**, *249*, 401.

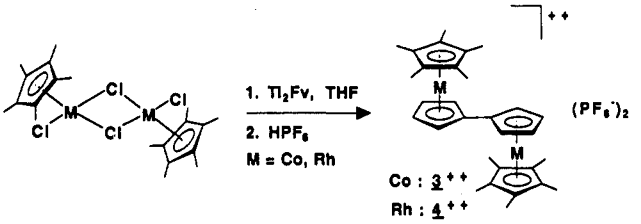
(9) (a) Escher, A.; Rutsch, W.; Neuenschwander, H. *Helv. Chim. Acta* **1986**, *69*, 1644. (b) Jutzi, P.; Schwartzen, K. H.; Mix, A. *Chem. Ber.* **1990**, *123*, 837.

(10) (a) Bunuel, E. E.; Valle, L.; Manriquez, J.-M. *Organometallics* **1985**, *4*, 1680. (b) For $[Fe_2FvCp_2]^{0/+}$, see: Cowan, D. O.; Kaufman, F. *J. Am. Chem. Soc.* **1970**, *92*, 219. Cowan, D. O.; Le Vanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1. Desbois, M.-H.; Rittinger, S.; Astruc, D. *J. Chem. Soc., Chem. Commun.*, in press.

(11) X-ray structure determination of 1: crystal dimensions 0.09 × 0.07 × 0.06 mm^3, measured on a Nicolet R3m/V diffractometer with Mo Kα radiation at 110 K; cell dimensions a = 8.217 (3) Å, b = 8.470 (2) Å, c = 9.004 (2) Å, α = 96.05 (2)°, β = 102.87 (2)°, γ = 91.34°, V = 607.4 (3) $Å^3$; $Z = 1$, d_{calcd} = 1.369 g cm^{-3}, μ = 1.21 mm^{-1}, triclinic, space group $P\bar{1}$, data collection of 1582 unique intensities ($2\theta_{max}$ = 35°), 1321 observed ($F_o > 4\sigma(F)$), structure solution with direct methods and refinement with full-matrix least squares, 146 parameters, rigid groups for hydrogen atoms; common isotropic U values for H atoms and anisotropic thermal parameters for all other atoms, which revealed some disorder of the iron atoms along the local C_5 axis, R = 0.073, R_w = 0.077, $w^{-1} = \sigma^2(F_o) + (6.21 \times 10^{-3})F_o^2$.

of $1^+PF_6^-$ show two doublets from 4 to 330 K which correspond to the Fe^{II} and Fe^{III} metallocene parameters,[12] indicating *localized mixed valency*[10b] (at 4 K IS (mm/s vs Fe) = 0.512 (1) and SQ (mm/s) = 2.143 (2) for Fe^{II} and IS (mm/s vs Fe) = 0.514 (2) and SQ (mm/s) = 0.396 (3) for Fe^{III}; the absorption factor is larger for Fe^{III} than for Fe^{II} in the ratio 1:0.39 at 300 K).

The 36e yellow dicobalt complex $[Co_2FvCp^*_2]^{2+}(PF_6^-)_2$ ($3^{2+}(PF_6^-)_2$) was synthesized in 54% yield by reacting $[CoCp^*Cl_2]_2$[13] with $[Tl_2Fv]$ (THF, 4 days) followed by oxidation using C_2Cl_6, precipitation using aqueous HPF_6, and recrystallization from acetone. The dirhodium analogue $[Rh_2FvCp^*_2]^{2+}(PF_6^-)_2$ ($4^{2+}(PF_6^-)_2$) was also made by refluxing $[RhCp^*Cl_2]_2$[14] with $[Tl_2Fv]$ for 1 week in THF. Workup using water and neutralization with aqueous HCl followed by precipitation using aqueous HPF_6 and recrystallization from acetone yields 44% of colorless crystals of $4^{2+}(PF_6^-)_2$[15] (for the X-ray structure[16] see the ORTEP plot in Figure 2).



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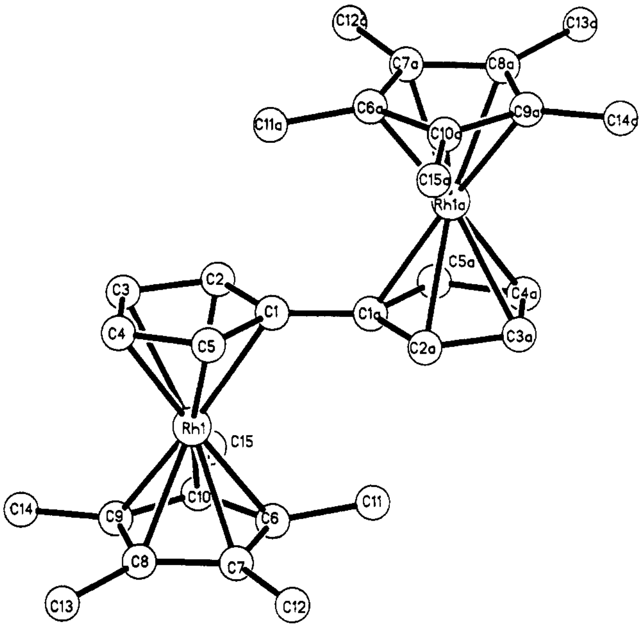

Figure 2. Molecular structure of the centrosymmetric molecule of 4^{2+}. Atomic distances (Å) and angles (deg): Rh–C(1–5), mean value 2.186 (0.011); Rh–C(6–10), mean value 2.156 (0.017); Rh–cent(Cp*) and Rh–cent(Fv), 1.79 and 1.82 (and 1.84), respectively; cent(Cp)–Rh–cent(Cp*), 173.4 and 171.4. The PF_6^- counterions are omitted.

Both 36e dications were also characterized by standard spectroscopic techniques, but cyclic voltammetry at 20 °C showed distinct behavior upon reduction. The dicobalt complex $3^{2+}(PF_6^-)_2$ shows three one-electron reversible waves ($E°$ = −0.85, −1.25, −2.08 V vs SCE) and a partly chemically and electrochemically reversible one-electron wave ($E°$ = −2.5 V vs SCE, ΔE = 70–130 mV), indicating the redox cascade (Hg cathode, DMF, 0.1 M $n\text{-}Bu_4NBF_4$)

$$3^{2+}\ (36e) \rightleftharpoons 3^{+}\ (37e) \rightleftharpoons 3\ (38e) \rightleftharpoons 3^{-}\ (39e) \rightleftharpoons 3^{2-}\ (40e)$$

as for $[Fe_2Fv(arene)_2]$.[7c,d,f] On the other hand, the dirhodium analogue $4^{2+}(PF_6^-)_2$ shows two close one-electron reversible waves separated by only 120 mV ($E°$ = −1.32 and −1.44 V vs SCE) as for $[Fe_2Cp^*_2(biphenyl)]^{2+}$,[17] strongly suggesting (as for the latter) ligand rearrangement during the second electron-transfer step (36e → 37e → 36e) in accord with the known high ligand character of the SOMO of rhodocene.[18]

Further synthetic and physical studies of these and other decamethylbimetallocenes and of their salts are in progress.

Acknowledgment. Postdoctoral DFG grants to S.R. and D.B. are gratefully acknowledged.

Supplementary Material Available: Full listings of bond distances and angles, atomic coordinates, and thermal parameters for 1 and 4^{2+} (10 pages). Ordering information is given on any current masthead page.

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[12] (a) Collins, R. L. *J. Chem. Phys.* **1965**, *42*, 1072. (b) Greenwood, N. N.; Gibb, T. C. *Mossbauer Spectroscopy*; Chapman and Hall Ed. London 1971.

[13] Kölle, U.; Khouzami, F.; Fuss, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 131; *Angew. Chem. Suppl.* **1982**, 230.

[14] Booth, B. L.; Haszeldine, R. N.; Hill, M. *J. Chem. Soc. A* **1969**, 1299.

[15] All the new compounds (1, $1^+PF_6^-$, $2^+PF_6^-$, $3^{2+}(PF_6^-)_2$, and $4^{2+}(PF_6^-)_2$) gave satisfactory elemental analyses and spectroscopic data. $1^+PF_6^-$: IR (KBr; ν cm^{-1}) 3430 (s), 2890 (w), 1632 (m), 1417 (m), 1024 (m), 836 (s, PF_6), 555 (s); vis–near-IR (CH_3CN; λ nm (ϵ, L mol^{-1} cm^{-1})) 554 (2120), 620 (1970), 1900 (1200). Anal. Calcd for $C_{30}H_{38}Fe_2PF_6$: C, 54.99; H, 5.84; P, 4.73. Found: C, 54.65; H, 5.82; P, 4.90. $2^+PF_6^-$: ESR (solid state, 8 K, 9.469 KHz) $g_1 = 4.42$, $g_2 = 1.28$; IR (KBr; ν, cm^{-1}) 3430 (m), 3108 (m), 2960 (w), 2930 (w), 1472 (m), 1418 (m), 1389 (s), 1027 (m), 861 (vs, PF_6), 555 (s); UV–vis (CH_3CN; λ, nm (ϵ, L mol^{-1} cm^{-1}) 734 (320). Anal. Calcd for $C_{15}H_{20}FePF_6$: C, 44.91; H, 5.03; P, 7.72. Found: C, 45.45; H, 5.03; P, 7.85. $3^{2+}(PF_6^-)_2$: ^1H NMR (250 MHz; δ vs TMS, acetone-d_6) 1.91 (s, 30 H), 5.79 (m, 4 H), 5.98 (m, 4 H); ^{13}C NMR (67.9 MHz, δ vs TMS, acetone-d_6) 10.0 (s), 84.0 (s), 89.7 (s), 93.4 (s), 99.2 (s). Anal. Calcd for $C_{15}H_{20}P_2F_{12}$: C, 44.68; H, 4.75. Found: C, 44.81; H, 4.73. $4^{2+}(PF_6^-)_2$: ^1H NMR (250 MHz, δ vs TMS, acetone-d_6) 2.02 (s, 30 H), 6.00 (m, 4 H), 6.26 (m, 4 H); ^{13}C NMR (67.9 MHz, δ vs TMS, acetone-d_6) 10.3 (s), 86.5 (br), 91.3 (br), 96.1 (D, $^1J_{Rh-C}$ = 8 Hz).

[16] X-ray structure determination of $4^{2+}(PF_6^-)_2$: crystal dimensions 0.71 × 0.21 × 0.50 mm^3 measured on a Nicolet-Siemens P3 diffractometer at 223 K; cell dimensions $a = 8.771$ (4) Å, $b = 2.142$ (1) Å, $c = 9.108$ (4) Å, $\alpha = \gamma = 90.00°$, $\beta = 87.95\ (4)°$, $V = 1709$ Å^3; $Z = 2$; $d_{calcd} = 1.455$ g cm^{-3}; $\mu = 1.06$ mm^{-1}; monoclinic, space group $P2_1/c$; data collection of 2528 unique intensities ($2\theta_{max} = 48°$), 2218 observed intensities ($F_o > 2\sigma(F)$), structure solution with direct methods and refinement with full-matrix least squares, 228 parameters, rigid groups for H atoms; common isotropic U values for H atoms and anisotropic thermal parameters for all other atoms; PF_6^- and C_5Me_5 groups disordered; $R = 0.0732$, $R_w = 0.0789$.

[17] Lacoste, M.; Rabâa, H.; Astruc, D.; Ardoin, N.; Varret, F.; Saillard, J.-Y.; Le Beuze, A. *J. Am. Chem. Soc.* **1990**, *112*, 9548.

[18] (a) Fischer, E. O.; Wawersik, H. *J. Organomet. Chem.* **1966**, *5*, 559. (b) Keller, H. J.; Wawersik, H. *J. Organomet. Chem.* **1967**, *8*, 185.