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Triple-Decker Complexes. 13.[1] Synthesis of the First Triple-Decker Complexes with a Bridging Phospholyl Ligand. Structures of the Triple-Decker Complex $[(\mu\text{-}C_4Me_4P)\{Fe(C_5Me_4CH_2C_6H_{11})\}(RuCp^*)]CF_3SO_3$ and the Related Sandwich Complex $Fe(C_4Me_4P)(C_5Me_4CH_2C_6H_{11})$

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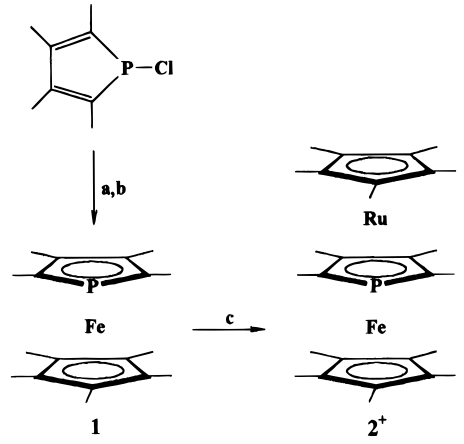
*Summary: The stacking reaction of the phosphaferrocene $Cp^*Fe(C_4Me_4P)$ (**1**) with the metallo-electrophiles $[Cp^*Ru(solv)_x]^+$ (solv = acetone, CH_2Cl_2) gives the 30e triple-decker complex $[(\mu\text{-}C_4Me_4P)(FeCp^*)(RuCp^*)]CF_3SO_3$ (**3**), the first compound with a central phospholyl ligand. The cyclohexylmethyl derivative $[(\mu\text{-}C_4Me_4P)\{Fe(C_5Me_4CH_2C_6H_{11})\}(RuCp^*)]CF_3SO_3$ (**10**) shows metal-to-phospholyl distances of 164.4(1) pm for Fe and 180.4(1) pm for Ru.*

Phospholyl ligands display a rich coordination chemistry,[2] but triple-decker complexes with bridging phospholyl ligands are as yet unknown. This seems astonishing, since the pentaphospholyl (P_5)[3] and 1,2,4-triphospholyl rings ($P_2(CR)_2P$ with R = Bu^t)[4] are known to act as bridging ligands in triple-decker structures. In this communication we describe the first synthesis of a triple-decker complex with a bridging 2,3,4,5-tetramethylphospholyl ligand.

We selected the phosphaferrocene $Cp^*Fe(C_4Me_4P)$ (**1**) as the starting compound and studied stacking reactions of **1** with metallo-electrophiles.[5] Complex **1**[6] was readily made from $[Cp^*Fe(NCMe)_3]PF_6$[7] and $Li(C_4Me_4P)$.[8] Dehalogenation of $[Cp^*RuCl]_4$ with $AgCF_3SO_3$ in acetone or CH_2Cl_2 produces the metallo-electrophiles $[Cp^*Ru(solv)_x]^+$ (solv = acetone, CH_2Cl_2). These undergo stacking reactions with the complex **1**. The 30e triple-decker cation $[(\mu\text{-}C_4Me_4P)(FeCp^*)(RuCp^*)]^+$ ($\mathbf{2}^+$) is formed within 1 h and could be isolated as the salt $(\mathbf{2})CF_3SO_3$ ($\equiv$**3**)[9] (Scheme 1).

Scheme 1[a]



[a] Legend: (a) 4 Li in THF; (b) $[Cp^*Fe(NCMe)_3]PF_6$ in THF; (c) $[Cp^*Ru(solv)_3]^+$ in acetone or CH_2Cl_2.

Two regiochemistries are conceivable for the stacking reaction of **1**, one which gives $\mathbf{2}^+$ and an alternative which would give a triple-decker cation with a bridging Cp* ligand. We note here that triple-decker complexes with terminal phospholyl ligands[10] as well as other ones with bridging pentamethylcyclopentadienyl ligands[11] are known. On the basis of the present experimental data we cannot decide whether $\mathbf{2}^+$ is the more stable isomer. The formation of $\mathbf{2}^+$ could also be the outcome of kinetic control. Attack of the metallo-electrophile at the open face of the phospholyl ligand of **1** could for

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(1) Part 12: Herberich, G. E.; Englert, U.; Ganter, B.; Lamertz, C. *Organometallics* **1996**, *15*, 5236.

(2) Mathey, F. *Coord. Chem. Rev.* **1994**, *137*, 1.

(3) (a) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1104. (b) Rink, B.; Scherer, O. J.; Heckmann, G.; Wolmershäuser, G. *Chem. Ber.* **1992**, *125*, 1011. (c) Scherer, O. J.; Brück, T.; Wolmershäuser, G. *Chem. Ber.* **1989**, *122*, 2049.

(4) Hitchcock, P. B.; Johnson, J. A.; Nixon, J. F. *Organometallics* **1995**, *14*, 4382.

(5) Herberich, G. E.; Englert, U.; Marken, F.; Hofmann, P. *Organometallics* **1993**, *12*, 4039.

(6) Preparation of **1**: To a solution of C_4Me_4PCl (1.56 g, 8.9 mmol) in THF was added freshly cut lithium metal (250 mg). After the reaction mixture was stirred for 4 h, unreacted lithium was removed from the solution. $[Cp^*Fe(NCMe)_3]PF_6$[7] (4.12 g, 8.9 mmol) was added, and the dark red mixture was stirred for 1 h. After removal of all volatiles under vacuum, the residue was dissolved in CH_2Cl_2, and the solution was filtered through silica (5 cm) using hexane (300 mL) as eluent. The orange solution was evaporated to dryness to give **1** (2.42 g, 82%) as orange crystals. Anal. Calcd for $C_{18}H_{27}FeP$: C, 65.47; H, 8.24. Found: C, 65.08; H, 8.17. ^1H NMR (500 MHz, $CDCl_3$): δ 1.64 (d, J_{PH} = 9.8 Hz, 2 Me_α), 1.74 (s, Cp*), 1.88 (s, 2 Me_β). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$): δ 10.03 (s, Cp*), 11.36 (s, 2 Me_β), 13.07 (d, J_{PC} = 23.8 Hz, 2 Me_α), 81.48 (s, Cp*), 91.61 (d, J_{PC} = 3.8 Hz, 2 C_β), 91.77 (d, 2C, J_{PC} = 53.6 Hz, 2 C_α). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ −61.2. MS (EI): m/z (I_{rel}) 330.2 (100, M^+), 315.0 (15, $M^+ - Me$).

(7) Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094.

(8) Douglas, T.; Theopold, K. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1367. See also: Nief, F.; Mathey, F.; Ricard, L.; Robert, F. *Organometallics* **1988**, *7*, 921.

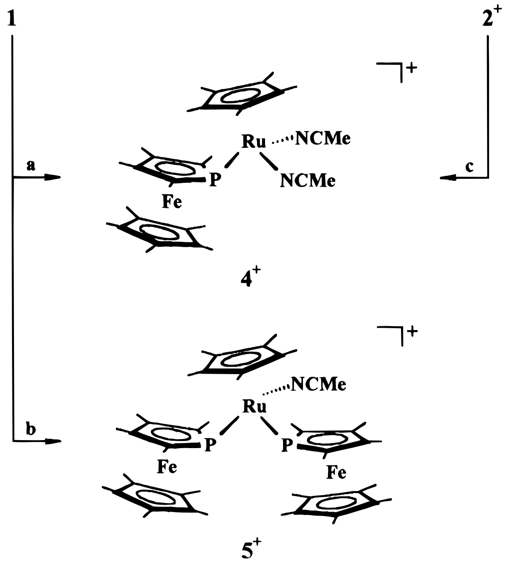
(9) Preparation of **3**: A suspension of $[Cp^*RuCl]_4$ (187 mg, 0.17 mmol) in acetone (or CH_2Cl_2) was cooled to 0 °C; $AgCF_3SO_3$ (176 mg, 0.68 mmol) was added, and the mixture was stirred for 30 min. The suspension was filtered through Kieselguhr into a Schlenk tube with **1** (226 mg, 0.68 mmol), and stirring was continued for 1 h. The reaction mixture was evaporated to dryness, dissolved in acetone (10 mL), and filtered through a layer of alumina (5% H_2O, 3 cm); the product was eluted with acetone. The solution was concentrated to a small volume and layered with Et_2O to give **3** (135 mg, 28%) as violet crystalline powder. Anal. Calcd for $C_{29}H_{42}F_3FeO_3PRuS$: C, 48.68; H, 5.92. Found: C, 48.62; H, 6.12. ^1H NMR (500 MHz, d_6-acetone): δ 1.67 (s, RuCp*), 1.81 (s, FeCp*), 1.94 (d, J_{PH} = 8.3 Hz, 2 Me_α), 2.66 (s, 2 Me_β). $^{13}C\{^1H\}$ NMR (125 MHz, d_6-acetone): δ 9.21 (s, FeCp*), 9.69 (s, RuCp*), 12.19 (s, 2 Me_β), 14.27 (d, J_{PC} = 15.9 Hz, 2 Me_α), 75.58 (d, J_{PC} = 85.0 Hz, 2 C_α), 76.61 (d, J_{PC} = 7.6 Hz, 2 C_β), 83.18 (s, FeCp*), 89.47 (s, RuCp*). $^{31}P\{^1H\}$ NMR (202 MHz, d_6-acetone): δ −39.5. SIMS: m/z (I_{rel}) 567.2 (100, M^+) from cation spectrum, 148.9 (100, $CF_3SO_3^-$) from anion spectrum.

(10) Chase, K. J.; Bryan, R. F.; Woode, M. K.; Grimes, R. N. *Organometallics* **1991**, *10*, 2631.

(11) Kudinov, A. R.; Rybinskaya, M. I.; Struchkov, Yu. T.; Yanovskii, A. I.; Petrovskii, P. V. *J. Organomet. Chem.* **1987**, *336*, 187.

S0276-7333(96)00985-5 CCC: $14.00

Scheme 2[a]



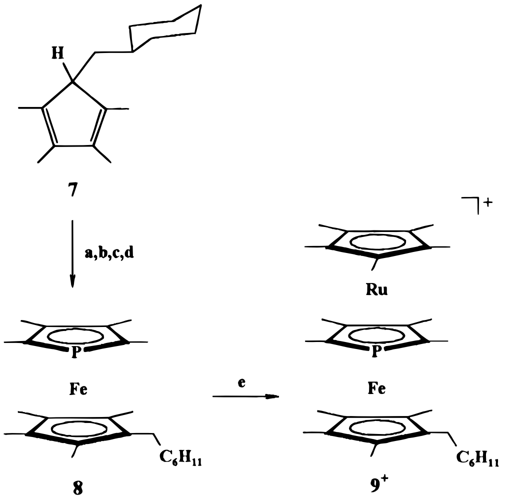
[a] Legend: (a) 0.5 $[Cp^*Ru(NCMe)_3]^+$; (b) 2 $[Cp^*Ru(NCMe)_3]^+$; (c) MeCN, slow.

instance be favored by an intermediate σ-coordination of the ruthenium to the phosphorus atom.

As one goes from **1** to **3**, the ^1H NMR signals show a downfield shift for the methyl groups of the phospholyl ring. The same trend has also been noted for triple-decker complexes with e.g. cyclopentadienyl ligands C_5H_4Me[12] and Cp*[11] rings as central ligands. Quite remarkably, the ^{31}P NMR resonance is also shifted downfield ($\delta(^{31}P)$ −61.2 for **1** and $\delta(^{31}P)$ −39.5 ppm for **3**).

When **3** is dissolved in acetonitrile, nucleophilic degradation takes place within 5−10 days at ambient temperature to give the complex $[Cp^*Ru(NCMe)_2(\mu\text{-}C_4Me_4P)FeCp^*]CF_3SO_3$ ((**4**)CF_3SO_3)[13] with a Ru−P σ-bond. On the other hand, mixtures of $[Cp^*Ru(NCMe)_3]^+$ [14] and **1** form the same species $\mathbf{4}^+$ as well as the complex $[Cp^*Ru(NCMe)\{(\mu\text{-}C_4Me_4P)FeCp^*\}_2]CF_3SO_3$ ((**5**)CF_3SO_3).[15] The σ-coordination of the phosphaferrocene **1** is indicated by a considerable downfield shift of the ^{31}P resonances ($\delta(^{31}P)$ 16.2 for $\mathbf{4}^+$ and $\delta(^{31}P)$ 1.4 ppm for $\mathbf{5}^+$).[16] With an excess of $[Cp^*Ru(NCMe)_3]^+$ only $\mathbf{4}^+$ is formed, while with an excess of **1** only $\mathbf{5}^+$ is seen (Scheme 2).[17] We conclude that these reactions are thermodynamically controlled, and the triple-decker cation $\mathbf{2}^+$ will only be formed if stabilizing ligands such as acetonitrile are absent.

Scheme 3[a]



[a] Legend: (a) $Fe(CO)_5$ in refluxing octane; (b) $[FeCp_2]PF_6$ in CH_2Cl_2/MeCN; (c) $h\nu$, MeCN; (d) $Li(C_4Me_4P)$ in THF; (e) $[Cp^*Ru(solv)_x]^+$ in acetone or CH_2Cl_2.

When **3** was recrystallized from acetone/ether/tetrahydropyran (THP), cocrystals with THP, **6**[18] (**6** ≡ **3**·THP), were obtained. The crystal structure of **6** showed an orientational disorder for the cations; therefore, the Fe and Ru positions were not distinguishable. In order to overcome this problem, we replaced the FeCp* fragment in $\mathbf{2}^+$ with a $Fe(C_5Me_4CH_2C_6H_{11})$ fragment. The required 1-(cyclohexylmethyl)-2,3,4,5-tetramethylcyclopentadiene (**7**) was prepared from $C_6H_{11}CH_2Br$, Li, and 2,3,4,5-tetramethylcyclopentenone (cf. the synthesis of Cp*H[19]). The subsequent synthetic steps, via the phosphaferrocene **8**[20] to the triple-decker complex (**9**)CF_3SO_3 (≡**10**),[21] closely follow the synthesis of **3** and are summarized in Scheme 3.

Compound **8** crystallizes in the monoclinic space group $P2_1/n$ with two independent molecules in the asymmetric unit;[22] the two molecules differ in the orientation of the cyclohexyl groups. The X-ray crystallographic study of compound **10** reveals a typical triple-decker structure (Figure 1).[23] The distances to the best phospholyl plane amount to 164.4(1) pm for Fe and 180.4(1) pm for Ru. These distances are almost equal

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(12) Salzer, A.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 930.

(13) NMR data for $\mathbf{4}^+$: ^1H NMR (500 MHz, CD_2Cl_2) δ 1.37 (d, J_{PH} = 9.8 Hz, 2 Me_α), 1.53 (d, J_{PH} = 2.7 Hz, RuCp*), 1.69 (s, FeCp*), 1.94 (s, 2 Me_β), 2.49 (d, J_{PH} = 1.5 Hz, 2 MeCN); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2) δ 16.2.

(14) (a) $[Cp^*Ru(NCMe)_3]PF_6$: Schrenk, J. L.; McNair, A. M.; McCormick, F. B.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 3501. (b) $[Cp^*Ru(NCMe)_3]CF_3SO_3$: Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

(15) NMR data for $\mathbf{5}^+$: ^1H NMR (500 MHz, CD_2Cl_2) δ 1.42 (d, J_{PH} = 11.9 Hz, 4 Me_α), 1.66 (s, 2 FeCp*), 1.69 (s, RuCp*), 1.96 (s, 4 Me_β), 2.43 (s, MeCN); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 1.4 (br).

(16) For reference data see: (a) Deschamps, B.; Mathey, F.; Fischer, J.; Nelson, J. H. *Inorg. Chem.* **1984**, *23*, 3455. (b) Nelson, J. H.; Mathey, F. In *Phosphorus-31 NMR spectroscopy in Stereoechemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Weinheim, Germany, 1987.

(17) There are no indications for the formation of the triply substituted species $[Cp^*Ru(\mathbf{1})_3]^+$, even with a large excess of **1**, presumably because of too much steric hindrance.

(18) A solution of **3** in a mixture of acetone (5 mL) and tetrahydropyran (5 mL) was layered with Et_2O (30 mL) to give **6** as violet crystals which were suitable for X-ray structure determination; they lose THP at room temperature.

(19) (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287. (b) Feitler, D.; Whitesides, G. M. *Inorg. Chem.* **1975**, *15*, 466.

(20) Data for **8**: Anal. Calcd for $C_{24}H_{37}FeP$: C, 69.90; H, 9.04. Found: C, 69.46; H, 9.11. ^1H NMR (500 MHz, $CDCl_3$): δ 0.85 (m, 2H, Cy), 1.10 (m, 3H, Cy), 1.15 (m, 1H, CH, Cy), 1.58 (m, 5H, Cy), 1.62 (d, J_{PH} = 9.8 Hz, 2 Me_α), 1.72 and 1.73 (s, C_5Me_4), 1.86 (s, 2 Me_β), 2.11 (d, J = 7.0 Hz, CH_2). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 10.10 and 10.69 (s, $C_5\mathit{Me}_4$), 11.41 (s, 2 Me_β), 13.16 (d, J_{PC} = 23.6 Hz, 2 Me_α), 26.40 (s, 2C, Cy), 26.51 (s, 1C, Cy), 33.47 (s, 2C, Cy), 33.79 (s, 1C, CH_2), 39.62 (s, 1C, Cy), 81.51 and 81.67 (s, C_5Me_4), 84.92 (s, $Fe\mathit{C}CH_2Cy$), 91.48 (d, J_{PC} = 53.2 Hz, 2 C_α), 91.56 (d, J_{PC} = 4.4 Hz, 2 C_β). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ −61.3. MS (EI): m/z (I_{rel}) 412.1 (95, M^+), 58.0 (100).

(21) Data for **10**: Anal. Calcd for $C_{35}H_{52}F_3FeO_3PRuS$: C, 52.70; H, 6.57. Found: C, 52.85; H, 6.77. ^1H NMR (500 MHz, d_6-acetone): δ 0.94 (m, 2H, Cy), 1.11 (m, 3H, Cy), 1.25 (m, $C\mathit{H}$, Cy), 1.53 (m, 2H, Cy), 1.61 (m, 3H, Cy), 1.66 (s, RuCp*), 1.82 and 1.84 (s, C_5Me_4), 1.94 (d, J_{PH} = 7.9 Hz, 2 Me_α), 2.38 (d, J = 7.3 Hz, CH_2), 2.65 (s, 2 Me_β). $^{13}C\{^1H\}$ NMR (125 MHz, d_6-acetone): δ 9.22 and 9.93 (s, $C_5\mathit{Me}_4$), 9.69 (s, RuCp*, 12.25 (s, 2 Me_β), 14.36 (d, J_{PC} = 15.9 Hz, 2 Me_α), 26.84 (s, 2C, Cy), 26.93 (s, 1C, Cy), 32.84 (s, 1C, CH_2), 33.82 (s, 2C, Cy), 39.56 (s, 1C, Cy), 75.52 (d, J_{PC} = 85.0 Hz, 2 C_α), 76.64 (d, J_{PC} = 7.6 Hz, 2 C_β), 83.15 and 83.71 (s, C_5Me_4), 86.06 (s, $Fe\mathit{C}CH_2Cy$), 89.47 (s, RuCp*). $^{31}P\{^1H\}$ NMR (202 MHz, d_6-acetone): δ −39.3. SIMS: m/z (I_{rel}) 649.2 (100, M^+) from cation spectrum, 148.9 (100, $CF_3SO_3^-$) from anion spectrum.

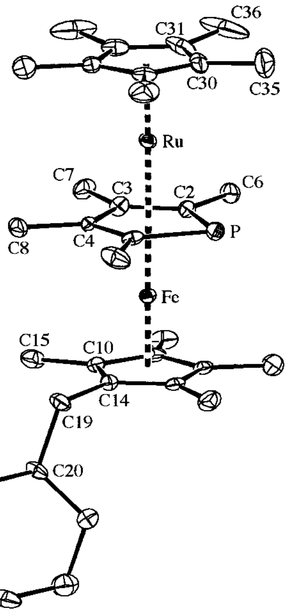

Figure 1. PLATON[25] plot of **10** (at the 30% probability level). Bond distances (pm): Ru−P, 241.2(2); Fe−P, 229.2(3); Ru−C2, 225.2(7); Ru−C3, 221.2(9); Ru−C4, 220.7(7); Ru−C5, 221.2(7); Fe−C2, 208.9(7); Fe−C3, 209.0(9); Fe−C4, 209.1(7); Fe−C5, 210.1(7); P−C2, 180.9(8); P−C5, 185.5(8); C2−C3, 145(1); C3−C4, 147(1); C4−C5, 143(1). Distances from ring planes (pm): Ru−(C_4Me_4P), 180.4; Ru−Cp*, 180.4; Fe−(C_4Me_4P), 164.4; Fe−($C_5Me_4CH_2C_6H_{11}$), 166.3. Bond angles (deg): Ru−P−Fe, 94.26(9); C2−P−C5, 88.2(3).

to those in comparable sandwich complexes (165.1(1) pm for **8** and 181.4 pm for Cp*Ru(2,5-$Bu^tC_4H_2P$)[24]).

Work is in progress in order to generalize the results presented here. Degradation reactions of triple-decker complexes with bridging phospholyl rings and phospholyl ligand transfer reactions are also currently under investigation.

Acknowledgment. We thank Dr. U. Englert for advice with the structure determinations. This work was generously supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: PLATON plots of **8** and tables of bond distances and angles, positional and anisotropic thermal parameters, and hydrogen atom coordinates for **8** and **10** (21 pages). Ordering information is given on any current masthead page.

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(22) Crystal data for **8**: orange crystals, 0.60 × 0.45 × 0.25 mm, monoclinic, $a = 1687(1)$ pm, $b = 1474(1)$ pm, $c = 1773(1)$ pm, $\beta = 92.39(5)°$, $V = 4.405(8)$ nm^3, $Z = 8$, space group $P2_1/n$ (No. 14), $D_{calcd} = 1.244$ g cm^{-3}, $\mu = 7.60$ cm^{-1}, $F(000) = 1776$. Data collection: ENRAF-Nonius CAD4, Mo Kα radiation, graphite monochromator, ω scan ($3 < \theta < 27°$) at 203 K, 10 291 reflections measured, 5885 unique reflections with $I > \sigma(I)$. Solution[26] and refinement:[27] 749 parameters, $R = 0.067$, $R_w = 0.060$, $w^{-1} = \sigma^2(F_o)$, GOF = 1.426, non-hydrogen atoms were refined anisotropically, most of the hydrogen atoms were refined isotropically, the remaining hydrogen atoms were treated as riding.[28]

(23) Crystal data for **10**: violet crystals, 0.50 × 0.25 × 0.08 mm, monoclinic, $a = 1721(1)$ pm, $b = 1109.6(3)$ pm, $c = 1862.2(6)$ pm, $\beta = 92.81(4)°$, $V = 3.553(4)$ nm^3, $Z = 4$, space group Ia (No. 9), $D_{calcd} = 1.490$ g cm^{-3}, $\mu = 9.73$ cm^{-1}, $F(000) = 1656$. Data collection: ENRAF-Nonius CAD4, Mo Kα radiation, graphite monochromator, ω scan ($3 < \theta < 28°$) at 203 K, 10 298 reflections measured, 6445 unique reflections with $I > \sigma(I)$. Solution[26] and refinement:[27] 404 parameters, $R = 0.063$, $R_w = 0.054$, $w^{-1} = \sigma^2(F_o)$, GOF = 1.137, non-hydrogen atoms were refined anisotropically, all hydrogen atoms were treated as riding.[28]

(24) Carmichael, D.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1167.

(25) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(26) Sheldrick, G. M. SHELXS-86, Program for Crystal Structure Solution; University of Göttingen: Göttingen, Germany, 1986.

(27) MolEN, An Interactive Structure Solution Procedure; ENRAF-Nonius: Delft, The Netherlands, 1990.

(28) Further details of the crystal structure analyses are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-406301 for **8** and CSD-406302 for **10**, the names of the authors, and this journal citation.