Notes

Convenient Synthesis of $[(\eta^5\text{-}C_5Me_5)Ru(NCMe)_3]PF_6$ and the Phosphine Derivatives $[(\eta^5\text{-}C_5Me_5)Ru(PR_3)_2(NCMe)]PF_6$

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*Summary: A convenient, high-yield (91%) synthesis of $[(\eta^5\text{-}C_5Me_5)Ru(NCMe)_3]PF_6$ (**4**−PF_6) by zinc reduction of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_n$ (**1**) in acetonitrile solution is described. Two acetonitrile ligands of **4**−PF_6 are readily exchanged for either PMe_3 or the chelating diphosphines bis(dimethylphosphino)methane, (2S,3S)-bis(diphenylphosphino)butane, or (2S,4S)-bis(diphenylphosphino)pentane. The remaining nitrile ligand is still labile, allowing easy access to a number of substitution products $[(\eta^5\text{-}C_5Me_5)Ru(PR_3)_2(L)]$.*

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Introduction

Half-sandwich ruthenium complexes of the type [CpRu(L)(L′)(L″)] (Cp = η^5-C_5H_5, η^5-C_5Me_5) have a quite prominent role in the chemistry of the late transition metals.[1,2] The ruthenium−L bonds are kinetically stable, and the high π-donor capacity of the $[CpRu(L)_2]$ complex fragment may in turn be exploited to "tame" unstable π-acceptor ligands such as carbenes,[3] vinylidenes,[4] silylenes,[5] silenes,[6] thioaldehydes,[7] sulfenes,[8] sulfur monoxide,[9] or sulfur trioxide,[10] to name a few. In this regard, the pentamethylcyclopentadienyl complexes are even superior to their C_5H_5 congeners due to improved electron donation as well as increased steric shielding.Their synthesis usually starts out from the Ru(III) complex $[(\eta^5\text{-}C_5Me_5)RuCl_2]_n$ (**1**), which is readily obtained from $RuCl_3{\cdot}3H_2O$ and HC_5Me_5.[11] Reduction of **1** with zinc or $LiHBEt_3$ gives the Ru(II) tetramer $[(\eta^5\text{-}C_5Me_5)RuCl]_4$[12,13] (**2**), which upon ligand addition yields pseudotetrahedral complexes $[(\eta^5\text{-}C_5Me_5)Ru(L)_2Cl]$ (**3**).[4e,13b,14] In favorable cases **1** may be converted directly to **3** using excess phosphine or olefin as the reductant.[11,15] In polar solvents the chloride is readily exchanged for neutral ligands such as acetonitrile, which offers an easy route to a vast variety of cationic complexes $[(\eta^5\text{-}C_5Me_5)Ru(L)_2(L')]^+$. In particular, the tris(acetonitrile) complex $[(\eta^5\text{-}C_5Me_5)Ru(NCMe)_3]^+$ (**4**) has been used in the synthesis of cationic arene complexes for purposes as different as activating arenes for nucleophilic substitutions or tagging arene groups in biomolecules.[16] Additional interest in $(\eta^5\text{-}C_5Me_5)Ru$ complexes arises from their ability to form isolable,

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coordinatively unsaturated 16-electron complexes[17] and to catalyze oligomerization reactions of alkenes and alkynes.[18] In the course of our work on the use of $[(\eta^5\text{-}C_5H_5)Ru(chir)]^+$ (chir = (2*S*,3*S*)-bis(diphenylphosphino)-butane) as a chiral auxiliary[7c,19] the need to develop a facile synthesis of complexes $[(\eta^5\text{-}C_5Me_5)Ru(PR_3)_2(NCMe)]^+$ (**5**) arose. Here, we report on the preparation of **4**−PF_6 by zinc reduction of **1** in acetonitrile and the use of **4** in ligand exchange reactions.

Experimental Section

All experiments were carried out in Schlenk tubes under an atmosphere of nitrogen. Acetonitrile and dichloromethane were refluxed over P_4O_{10} and distilled under nitrogen; hexanes were refluxed over Na/K alloy and distilled under nitrogen. $[(\eta^5\text{-}C_5Me_5)RuCl_2]_n$ (**1**) was obtained as described in the literature.[11] All other chemicals were used as obtained commercially. Sonications were performed by immersing the Schlenk tube into a small ultrasonic cleaning bath. NMR spectra were recorded on a JEOL Lambda 300 spectrometer (^{1}H, 300 MHz, TMS; ^{13}C, 75 MHz, TMS; ^{31}P, 122 MHz, H_3PO_4). Elemental analyses were performed by the microanalytical laboratory of the Institut für Anorganische Chemie, Universität Würzburg.

$[(\eta^5\text{-}C_5Me_5)Ru(NCMe)_3]PF_6$ (4−PF_6). To a solution of **1** (1.20 g, 3.91 mmol) in acetonitrile (25 mL) were added zinc dust (0.50 g, 7.65 mmol) and dry $NaPF_6$ (0.92 g, 5.48 mmol). After stirring for 4 h at ambient temperature, the mixture was filtered and the solution evaporated to dryness. The residue was extracted with CH_2Cl_2 (20 mL), filtered, and evaporated again. The residue was suspended in hexanes and treated with ultrasound to remove traces of oily impurities. The yellow crystalline powder thus obtained was washed with hexanes and dried under vacuum. Yield: 1.79 g (91%). Mp: 127 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 1.58 (s, 15H, C_5Me_5), 2.32 (s, 9H, CH_3CN). ^{13}C NMR (CD_2Cl_2): δ 3.8 (s, *C*H_3CN), 9.6 (s, C_5*Me*$_5$), 80.3 (s, *C*$_5$Me$_5$), 123.4 (s, br, CH_3*C*N). ^{31}P NMR (CD_2Cl_2): δ −144.5 (sept, $^1J_{PF}$ = 709 Hz, PF_6^-). Anal. Calcd for $C_{16}H_{24}F_6N_3PRu$: C, 38.10; H, 4.80; N, 8.33. Found: C, 37.86; H, 4.86; N, 7.22.

$[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(NCMe)]PF_6$ (5a). To a solution of **4** (0.17 g, 0.34 mmol) in dichloromethane (10 mL) was added a solution of PMe_3 (70 μL, 0.68 mmol) in CH_2Cl_2 (10 mL) at 10 °C. The mixture was stirred for 2 h at 0 °C and a further 2 h at room temperature. The mixture was then taken to dryness and the residue suspended in hexanes and treated with ultrasound. The yellow crystalline powder thus obtained was washed with hexanes and dried under vacuum. Yield: 0.17 g (87%). Mp: 138 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 1.32−1.52 (m, 18H, 2 × PMe_3), 1.69 (t, 15H, C_5Me_5, $^3J_{HP}$ = 1.8 Hz), 2.40 (s, 3H, CH_3CN). ^{13}C NMR (CD_2Cl_2): δ 4.7 (s, *C*H_3CN), 10.8 (s, C_5*Me*$_5$), 20.1 (vt, P*Me*$_3$, $N = {}^1J_{CP} + {}^3J_{CP}$ = 15 Hz), 91.3 (s, *C*$_5$Me$_5$), 125.1 (s, CH_3*C*N). ^{31}P NMR (CD_2Cl_2): δ 0.6 (s, PMe_3), −144.5 (sept, $^1J_{PF}$ = 709 Hz, PF_6^-). Anal. Calcd for $C_{18}H_{36}F_6NP_3Ru$: C, 37.63; H, 6.26; N, 2.44. Found: C, 37.04; H, 6.26; N, 2.23.

$[(\eta^5\text{-}C_5Me_5)Ru(dmpm)(NCMe)]PF_6$ (5b). To a solution of **4** (0.34 g, 0.67 mmol) in dichloromethane (15 mL) was added bis(dimethylphosphino)methane (112 mL, 0.71 mmol). After stirring 4 h at room temperature the mixture was worked up as described above. Yield: 0.35 g (93%). Mp: 120 °C (dec). ^{1}H NMR (CD_3CN): δ 1.39 (vt, 6H, dmpm−CH_3, $N = {}^2J_{HP} + {}^4J_{HP}$ = 10.3 Hz), 1.58 (vt, 6H, dmpm−CH_3, $N = {}^2J_{HP} + {}^4J_{HP}$ = 10.3 Hz), 1.76 (t, 15H, C_5Me_5, $^3J_{HP}$ = 2.2 Hz), 2.40 (t, 3H, CH_3CN, $^5J_{HP}$ = 1.8 Hz; signal decreases in intensity due to exchange with solvent), 3.14 (dt, 1H, dmpm−CH_2, $^2J_{HH}$ = 15.0 Hz, $^2J_{HP}$ = 10.9 Hz), 3.54 (dt, 1H, dmpm−CH_2, $^2J_{HH}$ = 15.0 Hz, $^2J_{HP}$ = 10.5 Hz). ^{13}C NMR (CD_3CN): δ 10.6 (s, C_5*Me*$_5$), 15.5 (vt, dmpm−CH_3, $N = {}^1J_{CP} + {}^3J_{CP}$ = 27 Hz), 16.5 (vt, dmpm−CH_3, $N = {}^1J_{CP} + {}^3J_{CP}$ = 26 Hz), 49.4 (t, dmpm−CH_2, $^1J_{CP}$ = 23 Hz), 91.0 (s, *C*$_5$Me$_5$). ^{31}P NMR (CD_3CN): δ −17.7 (s, dmpm), −144.5 (sept, $^1J_{PF}$ = 709 Hz, PF_6^-). Anal. Calcd for $C_{17}H_{32}F_6NP_3Ru$: C, 36.56; H, 5.78; N, 2.51. Found: C, 36.03; H, 5.70; N, 2.28.

$[(\eta^5\text{-}C_5Me_5)Ru(chir)(NCMe)]PF_6$ (5c). 5c was prepared similarly from **4** (0.75 g, 1.46 mmol) and (2*S*,3*S*)-bis(diphenylphosphino)butane (0.66 g, 1.54 mmol). Yield: 1.17 g (94%). Mp: 144 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 0.99 (dd, 3H, chir−CH_3, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 11.5 Hz), 1.23 (dd, chir−CH_3, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 11.2 Hz), 1.37 (s, 15H, C_5Me_5), 1.61 (s, 3H, CH_3CN), 2.30−2.48 (m, 1H, chir−CH), 2.55−2.73 (m, 1H, chir−CH). ^{13}C NMR (CD_2Cl_2): δ 3.5 (s, *C*H_3CN), 9.5 (s, C_5*Me*$_5$), 13.2 (dd, chir−CH_3, $^2J_{CP}$ = 18 Hz, $^3J_{CP}$ = 6 Hz), 15.2 (dd, chir−CH_3, $^2J_{CP}$ = 16 Hz, $^3J_{CP}$ = 5 Hz), 35.5 (dd, chir−CH, $^1J_{CP}$ = 29 Hz, $^2J_{CP}$ = 16 Hz), 43.9 (dd, chir−CH, $^1J_{CP}$ = 27 Hz, $^2J_{CP}$ = 20 Hz), 92.3 (t, *C*$_5$Me$_5$, $^2J_{CP}$ = 2 Hz), 124.4 (s, CH_3*C*N). ^{31}P NMR (CD_2Cl_2): δ 82.4 (d, J_{PP} = 35 Hz), 75.3 (d, J_{PP} = 35 Hz), −144.5 (sept, $^1J_{PF}$ = 709 Hz, PF_6^-). Anal. Calcd for $C_{40}H_{46}F_6NP_3Ru$: C, 56.60; H, 5.46; N, 1.65. Found: C, 56.64; H, 5.40; N, 1.58.

$[(\eta^5\text{-}C_5Me_5)Ru(bdpp)(NCMe)]PF_6$ (5d). 5d was obtained from **4** (0.26 g, 0.52 mmol) and (2*S*,4*S*)-bis(diphenylphosphino)-pentane (0.24 g, 0.54 mmol) as described above for **5b**. Yield: 0.40 g (89%). Mp: 131 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 0.76 (dd, 3H, bdpp−CH_3, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 13.9 Hz), 1.02 (dd, 3H, bdpp−CH_3, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 10.6 Hz), 1.12 (s, 15H, C_5-Me_5), 1.61 (s, 3H, CH_3CN), 1.85−2.18 (m, 2H, bdpp−CH_2), 2.92−3.15 (m, 2H, 2 × bdpp−CH). ^{13}C NMR (CD_2Cl_2): δ 5.4 (s, *C*H_3CN), 8.9 (s, C_5*Me*$_5$), 18.2 (s, bdpp−*C*H_3), 19.5 (d, bdpp−*C*H_3, $^2J_{CP}$ = 7 Hz), 23.9 (dd, bdpp−*C*H, $^1J_{CP}$ = 24 Hz, $^3J_{CP}$ = 3 Hz), 36.8 (d, bdpp−*C*H, $^1J_{CP}$ = 22 Hz), 38.6 (t, bdpp−*C*H_2, $^2J_{CP}$ = 6 Hz), 92.7 (s, *C*$_5$Me$_5$), 126.4 (s, CH_3*C*N). ^{31}P NMR (CD_2Cl_2): δ 51.9 (d, J_{PP} = 47 Hz), 41.4 (d, J_{PP} = 47 Hz), −144.5 (sept, $^1J_{PF}$ = 709 Hz, PF_6^-). Anal. Calcd for $C_{41}H_{48}F_6NP_3Ru$: C, 57.07; H, 5.61; N, 1.62. Found: C, 56.60; H, 5.64; N, 1.70.

$[(\eta^5\text{-}C_5Me_5)Ru(chir)Cl]$ (3c). A solution of **5c** (0.40 g, 0.47 mmol) in *n*-propanol (20 mL) was treated with KCl (0.18 g, 2.41 mmol). Ten milliliters of the solvent was distilled out of the reaction mixture (97 °C). The remaining solvent was removed under vacuum at room temperature, and the residue was chromatographed over silica with hexanes/Et_2O. The first orange band was collected and evaporated to give an orange crystalline powder. Yield: 0.20 g (60%). Mp: 237 °C (dec). ^{1}H NMR (C_6D_6): δ 0.95−1.05 (m, 6H, 2 × chir−CH_3), 1.40 (s, 15H, C_5Me_5), 1.82−2.02 (m, 1H, chir−CH), 3.22−3.42 (m, 1H, chir−CH). ^{13}C NMR (C_6D_6): δ 9.6 (s, C_5*Me*$_5$), 15.2 (dd, chir−CH_3, $^2J_{CP}$ = 14 Hz, $^3J_{CP}$ = 6 Hz), 17.4 (dd, chir−CH_3, $^2J_{CP}$ = 14 Hz, $^3J_{CP}$ = 6 Hz), 38.7 (dd, chir−CH, $^1J_{CP}$ = 22 Hz, $^2J_{CP}$ = 17 Hz), 39.7 (dd, chir−CH, $^1J_{CP}$ = 29 Hz, $^2J_{CP}$ = 17 Hz), 89.3 (t, *C*$_5$-Me$_5$, $^2J_{CP}$ = 3 Hz). ^{31}P NMR (C_6D_6): δ 81.1 (d, J_{PP} = 35 Hz), 71.3 (d, J_{PP} = 35 Hz). Anal. Calcd for $C_{38}H_{43}ClP_2Ru$: C, 65.37; H, 6.21. Found: C, 64.97; H, 6.07.

$[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(SO_2)]PF_6$ (6a). In a small pressure tube equipped with a Teflon needle valve, a solution of **5a** (57 mg, 0.10 mmol) in dichloromethane (10 mL) was saturated with SO_2 at 0 °C. The valve was closed and the mixture stirred at room temperature for an additional 24 h. Then the tube was vented, and all volatiles were removed under vacuum. The residue was suspended in hexanes and treated with ultrasound

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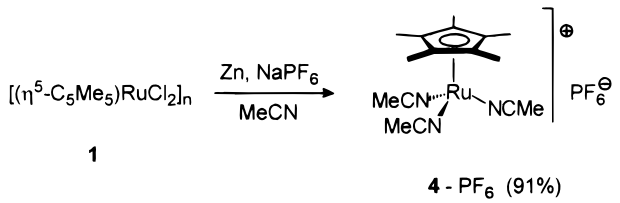
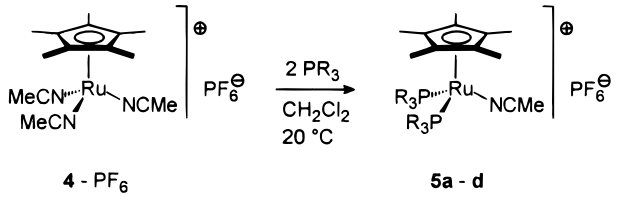
Scheme 1

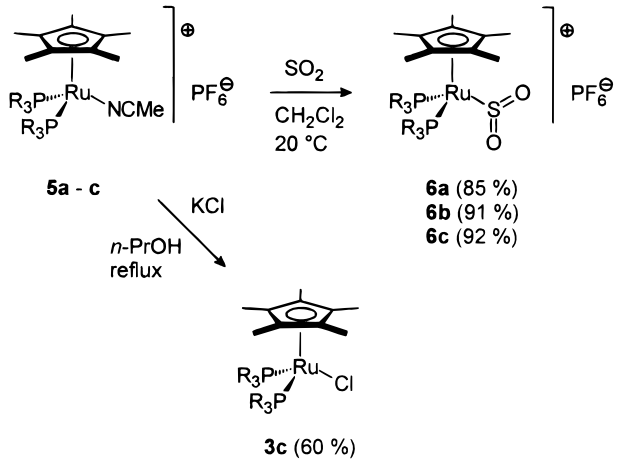


Scheme 2



$(PR_3)_2$ = $(PMe_3)_2$ (**5a**, 87%), $Me_2PCH_2PMe_2$ (**5b**, 93%), (*S,S*)-$Ph_2PCHMeCHMePPh_2$ (**5c**, 94%), (*S,S*)-$Ph_2PCHMeCH_2CHMePPh_2$ (**5d**, 89%)

Scheme 3



to improve crystallization. A yellow crystalline powder formed, identical with known **6a**.[20] Yield: 50 mg (85%).

[(η^5-C_5Me_5)Ru(dmpm)(SO_2)]PF_6 (6b). This compound was prepared similarly from **5b** (0.10 g, 0.18 mmol). Yield: 0.10 g (95%). Mp: 180 °C (dec). ^{1}H NMR (acetone-d_6): δ 1.80 (vt, 6H, dmpm−CH_3, N = $^2J_{HP} + {}^4J_{HP}$ = 12.1 Hz), 1.82 (vt, 6H, dmpm-CH_3, $N = {}^2J_{HP} + {}^4J_{HP}$ = 11.7 Hz), 1.96 (t, 15H, C_5Me_5, $^3J_{HP}$ = 2.0 Hz), 3.66−3.98 (m, 2H, dmpm−CH_2). ^{13}C NMR (acetone-d_6): δ 10.0 (s, C_5Me_5), 14.8 (vt, dmpm−CH_3, $N = {}^1J_{CP} + {}^3J_{CP}$ = 28 Hz), 17.6 (vt, dmpm−CH_3, $N = {}^1J_{CP} + {}^3J_{CP}$ = 34 Hz), 45.9 (t, dmpm−CH_2, $^1J_{CP}$ = 29 Hz), 103.2 (s, C_5Me_5). ^{31}P NMR (acetone-d_6): δ −24.3 (s, dmpm), −144.1 (sept, $^1J_{PF}$ = 709 Hz, PF_6^-). IR (Nujol): ν(S=O) 1254 (w), 1096 (m) cm^{-1}. Anal. Calcd for $C_{15}H_{29}F_6O_2P_3RuS$: C, 30.99; H, 5.03; S, 5.51. Found: C, 30.87; H, 4.87; S, 5.55.

[(η^5-C_5Me_5)Ru(chir)(SO_2)]PF_6 (6c). This compound was prepared similarly from **5c** (0.32 g, 0.38 mmol). Yield: 0.30 g (92%). Mp: 153 °C (dec). ^{1}H NMR (acetone-d_6): δ 1.23 (dd, 3H, chir−CH_3, $^3J_{HH}$ = 6.6 Hz, $^3J_{HP}$ = 13.4 Hz), 1.57 (dd, chir−CH_3, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 12.4 Hz), 1.62 (s, 15H, C_5Me_5), 2.87−3.10 (m, 1H, chir−CH), 3.43−3.62 (m, 1H, chir−CH). ^{13}C NMR (acetone-d_6): δ 9.4 (s, C_5Me_5), 14.6 (dd, chir−CH_3, $^2J_{CP}$ = 19 Hz, $^3J_{CP}$ = 6 Hz), 15.9 (dd, chir−CH_3, $^2J_{CP}$ = 17 Hz, $^3J_{CP}$ = 5 Hz), 35.2 (dd, chir−CH, $^1J_{CP}$ = 32 Hz, $^2J_{CP}$ = 14 Hz), 45.5 (dd, chir−CH, $^1J_{CP}$ = 30 Hz, $^2J_{CP}$ = 16 Hz), 104.2 (s, C_5Me_5). ^{31}P NMR (acetone-d_6): δ 73.7 (d, J_{PP} = 33 Hz), 69.3 (d, J_{PP} = 33 Hz), −144.1 (sept, $^1J_{PF}$ = 709 Hz, PF_6^-). IR (Nujol): ν(S=O) 1269 (w), 1108 (m) cm^{-1}. Anal. Calcd for $C_{38}H_{43}F_6O_2P_3RuS$: C, 52.35; H, 4.97; S, 3.68. Found: C, 52.11; H, 4.84; S, 3.71.

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Results and Discussion

[(η^5-C_5Me_5)Ru(NCMe)$_3$]$^+$ had been synthesized previously as the triflate salt **4**−OTf from **2** and AgOTf in acetonitrile[21] or as **4**−PF_6 by irradiating the sandwich complex [(η^5-C_5Me_5)Ru(C_6H_6)]PF_6 in acetonitrile.[22] As we have found now, stirring a solution of **1** in acetonitrile in the presence of $NaPF_6$ and zinc dust gives a high yield of **4**−PF_6 (Scheme 1). The complex [(η^5-C_5Me_5)-Ru(H_2O)$_2$($OCMe_2$)]PF_6 had previously been obtained using a similar procedure.[12]

In the iron complex [(η^5-C_5H_5)Fe(NCMe)$_3$]PF_6, the acetonitrile ligands can be exchanged to give a whole series of substitution products [(η^5-C_5H_5)Fe(L)$_n$(NCMe)$_{3-n}$]-PF_6 with good selectivity.[23] **4**−PF_6 reacts similarly with 2 equiv of PMe_3 or 1 equiv of the chelate phosphines $Me_2PCH_2PMe_2$ (dmpm), (2*S*,3*S*)-bis(diphenylphosphino)butane (chir), or (2*S*,4*S*)-bis(diphenylphosphino)-pentane (bdpp), giving the acetonitrile−bis(phosphine) complexes **5a**−**d** in excellent yields (Scheme 2). **5a**−**d** are yellow crystalline compounds which are soluble only in polar organic media. Their ^{1}H and ^{13}C NMR spectra show all the expected signals except for the nitrile carbon, which in some instances could not be detected due to slow relaxation and quadrupole broadening. The ^{13}C NMR signals of the P−CH_3 groups appear as virtual triplets, indicating strong P−P coupling. The high-field ^{31}P NMR signal of **5b** is typical of a four-membered chelate ring[24] and allows us to exclude the possible formation of a dmpm-bridged binuclear species. The chiral complexes **5c** and **5d** give widely separated ^{31}P signals with the typical P−P coupling for the diastereotopic phosphorus nuclei.

We have shown recently that, in the cation [(η^5-C_5H_5)-Ru(dppm)(NCMe)]$^+$, the nitrile ligand can be exchanged even at 20 °C for SO_2.[8c] **5a**−**c** react similarly, giving known [(η^5-C_5Me_5)Ru(PMe_3)$_2$(SO_2)]PF_6 (**6a**)[20] and the analogous complexes **6b**,**c**. **6c** is the first chiral, enantiomerically pure complex of sulfur dioxide. The weaker ligand Cl^- may be introduced under slightly more forcing conditions: Heating **5c** in *n*-propanol solution in the presence of potassium chloride gives, after chromatographic workup, the orange crystalline chloride complex [(η^5-C_5Me_5)Ru(chir)Cl] (**3c**) in good yield (Scheme 3).

Conclusions

An easy route to [(η^5-C_5Me_5)Ru(NCMe)$_3$]PF_6 and several phosphine substitution products [(η^5-C_5Me_5)Ru-(PR_3)$_2$(NCMe)]PF_6 is described. Of the latter the re-

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maining nitrile ligand is still readily exchanged, allowing easy access to a variety of mixed ligand complexes $[(\eta^5\text{-}C_5Me_5)Ru(PR_3)_2(L)]$.

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Supporting Information Available: ^{1}H NMR spectra of **4**−PF_6, **5a**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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