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Synthesis of 2-silyl substituted phospharuthenocenes and an elaboration into the first phospharuthenocene-phosphine

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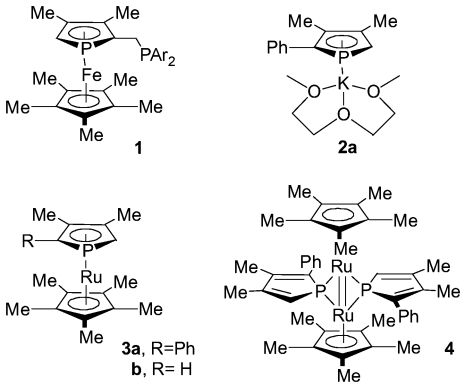
A [1,5] shift protocol transiently hindering the 2-position of phospholide anions provides an access to sterically unencumbered phospharuthenocenes and the first phospharuthenocene-phosphine.

The potential of phosphametallocenes as ligands for enantioselective catalysis,[1] a promising area currently dominated by iron derivatives,[2] has been underlined *inter alia* by recent reports of the spectacular performance of the phosphaferrocene-phosphine ligand (+)**1**[3,4] in the enantioselective isomerisation of unprotected allylic alcohols.[4] Ruthenium-based homologues provide an obvious means of varying the electronic and steric properties of the phosphametallocene ligand but they have not found uses in catalysis to date, presumably because the few known (monophospholyl)ruthenocenes[5] all bear sterically demanding groups which are likely to impede coordination at the phosphorus lone pair. Given (*a*) the stability of phospharuthenocenes across the range of mono-,[5] di- and tri-[6] and penta[7]-phospholyl ligands, (*b*) the potential for elaborating phospharuthenocenes by simple electrophilic aromatic substitution reactions[8] and (*c*) precedents for increasing either catalyst TOF[9] or enantioselectivity[10] through judiciously substituting Fe by Ru, it seemed important to prepare, investigate and functionalise a simple monophospharuthenocene.



Previous studies have suggested that only phospharuthenocenes bearing bulky groups are easily accessible[5] and our exploratory reactions between non-encumbered phospholides and $[RuCp^*Cl]_4$ showed that hindrance blocks a kinetically facile formation of phospholyl-bridged dimers. Thus reaction of $[RuCp^*Cl]_4$ with phospholide **2a**[11] gave only traces (< 5%) of the desired phospharuthenocene **3a**, with the product being predominantly (> 80%) a 1:1 mixture of two complexes showing ^{31}P NMR resonances (201 and 203 ppm) in a zone indicative of ligands bridging metal–metal bonds.[12]† One of these compounds, the dimer **4**, was obtained as monocrystals suitable for an X-ray structural determination (Fig. 1).‡ Its thermal conversion into **3a** (toluene, 110 °C, 2 days) was unsatisfactory and provoked extensive decomposition.

To encumber the phospholide anion reversibly and activate the phospharuthenocene products towards electrophilic aromatic substitution, a simple and potentially general synthesis of 2-silylphospholide anions[13] was developed (Scheme 1). After treatment of potassium phospholides **2a,b** with *i*-Pr_3SiCl,[14] a KO*t*-Bu-induced [1,5] silyl shift-deprotonation sequence[11] provided the corresponding 2-triisopropylsilylphospholides **5a,b** in excellent yield. These anions were conveniently complexed to $[RuCp^*Cl]_4$ *in situ* and the pale yellow air-stable phospharuthenocene products $[RuCp^*(PC_4Me_2\{i\text{-}Pr_3Si\}R)]$

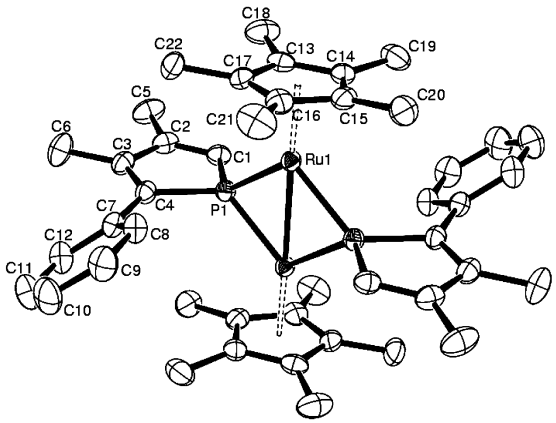
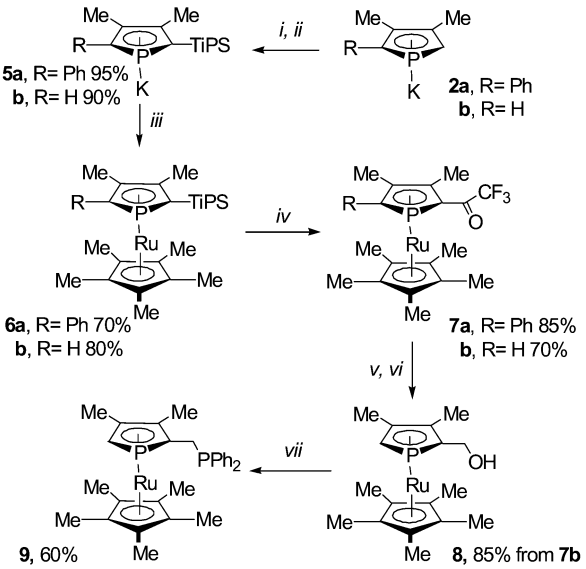


Fig. 1 Molecular structure of $[RuCp^*(PC_4PhHMe_2)]_2$ **4**. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(1′), 2.6471(8); Ru(1)–P(1), 2.250(1); Ru(1)–P(1)′, 2.240(1); P(1)–C(1), 1.798(3); C(1)–C(2), 1.339(4); C(2)–C(3), 1.476(4); C(3)–C(4), 1.359(3); P(1)–C(4), 1.825(3); Ru(1)–P(1)–Ru(1)′, 72.25(3); P(1)–Ru(1)–P(1)′, 107.75(3). Primed and unprimed atoms are related by a centre of symmetry.



Scheme 1 *Reagents and conditions*: *i*: *i*-Pr_3SiCl (1 eq.), THF, 20 °C, 30 min, *ii*: KO*t*–Bu (1 eq.), THF, −78 °C to rt, 1 h, *iii*: $[Cp^*RuCl]_4$ (0.25 eq.), THF, 20 °C, 5 min, *iv*: $(CF_3CO)_2O$ (2 eq.), BF_3OEt_2 (2 eq.), CH_2Cl_2, rt, 2 h, *v*: NaOMe (1 eq.), THF, −78 °C to rt, 30 min, *vi*: $LiAlH_4$ (2 eq.), THF, 20 °C, 10 min, *vii*: MsOH (1.2 eq.), CH_2Cl_2–MeOH, −78 °C, 30 s, then $HPPh_2$ (2 eq.), rt, 20 min.

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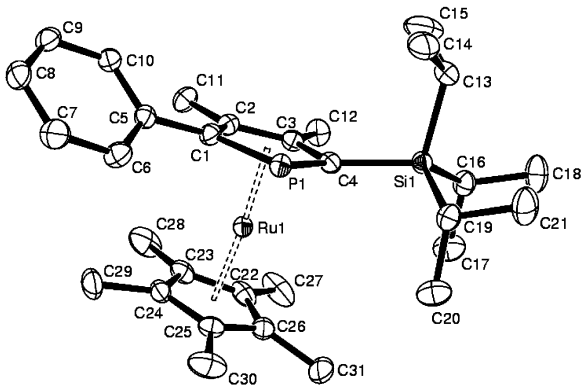

Fig. 2 Molecular structure of [RuCp*(PC_4Ph(Si*i*-Pr_3)Me_2)] **6a**. Selected bond lengths (Å): Ru(1)–P(1), 2.405(1); Ru(1)–C(1), 2.228(2); Ru(1)–C(2), 2.186(2); Ru(1)–C(3), 2.195(2); Ru(1)–C(4), 2.275(2); P(1)–C(1), 1.798(2); C(1)–C(2), 1.431(2); C(2)–C(3), 1.436(2); C(3)–C(4), 1.439(2); P(1)–C(4), 1.795(2).

6a,b were isolated by chromatography (silica, pentane, **6b**, *rf ca*. 0.2) or crystallisation (MeOH, **6a**). Crowding in **6a** is clearly reflected in the centroid-C(4)–Si(1) angle of 18.0° (Fig. 2).

As anticipated, compounds **6** show useful reactivity towards electrophiles. Protodesilylation using TMSCl–methanol led quantitatively to the parent phospharuthenocenes **3** and treatment of either **3** or **6** with $[CF_3CO]^+[F_3BO_2CCF_3]^-$ [2b,15] gave the corresponding 2-(trifluoroacetyl)phospharuthenocenes **7**. The utility of these complexes was confirmed by transformation of **7b** into the potentially versatile[10,16] (2-phospharuthenocene)-methanol derivative **8** and its classical elaboration into the target (2-phospharuthenocene)methylphosphine **9** (Scheme 1).

It seems clear that the methodology developed above provides the means to transform readily available phospholide anions into a wide variety of α-functionalised phospharuthenocenes. No organic phospharuthenocene chemistry has been described prior to this article but complexes **3**–**9** are stable and easy to handle, and the simplicity of their functional group transformations makes them good candidates for more sophisticated elaboration. The approach described here is particularly well-suited to the synthesis of Cp*-substituted phosphametallocenes which, when employed as enantiopure ligands, seem likely to deliver better ee's than their Cp-derived analogues. Given the relationship of **9** to the ligand class exemplified by **1**, further phospharuthenocene work is in progress.

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Notes and references

† Selected spectroscopic data: **3a**: ($CDCl_3$, 298 K) ^{31}P NMR δ −42.7 [d, $^2J_{PH}$ 35.8 Hz] ppm. **3b**: ($CDCl_3$, 298 K) ^{31}P{^{1}H} NMR δ −54.1 ppm. ^{13}C{^{1}H} NMR δ 93.0 [d, $^2J_{PC}$ 7.4 Hz, *C*Me], 87.4 [s, Cp*], 80.7 [d, $^1J_{PC}$ 59.6 Hz, P*C*H], 13.4 [s, C*Me*], 11.1 [s, Cp*] ppm. MS (EI, 70 eV): *m*/*z* (%) 347 (100) [M$^+$ − H], 332 (58) [M$^+$ − H − CH_3]. **4**: (C_6D_6, 333 K) ^{31}P{^{1}H} NMR δ 203.1 ppm. **5a**: (THF, 298 K) ^{31}P{^{1}H} NMR δ 123.8 ppm. **5b**: ^{31}P{^{1}H} NMR δ 113.3 ppm. **6a**: (THF, 298 K) ^{31}P{^{1}H} NMR δ −2.6 ppm. **6b**: ($CDCl_3$, 298 K) ^{31}P{^{1}H} NMR δ −21.1 ppm. ^{13}C{^{1}H} NMR δ 97.3 [d, $^2J_{PC}$ 4.5 Hz, *C*Me], 96.3 [d, $^2J_{PC}$ 8.2 Hz, *C*Me], 87.3 [s, Cp*], 83.7 [d, $^1J_{PC}$ 62.2 Hz, P*C*H], 83.4 [d, $^1J_{PC}$ 81.3 Hz, P*C*Si], 19.4 [4C, s, Si*CC*H], 19.3 [2C, s, Si*CC*H], 15.0 [s, C*Me*], 14.3 [s, C*Me*], 12.7 [2C, s, Si*C*H], 12.6 [1C, s, Si*C*H], 11.0 [s, Cp*] ppm. MS (EI, 70 eV): *m*/*z* (%) 505 (87) [MH$^+$], 462 (100) [MH$^+$-C_3H_7]. **7a**: ($CDCl_3$, 298K) ^{31}P{^{1}H} NMR δ −20.4 [q, $^4J_{PF}$ 59.5 Hz] ppm. **7b**: ($CDCl_3$, 298 K) ^{31}P{^{1}H} NMR δ −28.1 [q, $^4J_{PF}$ 61.4 Hz] ppm. ^{13}C{^{1}H} NMR δ 187.0 [dq, $^2J_{PC}$ 23.0 Hz $^2J_{FC}$ 33.3 Hz, *C*$COCF_3$], 112.4 [q, $^1J_{FC}$ 294.3 Hz, C], 100.4 [d, $^2J_{PC}$ 8.0 Hz, *C*Me], 94.1 [d, $^2J_{PC}$ 4.6 Hz, *C*Me], 90.2 [s, Cp*], 87.0 [dq, $^1J_{PC}$ 58.6, $^3J_{FC}$ 4.6 Hz, P*C*CO], 81.0 [d, $^1J_{PC}$ 71.3 Hz, P*C*H], 13.9 [s, C*Me*], 12.5 [s, C*Me*], 10.4 [s, Cp*] ppm. MS (EI, 70 eV): *m*/*z* (%) 444 (54) [M$^+$], 428 (37) [M$^+$ − O], 344 (33) [M$^+$ − $COCF_3$], 57 (100). **8**: ($CDCl_3$, 298 K) ^{31}P{^{1}H} NMR δ −48.0 ppm. ^{13}C{^{1}H} NMR δ 98.3 [d, $^1J_{PC}$ 58.3 Hz, P*C*CH_2], 96.1 [d, $^2J_{PC}$ 6.8 Hz, *C*Me], 92.0 [d, $^2J_{PC}$ 4.5 Hz, *C*Me], 88.1 [s, Cp*], 80.8 [d, $^1J_{PC}$ 58.8 Hz, P*C*H], 60.6 [d, $^2J_{PC}$ 23.6 Hz, CH_2O], 14.2 [s, C*Me*], 11.3 [s, Cp*], 10.5 [s, C*Me*] ppm. MS (EI, 70 eV): *m*/*z* (%) 377 (100) [M$^+$ − H], 359 (53) [M$^+$ − H_3O], 346 (35) [M$^+$ − CH_4O]. **9**: ($CDCl_3$, 298 K) ^{31}P{^{1}H} NMR δ −12.7 [d, $^3J_{PP}$ 28.7 Hz, *P*Ph_2], −44.9 [d, $^3J_{PP}$ 28.7 Hz, *P*Ru] ppm. ^{13}C{^{1}H} NMR δ 140–127 [Ar*C*], 94.5 [d, $^2J_{PC}$ 6.7 Hz, *C*Me], 93.3 [dd, J_{PC} 58.4, 18.9 Hz, P*C*CH_2], 92.1 [dd, J_{PC} 8.3, 6.4 Hz, *C*Me], 87.4 [s, Cp*], 80.3 [d, $^1J_{PC}$ 59.0 Hz, P*C*H], 29.7 [dd, J_{PC} 19.2, 14.7 Hz, *C*H_2P], 14.6 [s, C*Me*], 11.2 [s, Cp*], 11.0 [d, $^4J_{PC}$ 2.3 Hz, C*Me*] ppm. MS (EI, 70 eV): *m*/*z* (%) 546 (2) [M$^+$], 360 (100) [M$^+$ − PPh_2H].

‡ *Crystal data*: *For* **4**: from THF. $C_{44}H_{54}P_2Ru_2$, *M* = 846.95, monoclinic, space group $P2_1/n$, *a* = 11.087(5), *b* = 14.757(5), *c* = 12.041(5) Å, β = 96.340(5)°, *U* = 1958.0(14) Å^3, *Z* = 2, D_c = 1.437 g cm^{-3}, *F*(000) = 872. Monochromated Mo-K_α radiation λ = 0.71070 Å. μ = 0.883 cm^{-1}, *T* = 150 K. Of 5702 independent reflections measured over *h*: −15 to 15, *k*: −20 to 18, *l*: −16 to 15° from an orange plate of *ca*. 0.20 × 0.20 × 0.12 mm on a Kappa CCD diffractometer, 4346 with $I > 2\sigma(I)$ were refined on F^2 using direct methods in SHELXL. wR_2 = 0.1072, R_1 = 0.0388, GoF = 1.075. *For* **6a**: $C_{31}H_{47}PRuSi$ from CH_2Cl_2–EtOH. *M* = 579.82, monoclinic, space group $P2_1/c$, *a* = 8.939(5), *b* = 42.464(5), *c* = 8.166(5) Å, β = 110.070(5)°, *U* = 2911(2) Å^3, *Z* = 4, D_c = 1.323 g cm^{-3}, *F*(000) = 1224, μ = 0.652 cm^{-1}. 8165 independent reflections from a pale yellow crystal of *ca*. 0.20 × 0.20 × 0. 20 mm were collected, over *h*: −12 to 12, *k*: −53 to 59, *l*: −11 to 11°, and 6814 were refined using the methods above. wR_2 = 0.0791, R_1 = 0.0313, GoF = 1.034. CCDC 193091 and 193092. See http://www.rsc.org/suppdata/cc/b2/b208736g/ for crystallographic files in CIF or other electronic format.

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