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Alcohol induced stereospecific P–C bond cleavage to afford Ru–phenyl derivatives containing three different types of stereogenicity: novel and unprecedented complexes of P(OH)(OR)Ph

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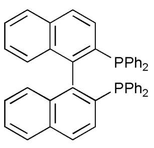
Alcohol induced stereospecific P–C bond cleavage in a Ru–$P(OH)Ph_2$ fragment affords new chiral-Binap and MeO-Biphep based complexes containing three different forms of stereogenicity: ligand atropisomerism plus stereogenic Ru and P atoms; these represent the first reported transition metal complexes of the ligands P(OH)(OR)Ph.

The atropisomeric chelating phosphines, Binap **1** and MeO-Biphep **2** are well known to be excellent chiral auxiliaries though there is relatively little known with respect to their Ru-organometallic chemistry.[1–5]



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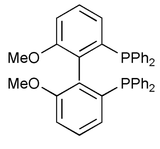
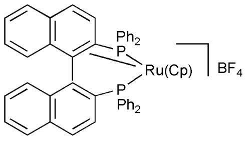


2

It is now known[6,7] that both of these bidentate ligands are capable of acting as six-electron donors to Ru(II), in that one of the biaryl double bonds, immediately adjacent to one of the two P-donors, can complex the metal, *e.g.* **3** and **4**.



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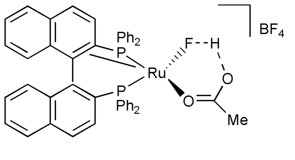
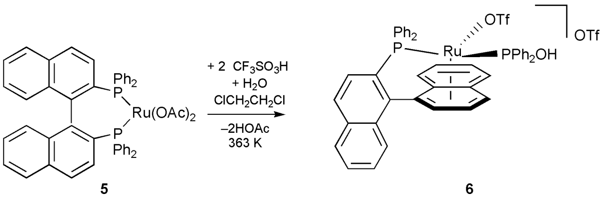


4

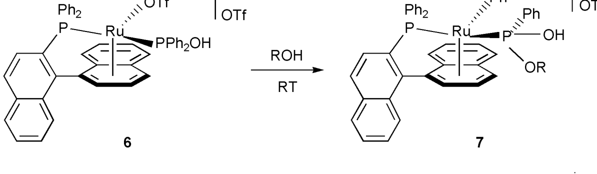
Once the proximate double bond complexes to Ru(II), it is relatively easy to cleave a P–C bond,[7] with the metal attaining an 18e configuration by sliding from the η^2 mode to the η^6 arene form, *e.g.* complex **6** of eqn. (1).



(1)

5 **6**

We report here an extension of the chemistry of eqn. (1) in which compound **6** reacts with aliphatic alcohols to afford the Ru–phenyl products, **7** [eqn. (2)]. These arise from a stereospecific P–C bond splitting and P–O bond making reaction of the $P(OH)Ph_2$ ligand to afford P(OH)(OR)Ph complexes.



(2)

6 **7**

a, R = Me, **b** R = Et, **c** R = Pr^i

The Binap complexes **7** and the MeO-Biphep analogues **8** have been prepared using MeOH, EtOH and Pr^iOH, by simply stirring the starting materials **6** in the appropriate alcohol[8] [eqn. (2)] The new phenyl complexes **7** and **8** are unique in that (a) they are produced in only *one* diastereomeric form, *i.e.* the phenyl migration and P–O bond formation are specific, (b) they contain *three* different forms of stereogenicity: atropisomerism, from the biaryl moiety,[9] a chiral transition metal and the newly formed stereogenic P atom and (c) these are the first reported transition metal complexes of the ligands P(OH)(OR)Ph. We know of only one example in which a marginally related species arises through P–C bond protonation, *i.e.* a Mo–P(OH)PhMe moiety can be formed by protonation of one of the two P–C phenyl bonds of a $PMePh_2$.[10] In this chemistry the $PMePh_2$ is complexed as an η^6-arene and not as a tertiary phosphine.

In solution the formation of **7a** from **6** is conveniently followed by ^{31}P NMR spectroscopy in that the disappearance of the signal for the complexed $P(OH)Ph_2$ ligand of **6**, δ = 114.5, is accompanied by the appearance of a new signal for the Ru–P(OH)(OMe)Ph moiety at δ = 144.7. The presence of the new P(OR) fragment was confirmed by a ^{31}P–^{1}H-correlation, *e.g.* see Fig. 1 for the ethanol analogue **7b**. This NMR spectrum shows cross-peaks for the P(OH), at high frequency, and the two non-equivalent (diastereotopic) methylene protons as multiplets (one of which is almost completely covered by the OCH_2 of the solvent, THF-d_8) all correlated to the new ^{31}P signal at δ 142.4. In addition cross-peaks are observed from the *ortho* (intense) and *meta* (weaker) P–phenyl aromatic protons. The *ipso* ^{13}C resonance of the new η^1 phenyl ligand is found at δ 150.3.

The solid-state structure of the Binap Pr^iOH analog **7c**, was determined by X-ray diffraction methods (Fig. 2).[12] The immediate coordination sphere consists of the two phosphorus atoms, the π-arene and the η^1-phenyl ligand. Whereas four of the Ru–C(arene) separations are normal,[11] the remaining two distances, from the bridgehead carbons C2 and C3, are quite long (see **9**) and suggest little or no bonding to the metal. Selected bond lengths and bond angles are given in the caption to Fig. 2.[13]

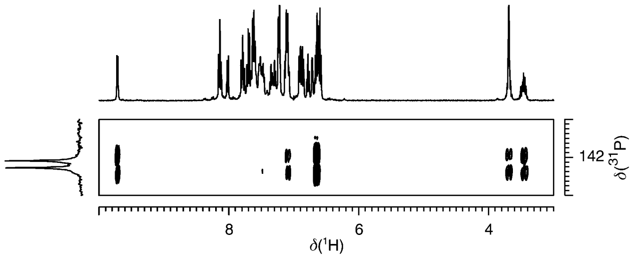


Fig. 1 Slice through the ^{31}P–^{1}H correlation (δ 142.4) showing the cross-peaks arising from the hydroxy P(OH), at high frequency, and the two non-equivalent methylene protons of the EtO moiety as multiplets (one of which is almost completely covered by the OCH_2 of the solvent, THF-d_8). There are also cross-peaks from the *ortho* and *meta* protons of the remaining P–phenyl ring.

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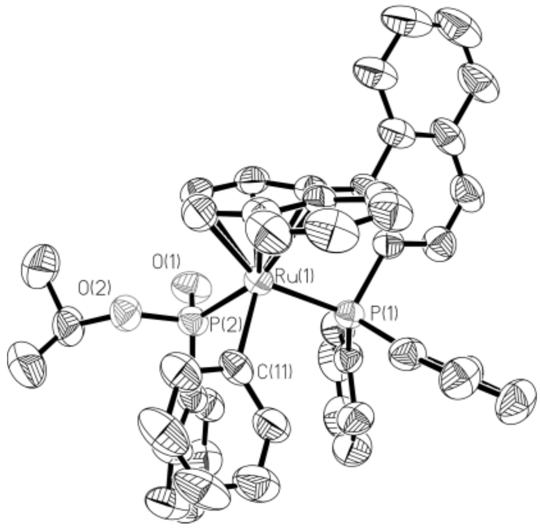
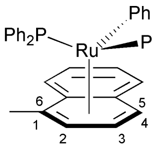


Fig 2 ORTEP view of the cation of **7c**. Selected bond lengths (Å) and angles (°): Ru–C(11), 2.105(6), Ru–P1 2.3074(16), Ru–P2 2.2507(16), Ru–C1 2.221(6), Ru–C2 2.430(5), Ru–C3 2.411(6), Ru–C4 2.275(6), Ru–C5 2.258(6), Ru–C6 2.268(6), C11–Ru–P1 97.14(18), C11–Ru–P2 81.30(16), P1–Ru–P2 98.09(6).



fragment **9**
Ru-C2 2.433(7) Å, Ru-C3 2.419(8) Å

Complexes **7** and **8** are relatively reactive and offer unique opportunities for studying the stereospecificity of subsequent reactions. Details of this chemistry are in preparation.

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8 Binap complex **6** (54 mg, 0.052 mmol) was dissolved in 12 ml MeOH and the solution stirred at room temperature for 30 min. The solvent was removed *in vacuo* and the remaining residue washed three times with diethyl ether. Product **7a** is obtained as an orange–yellow solid. Yield: 46 mg (96%). ^{1}H NMR (d^8-thf, 400 MHz): δ 9.64 (d, $^2J_{PH}$ 8.1 Hz, 1H, OH), 8.15 (d, $^3J_{HH}$ 7.5 Hz, 1H), 8.13 (d, $^3J_{HH}$ 8.1 Hz, 1H), 8.02 (d, $^3J_{HH}$ 8.53 Hz, 1H). 7.86 (d, $^3J_{HH}$ 8.4 Hz, 1H), 7.77 (m, 1H), 7.73 (t, $^3J_{HH}$ 7.7 Hz, 1H), 7.69 (m, 1H), 7.67 (m, 1H), 7.64 (m, 1H), 7.63 (m, 2H), 7.55 (m, 2H), 7.37 (m, 1H), 7.35 (m, 2H), 7.28 (d, $^3J_{HH}$ 7.6 Hz), 7.24 (t, $^3J_{HH}$ 7.8 Hz, 1H), 7.15 (m, 2H), 7,11 (m, 2H), 6.90 (m, 2H), 6.89 (d, $^3J_{HH}$ 5.5 Hz, 1H), 6.79 (t, $^3J_{HH}$ 7.1 Hz, 1H), 6.75 (m, 1H), 6.71 (m, 2H), 6.62 (m, 2H), 6.60 (d, $^3J_{HH}$ 7.9 Hz), 3.68 (d, $^3J_{PH}$ 11.9 Hz, 3H, CH_3). ^{13}C NMR (d^8-thf, 100 MHz): δ 150.3, 148.5, 147.3 (d, $^2J_{CP}$ 5.1 Hz), 140.9, 137.9, 135.6 (d, $^2J_{CP}$ 11.0 Hz), 134.8, 134.7, 133.9, 131.4, 131.0, 130.9, 130.8 (d, $^3J_{CP}$ 10.6 Hz), 130.6, 130.5, 129.4, 129.0, 128.6, 128.5, 127.9 (d, $^2J_{CP}$ 10.1 Hz), 127.7, 126.6, 126.1, 123.1, 117.8, 116.2, 106.8, 101.1 (d, $^3J_{CP}$ 5.4 Hz), 93.5, 91.6 (d, $^3J_{CP}$ 9.1 Hz), 53.6 (d, $^2J_{CP}$ 13.0 Hz). ^{19}F NMR (d^8-thf, 282 MHz): δ -78.17. ^{31}P NMR (d^8-thf, 162 MHz): δ 144.7 (d, $^2J_{PP}$ 61.2 Hz), 60.3 (d, $^2J_{PP}$ 61.2 Hz). MS (FAB): 773.0 (M^+), 695.0 ($M^+ - Ph$), 539.0 [$M^+ - PPh(OH)(OMe) - Ph$; 100%]. Elemental analysis: $C_{46}H_{37}F_3O_5P_2RuS \cdot H_2O$. Calc.: C, 58.78; H, 4.19. Found: C, 58.66; H, 4.78%.

9 Only one diastereomer is observed starting from optically pure (*R*)-MeO-Biphep. Interestingly the same diastereomer is observed starting from racemic MeO-Biphep (based on ^{31}P NMR results). This implies that a mixture containing *e.g.*, (*R*,*S*,*R*) and (*S*,*R*,*S*) [or (*R*,*R*,*R* and (*S*,*S*,*S*)] is present.

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12 *Crystal data* for **7c**: $C_{60}H_{41}F_3O_5P_2RuS$, $M = 1094.00$, monoclinic, space group $P2_1/n$, $a = 11.415(2)$, $b = 35.057(5)$, $c = 13.524(2)$ Å, $\beta = 100.54°$, $V = 5320.7(14)$ Å^3, $Z = 4$, $D_c = 1.381$ Mg m^{-3}, $\mu = 0.453$ mm^{-1}, $F(000) = 2232$, Crystal size $= 0.54 \times 0.40 \times 0.32$ mm. Data were collected on a Siemens SMART platform diffractometer equipped with a CCD detector using graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). Total number of reflections was 33233 of which 10942 were independent. The structure was solved by direct methods and refined on F^2, $R1 = 0.0772$, $wR2 = 0.1751$. The CF_3SO_3 molecule is disordered and was refined as a rigid group. Further, two molecules of disordered benzene solvent were found and refined in two different orientations. CCDC 182/1723.

13 There is no doubt as to the structure of the molecule; however, owing to disorder in several molecules of benzene, which co-crystallise, and some disorder in the triflate anion, the *R* factor is rather large. This does not interfere with a reasonable determination of the various Ru–(ligand atom) bond lengths.