Two isomers of a bis(diphenylphosphino)phosphinine, and the synthesis and reactivity of Ru arene / Cp* phosphinophosphinine complexes

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Synthesis and crystal structure of 7Fe

An ampoule was charged with 7 (100 mg, 0.13 mmol, 1 equiv.), anhydrous FeCl2 (17 mg, 0.13 mmol, 1 equiv.) and dry THF (10 cm³), sealed with a Teflon tap and heated to 70°C for 18 hours. All volatiles were removed under high vacuum and the resulting residue dissolved in dry dichloromethane (1 cm³). The solution was cannula filtered and layered with pet. ether (4 cm³), with yellow needles of the product produced over one week, which X-ray diffraction revealed to be 7.H2.O.FeCl2.HCl

31P{1H}-NMR (162 MHz, CDCl3): δ = 18.4 (bs).
Scheme S1. Reaction of 7 with FeCl$_2$ and trace HCl / H$_2$O (1 equivalent of each). Several potential resonance structures are given.

Figure S1. Molecular structure of 7Fe; thermal ellipsoids at 50% probability. All H-atoms have been removed for clarity except for those attached to N or P atoms.

Figure S2. $^{31}$P{$^{1}$H} NMR spectrum of 7Fe
Figure S3. $^1$H NMR spectrum of 5

Figure S4. $^{31}$P{$^1$H} NMR spectrum of 5
Figure S5. $^{13}$C($^1$H) NMR spectrum of 5
Figure S6. $^{13}$C$[^1]H$ NMR spectrum (aromatic region) of 5
Figure S7. MS (EI) of 5

Figure S8. $^1$H NMR spectrum of 6
Figure S9. $^{31}$P{^1}H NMR spectrum of 6

Figure S10. $^{31}$P{^1}H NMR spectrum (phosphinine region) of 6
Figure S11. $^{31}$P(1H) NMR spectrum (phosphine region) of 6
Figure S12. $^{13}$C($^1$H) NMR spectrum of 6
Figure S13. MS (EI) of 6

Figure S14. $^1$H NMR spectrum of 7
Figure S15. $^{31}$P($^1$H) NMR spectrum of 7

Figure S16. $^{31}$P($^1$H) NMR spectrum (phosphinine region) of 7
Figure S17. $^{31}$P($^1$H) NMR spectrum (phosphine region) of 7
Figure S18. $^{13}$C{¹H} NMR spectrum of 7
Figure S19. HRMS of 7
Figure S20. $^{31}$P{H} NMR spectrum of mixture of 2 & 8 (* = 2)
Figure S21. $^1$H NMR spectrum of 9.
Figure S22. $^{31}$P{$^{1}$H} NMR spectrum of 9

Figure S23. $^{31}$P{$^{1}$H} NMR spectrum ([PF$_6$] resonance) of 9
Figure S24. $^{19}$F NMR spectrum ([PF$_6$] resonance) of 9

Figure S25. HRMS of 9
Figure S26. $^1$H NMR spectrum of 10
Figure S27. $^{13}$C($^1$H) NMR spectrum of 10. Contains traces of petroleum ether.
Figure S28. $^{31}\text{P}[^1\text{H}]$ NMR spectrum of 10

Figure S29. $^{31}\text{P}[^1\text{H}]$ NMR spectrum (phosphinine region) of 10

Figure S30. $^{31}\text{P}[^1\text{H}]$ NMR spectrum (phosphine region) of 10
Figure S31. $^{29}\text{Si}[^1\text{H}]$ NMR spectrum of 10

Figure S32. HRMS of 10
Figure S33. $^1$H NMR spectrum of 11. * Contains silicone grease.
Figure S34. $^{31}$P($^1$H) NMR spectrum of 11

Figure S35. $^{29}$Si($^1$H) NMR spectrum of 11
Figure S36. HRMS of 11

Figure S37. $^1$H NMR spectrum of the transfer hydrogenation of benzophenone (20°C, 0.1 mol% 2, 24h: 70% yield)
Figure S38. $^1$H NMR spectrum of the transfer hydrogenation of benzophenone (82°C, 0.1 mol% 2, 4h: 95% yield)

Figure S39. $^1$H NMR spectrum of the transfer hydrogenation of 2-fluorobenzaldehyde (82°C, 1 mol% 2, 24h: 24% yield)
Figure S40. $^1$H NMR spectrum of the transfer hydrogenation of 4-methylcyclohexanone (82°C, 1 mol% Ru, 1h: 63% yield)

Figure S41. GC trace of the upgrading of ethanol and methanol to isobutanol (180°C, 0.1 mol% trans-[Ru(III)(dppm)]$_2$, 2h: 64.6% yield). This catalytic sample was analysed using a different method to the other samples: Method: oven temperature starts at 35 °C for 3.5 minutes, heat to 200 °C at 20 °C min$^{-1}$ then to 250 °C at 50 °C min$^{-1}$ then hold at 250 °C for 5 minutes. Flow rate 1.8 cm$^3$ min$^{-1}$. n-Pentanol was used as a standard
Figure S42. GC trace of the upgrading of ethanol and methanol to isobutanol (180°C, 0.1 mol% 2, 2h: 38.1% yield). Hexadecane was used as a standard.

Figure S43. GC trace of the upgrading of ethanol and methanol to isobutanol (180°C, 0.1 mol% 9, 2h: 11.1% yield). Hexadecane was used as a standard.
Reactivity studies

Reaction of 1 with [{RuCl₂(C₆Me₆)}₂] and dried NH₄PF₆

Under a nitrogen atmosphere, a Schlenk flask was charged with 1 (20 mg, 0.06 mmol, 1 equiv.), [{RuCl₂(C₆Me₆)}₂] (18 mg, 0.03 mmol, 0.5 equiv) and NH₄PF₆ (9 mg, 0.06 mmol, 1 equiv.). Dry dichloromethane (2 cm³) was then added via syringe and the reaction stirred for two hours. All volatiles were then removed in vacuo before dry CDCl₃ (0.8 cm³) was added. The crude reaction mixture was then analysed by ³¹P{¹H} NMR spectroscopy.

Figure S44. ³¹P{¹H} NMR spectrum of the reaction of 1 with [{RuCl₂(C₆Me₆)}₂] and dry NH₄PF₆

Figure S45. ³¹P{¹H} NMR spectrum of the reaction of 1 with [{RuCl₂(C₆Me₆)}₂] and dry NH₄PF₆ (magnification of low frequency area). * = 9
Reaction of 1 with $\left[\{\text{RuCl}_2(\text{C}_6\text{Me}_6)\}_2\right]$ without any additional anions

An NMR tube was charged with 1 (20 mg, 0.06 mmol) and $\left[\{\text{RuCl}_2(\text{C}_6\text{Me}_6)\}_2\right]$ (18 mg, 0.03 mmol, 0.5 equiv), then an approx. 1:1 mixture of $\text{C}_6\text{D}_6$ : fluorobenzene (used to aid solubility of the Ru dimer) was added and the tube sealed with a J Young tap. The tube was heated to 90°C overnight and the contents analysed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, which revealed formation of 2 as the major product.

**Figure S46.** $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of 1 with $\left[\{\text{RuCl}_2(\text{C}_6\text{Me}_6)\}_2\right]$

**Figure S47.** $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of 1 with $\left[\{\text{RuCl}_2(\text{C}_6\text{Me}_6)\}_2\right]$ (magnification of high frequency area).

* = 2

*
Figure S48. $^{31}$P$^{[1]H}$ NMR spectrum of the reaction of 1 with [[RuCl$_2$(C$_6$Me$_6$)$_2$]] (magnification of low frequency area). $^*$ = 2
Reaction of 10 with water
An NMR tube was charged with a solution of 10 (20 mg, 0.03 mmol) in dry THF-d₈ (0.6 cm³). Water (3 drops) was then added and the tube was then sealed with a J Young tap and thorough shaken. After an hour, the reaction was analysed by $^{31}$P{$^1$H} NMR which revealed formation of mainly 11 as well as minor side products and unconsumed 10.

Figure S49. $^{31}$P{$^1$H} NMR spectrum of the reaction of 10 with excess water

Figure S50. $^{31}$P{$^1$H} NMR spectrum of the reaction of 10 with excess water (magnification of low frequency region).

* = 11