SUPPORTING INFORMATION

Heterobimetallic Ruthenium-Zinc Complexes with Bulky N-Heterocyclic Carbenes: Syntheses, Structures and Reactivity

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Figure S1. $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298 K) of [Ru(2)(CO)ZnMe][BAr$_{6}$]$_6$ (7).

Figure S2. $^{13}$C{H} PENDANT NMR spectrum (101 MHz, CD$_2$Cl$_2$, 298 K) of [Ru(2)(CO)ZnMe][BAr$_{6}$]$_6$ (7).
Figure S3. High frequency region of the $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298 K) of [Ru(IPr)$_2$(CO)(η$^2$-H)$_2$(H)$_2$ZnMe][BAr$_{5}$F$_4$] (8).

Figure S4. Variable temperature proton NMR spectra of the low frequency region of the $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$) of [Ru(IPr)$_2$(CO)(η$^2$-H)$_2$(H)$_2$ZnMe][BAr$_{5}$F$_4$] (8).
Figure S5. $^{13}$C\{H\} PENDANT NMR spectrum (101 MHz, CD$_2$Cl$_2$, 298 K) of [Ru(IPr)$_2$(CO)(η$^2$-H$_2$)(H)$_2$ZnMe][BAR$_6$$_4$] (8).

Figure S6. $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298 K) of [Ru(IPr)$_2$(CO)(H)$_2$ZnMe][BAR$_6$$_4$] (9).
Figure S7. $^{13}$C{$^1$H} PENDANT NMR spectrum (101 MHz, CD$_2$Cl$_2$, 298 K) of [Ru(IPr)$_2$(CO)(H)ZnMe][BAr$_x$$_y$] (9).

Figure S8. $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$, 223 K) of [Ru(IBiox)$_2$(CO)HCl] (10).
Figure S9. $^{13}$C{\textsuperscript{1}H} PENDANT NMR spectrum (126 MHz, CD$_2$Cl$_2$, 223 K) of [Ru(IIbox$_6$)$_2$(CO)HCl] (10).

Figure S10. $^1$H NMR spectrum (500 MHz, THF-$d_8$, 298 K) of [Ru(IIbox$_6$)$_2$(CO)(THF)H][BAR$_4$] (11).
Figure S11. High (top) and lower (bottom) frequency regions of the $^{13}$C{^1}H PENDANT NMR spectrum (126 MHz, THF-$d_8$, 298 K) of [Ru(Biox6)2(CO)(THF)H][BAr$_4^-$] (11).
Figure S12. $^1$H NMR spectrum (500 MHz, THF-$d_8$, 298 K) of [Ru(IBiox6)$_2$(CO)(THF)ZnMe][BAr$_4^-$] (12).  

Figure S13. $^{13}$C{$^1$H} PENDANT NMR spectrum (126 MHz, THF-$d_8$, 298 K) of [Ru(IBiox6)$_2$(CO)(THF)ZnMe][BAr$_4^-$] (12).
Figure S14. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K) of [Ru(IBioxMe)$_2$(CO)HCl] (13).

Figure S15. $^{13}$C{$^1$H} PENDANT NMR spectrum (126 MHz, CDCl$_3$, 298 K) of [Ru(IBioxMe)$_2$(CO)HCl] (13).
Figure S16. $^1$H NMR spectrum (400 MHz, THF-$d_8$, 298 K) of [Ru(IBioxMe$_4$)$_2$(CO)(THF)H][BAr$_4$F$_4$] (14).

Figure S17. $^{13}$C{$^1$H} NMR spectrum (101 MHz, THF-$d_8$, 298 K) of [Ru(IBioxMe$_4$)$_2$(CO)(THF)H][BAr$_4$F$_4$] (14).
[Ru(IMes)(PPh₃)(CO)HCl]. The compound was synthesised by a minor modification of the literature procedure.¹ IMes (200 mg, 0.655 mmol) was added to the suspension of finely powdered [Ru(PPh₃)₃(CO)HCl]·CH₂Cl₂ (426 mg, 0.410 mmol) in toluene (5 mL). The solution was stirred overnight, after which time reaction was complete by $^{31}$P{$^1$H} NMR spectroscopy. The solvent was concentrated under vacuum to ca. 0.5 mL and treated with hexane (8 mL) at room temperature. A yellow-orange microcrystalline precipitate was filtered off, washed with hexane (3 x 5 mL) and dried under vacuum. Yield 256 mg (85%).

Figure S18. $^1$H NMR spectrum (500 MHz, C₆D₆, 298 K) of [Ru(IMes)(PPh₃)(CO)ZnMe] (15).
**Figure S19.** $^1$H NMR spectrum (500 MHz, THF-$d_8$, 298 K) of [Ru(IMes)(PPh$_3$)(CO)ZnMe] (15).

**Figure S20.** $^{31}$P{$^1$H} NMR spectrum (162 MHz, C$_6$D$_6$, 298 K) of [Ru(IMes)(PPh$_3$)(CO)ZnMe] (15).
Figure S21. $^{31}$P $^1$H NMR spectrum (162 MHz, THF-$d_8$, 298 K) of [Ru(IMes)(PPh$_3$)(CO)ZnMe](15).
Figure S22. $^{13}$C-{$^1$H} PENDANT NMR spectrum (101 MHz, C$_6$D$_6$, 298 K) of [Ru(IMes)(PPh$_3$)(CO)ZnMe] (15).

Figure S23. $^{13}$C-{$^1$H} DEPTQ NMR spectrum (126 MHz, THF-$d_8$, 298 K) of [Ru(IMes)(PPh$_3$)(CO)ZnMe] (15).
IMes cyclometallated region (Ru-CH₂):

Figure S24. $^1$H-$^13$C HSQC spectra (THF-$d_8$, 298 K) of [Ru(IMes)(PPh₃)(CO)ZnMe] (15).
IMes cyclometallated region (Ru-CH$_2$):

Figure S25. NOESY NMR spectra (400 MHz, THF-$d_8$, 298 K) of [Ru(IMes)(PPh$_3$)(CO)ZnMe] (15). The exchange peaks are labelled.
[Ru(IMes)(PPh₃)(CO)(ZnMe)Cl] (16). The slow, dropwise addition of ZnMe₂ (0.60 mL of 1.2 M in toluene, 0.72 mmol) to a THF (4 mL) solution of [Ru(IMes)(PPh₃)(CO)HCl] (105 mg, 0.143 mmol) brought about a colour change from yellow to dark orange. After stirring for 1 h, the volatiles were removed under vacuum and the residue treated with Et₂O (15 mL). This afforded a yellow precipitate of 16, which was separated and dried in vacuum. Yield 20 mg (17 % yield). ¹H NMR: δH (400 MHz, C₆D₆, 298 K) 7.66-7.55 (m, 6H, PPh₃), 6.99 (br s, 9H, PPh₃), 6.79 (s, 2H, Ar), 6.76 (s, 2H, Ar), 6.18 (s, 2H, NCH=NCH), 2.43 (s, 6H, CH₃), 2.31 (br s, 6H, CH₃), 2.19 (s, 6H, CH₃), -0.51 (s, 3H, ZnCH₃). ³¹P{¹H} NMR: δP (162 MHz, C₆D₆, 298 K) 40.3 (s). Selected ¹³C{¹H} NMR: δC (101 MHz, C₆D₆, 298 K) 200.8 (d, ²JCP = 13 Hz, Ru-CO), 192.2 (d, ²JCP = 95 Hz, Ru-C₃H₃), 134.7 (d, JCP = 11 Hz, PPh₃), 129.3 (d, JCP = 2 Hz, PPh₃), 21.3 (s, CH₃), 19.0 (br s, CH₃), -2.7 (d, ³JCP = 3 Hz, ZnCH₃). IR (KBr, cm⁻¹): 1878 (νCO).

Figure S26. ¹H NMR spectrum (400 MHz, C₆D₆, 298 K) of [Ru(IMes)(PPh₃)(CO)(ZnMe)Cl] (16).

Figure S27. ³¹P{¹H} NMR spectrum (162 MHz, C₆D₆, 298 K) of [Ru(IMes)(PPh₃)(CO)(ZnMe)Cl] (16).
Figure S28. $^{13}$C{${}^1$H} PENDANT NMR spectrum (101 MHz, C$_6$D$_6$, 298 K) of [Ru(IMes)(PPh$_3$)(CO)(ZnMe)Cl] (16).

Figure S29. $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 298 K) of [Ru(IMes)(PPh$_3$)(CO)(H)$_2$ZnMe] (17).
Figure S30. $^{31}$P{1H} NMR spectrum (202 MHz, C₆D₆, 298 K) of [Ru(IMes)(PPh₃)(CO)(H)₂ZnMe] (17).

Figure S31. $^{13}$C{1H} PENDANT NMR spectrum (126 MHz, C₆D₆, 298 K) of [Ru(IMes)(PPh₃)(CO)(H)₂ZnMe] (17).
Figure S32. $^1$H-$^{13}$C HSQC spectrum (THF-$d_8$, 298 K) of [Ru(IMes)(PPh$_3$)(CO)(H)$_2$ZnMe] (17), with expansion of the cyclometallated (Ru-CH$_2$) region.