Supporting Information for:

Integration of Phosphine Ligand and Ionic Liquid Both in Structure and Property: An Efficient and Economical Catalytic System for Homogeneous-Catalyst Recycling

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1 Experimental Procedure

1.1 General procedure for recycling of Rh-2a catalyst in Rh-2a/1-octene/MeOH-HCBS hydroformylation system

Under an argon atmosphere, a 60 mL autoclave was loaded with Rh(acac)(CO)$_2$ (1.0 mg, 3.88×10$^{-3}$ mmol), 20 equivalents of 2a (110 mg, 7.76×10$^{-2}$ mmol) and MeOH (3 mL). Subsequently, 5×10$^3$ equivalents of 1-octene (3 mL, 19.4 mmol) and the internal standard were added, and the reaction temperature and syngas pressure were raised to 100 °C and 5.0 MPa, respectively, with an intense stirring. After 1 h, the reaction was terminated by placing the autoclave in an ice bath. Upon releasing the syngas and after a GC analysis, the methanol was removed in vacuo and n-heptane (4.5 mL) was added to extract the aldehydes. The upper organic phase was removed, then the fresh 1-octene and methanol were replenished to the IL phase for next run. (Note: 1.0 μL of N, N, N’, N’-tetramethylguanidine was added in runs 1, 6 and 9)

1.2 General procedure for recycling of Rh-3a catalyst in Rh-3a/1-octene/EtOH-HCBS hydroformylation system

Under an argon atmosphere, a 60 mL autoclave was loaded with Rh(acac)(CO)$_2$ (1.0 mg, 3.88×10$^{-3}$ mmol), 20 equivalents of 3a (105 mg, 7.76×10$^{-2}$ mmol) and EtOH (5 mL). Subsequently, 5×10$^3$ equivalents of 1-octene (3 mL, 19.4 mmol) and the internal standard were added, and the reaction temperature and syngas pressure were raised to 100 °C and 5.0 MPa, respectively, with an intense stirring. After 6 h, the reaction was terminated by placing the autoclave in an ice bath. Upon releasing the syngas and after a GC analysis, the ethanol was removed in vacuo and n-heptane (4.5 mL) was added to extract the aldehydes. The upper organic phase was removed, then the fresh 1-octene and ethanol were replenished to the IL phase for next run. (Note: 1.0 μL of N, N, N’, N’-tetramethylguanidine was added in cycles 2, 4 and 6)

1.3 General procedure for recycling of Rh-2b catalyst in Rh-2b/1-octene/MeOH-HCBS hydrogenation system

Under an argon atmosphere, a 60 mL autoclave was loaded with RhCl$_3$·3H$_2$O (1.0 mg, 3.8×10$^{-3}$ mmol), 20 equivalents of 2b (228 mg, 7.6×10$^{-2}$ mmol) and MeOH. Subsequently, 1×10$^3$ equivalents of 1-octene (0.6 mL, 3.8 mmol) and the internal standard were added, and the reaction temperature and H$_2$ pressure were raised to 80 °C and 6.0 MPa, respectively, with an intense stirring. After 5 h, the reaction was terminated by placing the autoclave in an ice bath. Upon releasing the gas and after a GC analysis, the methanol and products were removed in vacuo, then the fresh 1-octene and methanol were replenished to the IL phase for next run.
2 NMR Spectra

2.1 $^1$H NMR spectrum of 2a

Figure S1. $^1$H NMR spectrum of 2a (500.0 MHz, D$_2$O)
2.2 $^{13}$C NMR spectrum of 2a

Figure S2. $^{13}$C NMR spectrum of 2a (125.7 MHz, CDCl$_3$)
2.3 $^{31}$P NMR spectrum of 2a

![P NMR spectrum of 2a](image.png)

Figure S3. $^{31}$P NMR spectrum of 2a (202.4 MHz, D$_2$O)
2.4 $^1$H NMR spectrum of 2b

Figure S4. $^1$H NMR spectrum of 2b (500.0 MHz, D$_2$O)
Figure S5. $^{13}$C NMR spectrum of 2b (125.7 MHz, CDCl$_3$)
2.6 $^{31}$P NMR spectrum of 2b

Figure S6. $^{31}$P NMR spectrum of 2b (202.4 MHz, D$_2$O)
2.7 $^1$H NMR spectrum of 2c

Figure S7. $^1$H NMR spectrum of 2c (500.0 MHz, D$_2$O)
2.8 $^{13}$C NMR spectrum of 2c

Figure S8. $^{13}$C NMR spectrum of 2c (150.9 MHz, CDCl$_3$)
2.9 $^{31}\text{P}$ NMR spectrum of 2c

Figure S9. $^{31}\text{P}$ NMR spectrum of 2c (202.4 MHz, D$_2$O)
2.10 $^1$H NMR spectrum of 2d

Figure S10. $^1$H NMR spectrum of 2d (500.0 MHz, D$_2$O)
2.11 $^{13}$C NMR spectrum of 2d

Figure S11. $^{13}$C NMR spectrum of 2d (150.9 MHz, CDCl$_3$)
2.12 $^{31}$P NMR spectrum of 2d

Figure S12. $^{31}$P NMR spectrum of 2d (202.4 MHz, D$_2$O)
2.13 $^1$H NMR spectrum of 3a

Figure S13. $^1$H NMR spectrum of 3a (500.0 MHz, D$_2$O)
2.14 $^{13}$C NMR spectrum of 3a

Figure S14. $^{13}$C NMR spectrum of 3a (125.7 MHz, CD$_2$OD)
2.15 $^{31}$P NMR spectrum of 3a

![NMR spectrum of 3a](attachment:image.png)

**Figure S15.** $^{31}$P NMR spectrum of 3a (202.4 MHz, D$_2$O)
2.16 $^1$H NMR spectrum of 3b

Figure S16. $^1$H NMR spectrum of 3b (500.0 MHz, D$_2$O)
2.17 $^{13}$C NMR spectrum of 3b

Figure S17. $^{13}$C NMR spectrum of 3b (125.7 MHz, CD$_3$OD)
2.18 $^{31}$P NMR spectrum of 3b

Figure S18. $^{31}$P NMR spectrum of 3b (202.4 MHz, D$_2$O)
2.19 $^1$H NMR spectrum of 3c

Figure S19. $^1$H NMR spectrum of 3c (500.0 MHz, D$_2$O)
2.20 $^{13}$C NMR spectrum of 3c

Figure S20. $^{13}$C NMR spectrum of 3c (125.7MHz, CD$_3$OD)
2.21 $^{31}$P NMR spectrum of 3c

Figure S21. $^{31}$P NMR spectrum of 3c (202.4 MHz, D$_2$O)
2.22 $^1$H NMR spectrum of 3d

Figure S22. $^1$H NMR spectrum of 3d (500.0 MHz, D$_2$O)
2.23 $^{13}$C NMR spectrum of 3d

Figure S23. $^{13}$C NMR spectrum of 3d (150.9 MHz, CD$_3$OD)
2.24 $^{31}$P NMR spectrum of 3d

Figure S24. $^{31}$P NMR spectrum of 3d (202.4 MHz, D$_2$O)
3 HRMS Spectra

3.1 Mass spectrum (ES+) of 2a

Figure S25. Mass spectrum (ES+) of 2a
3.2 Mass spectrum (ES-) of 2a

Figure S26. Mass spectrum (ES-) of 2a
3.3 Mass spectrum (ES+) of 2b

![Mass spectrum (ES+) of 2b](image)

Figure S27. Mass spectrum (ES+) of 2b
3.4 Mass spectrum (ES-) of 2b

Figure S28. Mass spectrum (ES-) of 2b
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Figure S37. Mass spectrum (ES+) of 3c
3.14 Mass spectrum (ES-) of 3c

Figure S38. Mass spectrum (ES-) of 3c
3.15 Mass spectrum (ES+) of 3d

Figure S39. Mass spectrum (ES+) of 3d
3.16 Mass spectrum (ES-) of 3d

![Mass spectrum](image)

Figure S40. Mass spectrum (ES-) of 3d
4 $^{31}$P NMR Spectra of Fresh and Spent Catalyst

4.1 $^{31}$P NMR spectrum of fresh catalyst

Figure S41. $^{31}$P NMR spectrum of fresh Rh-2a catalyst (161.9 MHz, CDCl$_3$, 85% phosphoric acid as the internal standard)
4.2 $^{31}$P NMR spectrum of spent catalyst

Figure S42. $^{31}$P NMR spectrum of spent Rh-2a catalyst (161.9 MHz, CDCl$_3$, 85% phosphoric acid as the internal standard)