Supplementary material to:

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Table S1 Melting temperatures for $CpRu(CO)_2I + PR_3$ (1:1) mixtures.

Mixture	Melting point/°C
$CpRu(CO)_2I + PPh_3$	70
$CpRu(CO)_2I + P(p\text{-}OCH_3C_6H_4)_3$	97
$CpRu(CO)_2I + P(m\text{-}CH_3C_6H_4)_3$	88
$CpRu(CO)_2I + P(p\text{-}FC_6H_4)_3$	70
$CpRu(CO)_2I + P(p\text{-}ClC_6H_4)_3$	87

Table S2 Reactions of $CpRu(CO)_2I$ and PR_3 ligands at 100 °C.

Ligand (L)	Time/h	Uncatalyzed		Catalyzed	
		2	3	2	3
PPh_3	0.5	29	13	58	34
	4	50	19	35	65
$P(p\text{-}OCH_3C_6H_4)_3$	0.5	18	0	66	22
	4	44	8	0	100
$P(m\text{-}CH_3C_6H_4)_3$	0.5	0	0	5	95
	4	27	8	0	100
$P(p\text{-}FC_6H_4)_3$	0.5	0	15	0	100
	4	0	100	0	100
$P(p\text{-}ClC_6H_4)_3$	0.5	0	9	31	69
	4	10	17	0	100

Table S3 Melting temperatures of $MeCpRu(CO)_2I + PR_3$ mixtures (1:1 ratio).

Mixture	Melting point/°C
$CH_3CpRu(CO)_2I + PPh_3$	36
$CH_3CpRu(CO)_2I + P(p\text{-}MeC_6H_4)_3$	42
$CH_3CpRu(CO)_2I + P(m\text{-}MeC_6H_4)_3$	38
$CH_3CpRu(CO)_2I + P(p\text{-}FC_6H_4)_3$	36
$CH_3CpRu(CO)_2I + P(p\text{-}ClC_6H_4)_3$	40

Table S4 Reactions of $MeCpRu(CO)_2I$ and PR_3 ligands at 70 °C.

Ligand (L)	Time/h	Uncatalyzed		Catalyzed	
		2	3	2	3
PPh_3	0.5	0	0	30	0
	4	0	0	100	0
$P(p\text{-}OCH_3C_6H_4)_3$	0.5	0	0	0	0
	4	0	0	10	0
$P(m\text{-}CH_3C_6H_4)_3$	0.5	0	0	0	0
	4	0	0	19	0
$P(p\text{-}FC_6H_4)_3$	0.5	0	0	0	0
	4	0	0	0	0
$P(p\text{-}ClC_6H_4)_3$	0.5	0	0	0	0
	4	0	0	0	0