Comment on "Conformational analysis of triphenylphosphine ligands in stereogenic monometallic complexes: tools for predicting the preferred configuration of the triphenylphosphine rotor" by J. F. Costello, S. G. Davies, E. T. F. Gould and J. E. Thomson, *Dalton Trans.*, 2015, **44**, 5451

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Table S1. $Cp^{(*)}M\text{-}PPh_3$ complexes (M = Fe, Ru or Re): Variants A and B, torsion angles M-P-C_i-C_o <90°, and distances $^{in}C_oH\text{-}C_i$, $^{in}C_oH\text{-}^{in}C_o$, and $^{in}C_oH\text{-}^{out}C_o$

Entry **vari-ant**	CSD symbol[a]	Formula[b]	C_o-C_i- P-M **Ph1**	**3→1** (Å) $^{in}C_oH\text{-}C_i$ $^{in}C_oH\text{-}C_o$[c]	C_o-C_i- P-M **Ph2**	**1→2** (Å) $^{in}C_oH\text{-}C_i$ $^{in}C_oH\text{-}C_o$[c]	C_o-C_i- P-M **Ph3**	**2→3** (Å) $^{in}C_oH\text{-}C_i$ $^{in}C_oH\text{-}^{out}C_o$
1 no H[d]	CIBSFE	$[CpFe(CO)PPh_3SO_2CH_2{}^iPr]$	11.8°		-51.9°		-64.5°	
2 **A**	ZISSEZ[e]	$[CpFe(CO)PPh_3\text{-}PMe(NMeCH_2\text{-}CH_2NMe)]BF_4$	11.4°	**2.69** 2.80^{in}	-58.9°	**2.94** -	-79.1°	**2.76** 2.50^{out}
3 **A**	FIHTUL[e]	$[CpFe(CO)PPh_3\text{-}COCH(SPh)CHPhOH]$	9.0°	**2.63** 2.65^{in}	-65.7°	**2.96** -	-68.1°	**2.76** 2.57^{out}
4 **A**	LEZVAN	$[CpFe(CO)PPh_3CO^nBu]$	8.6°	**2.68** 2.79^{in}	-33.3°	- 2.82^{in}	-78.1°	**2.65** 2.70^{out}
5 **A**	FUGWOT[e]	$[CpRe(NO)PPh_3\text{-}CH{=}CHCH_2Ph]$-(*E*)	7.8°	**2.72** -	-37.4°	**3.00** 2.86^{in}	-83.3°	**2.76** 2.76^{out}
6 **A**	QUNTEY[e]	$[CpFe(CO)PPh_3\text{-}Sb(O(R)Ar)O(R')Ar']$	2.7°	**2.55** 2.58^{in}	-53.7°	**2.91** -	-68.6°	**2.63** 2.53^{out}
7 **A**	LAPJIV(1)[e]	$[Cp^*Re(NO)PPh_3COCH_2\text{-}Re(CO)_4PPh_3]$	1.6°	**2.62** 2.78^{in}	-52.6°	**2.87** -	-71.0°	**2.70** 2.55^{out}
8 **A**	ZONDAH[e]	$[CpFe(CO)PPh_3SiMePhCl]$	1.2°	**2.64** 2.81^{in}	-68.1°	**2.92** -	-68.9°	**2.81** 2.67^{out}
9 **A**	BOFGOS	$[CpFe(CO)PPh_3\text{-}SiPh(CH_2)_5]$	1.1°	**2.51** 2.66^{in}	-66.0°	**2.81** -	-69.4°	**2.82** 2.57^{out}
10 **A**	JACXIU10[e]	$[Cp^*Re(NO)PPh_3\text{-}COCHMeCORe(CO)_4]$	0.4°	**2.79** -	-72.4°	- -	-60.5°	**2.83** 2.54^{out}
11 no H[d]	JEJXUR	$[CpRe(NO)PPh_3Ph]$	0.3°		-49.2°		-65.4°	
12 no H[d]	VULCIO	$[CpRu(CO)PPh_3\text{-}SO(Me)^tBu]SbF_6$	0.0°		-48.8°		-66.2°	
13 **A**	DOKXIK	$[CpFe(CO)PPh_3\text{-}CO(CH_2)_2OC_{10}H_{19}]$, $C_{10}H_{19}$ = menthyl	-1.4°	**2.60** 2.72^{in}	-57.7°	**2.83** -	-70.3°	**2.73** 2.58^{out}
14 **A**	FUGWUZ	$[CpRe(NO)PPh_3\text{-}C(OMe){=}CHCH_2Ph]$-(*Z*)	-3.1°	**2.63** 2.94^{in}	-40.5°	**2.78** 2.75^{in}	-71.3°	**2.71** 2.80^{out}
15 **A**	VOWTUW[1]	$[CpFe(CO)PPh_3\text{-}COC(=CH_2)O\text{-}CH_2Ph]$	-3.1°	**2.60** 2.68^{in}	-49.3°	**2.79** 2.82^{in}	-65.7°	**2.58** 2.60^{out}
16 **A**	DEXGAO	$[CpRu(Cl)PPh_3\text{-}PPh_2CH_2Ph]$	-3.5°	**2.66** 2.54^{in}	-71.2°	**2.75** -	-49.9°	**2.69** 2.71^{out}
17 **A**	PIRDOJ[e]	$[CpFe(CO)PPh_3\text{-}COCH_2C(OH)RR']$	-3.5°	**2.60** 2.65^{in}	-56.6°	**2.85** -	-63.2°	**2.59** 2.52^{out}
18 **A**	KEWSEK[e]	$[CpFe(CO)PPh_3\text{-}COCH_2CHPh\text{-}OTiCp_2Cl]$	-3.6°	**2.66** 2.92^{in}	-26.7°	**2.95** 2.72^{in}	-75.8°	- -
19 no H[d]	CUXBIG10	$[CpFe(CO)PPh_3\text{-}COCH_2CHPhOH]$	-3.8°	**2.69** 2.70^{in}	-57.9°		-60.2°	
20 **A**	LADFEB(1)[e]	$[CpFe(CO)PPh_3\text{-}CO_2Re(CO)_4PPh_3]$	-5.3°	**2.53** 2.69^{in}	-59.2°	**2.80** -	-67.0°	**2.72** 2.61^{out}
21 no H[d]	WAJYOV	$[CpFe(CO)PPh_3\text{-}COCHPhCMe_2OH]$	-6.3°		-74.2°		-59.2°	
22 **A**	KOZRAS	$[CpRu(CO)PPh_3\text{-}CR(=CRPh)]$	-6.6°	**2.51** 2.84^{in}	-43.2°	**2.73** 2.60^{in}	-75.3°	**2.64** 2.65^{out}
23 **A**	KEWSIO	$[CpFe(CO)PPh_3\text{-}COCH_2CHPhOTiCp_2]BPh_4$	-6.9°	**2.58** 2.80^{in}	-36.3°	**2.94** 2.70^{in}	-63.0°	**2.58** 2.90^{out}
24 **A**	LAPJIV(2)[f]	$[Cp^*Re(NO)PPh_3COCH_2\text{-}Re(CO)_4PPh_3]$	-7.3°	**2.70** 2.68^{in}	-58.4°	**2.77** -	-55.0°	**2.63** 2.62^{out}
25 no H[d]	KISFEX[e]	$[CpRe(NO)PPh_3\text{-}Ge(Ph)_2OSO_2CF_3]$	-9.3°		-54.3°		-72.0°	
26 **A**	VIZLAR[e]	$[Cp^*Re(NO)PPh_3\text{-}COCH_2CORe(CO)_4PMe_3]$	-9.3°	**2.60** 2.65^{in}	-76.0°	**2.92** -	-59.0°	**2.76** 2.48^{out}

27 **A**	JUDNEB01	[CpFe(CO)PPh_3COCH_2Ph]	-9.8°	**2.57** 2.87^{in}	-50.6°	**2.76** 2.86^{in}	-68.4°	2.59 2.56^{out}
28 no H[d]	XIKFEC[e]	[CpFe(CO)PPh_3-COFc] Fc = ferrocenyl	-9.9°	- -	-71.5°	**2.77** -	-56.3°	**2.67** 2.49^{out}
29 **A**	FAMNAI	[CpFe(CO)PPh_3- $COCH_2CHPh$-NHPh]	-10.1°	**2.57** 2.64^{in}	-65.7°	**2.77** -	-57.9°	**2.70** 2.60^{out}
30 **A**	GIRYIP[1][e]	[CpFe(CO)$PPh_3CC_3F_5$]	-10.2°	**2.51** 2.68^{in}	-42.0°	**2.79** 2.75^{in}	-63.7°	**2.56** 2.70^{out}
31 **A**	NOCQEB	[CpFe(CO)PPh_3- $COCH_2C_6H_4$-*m*-Me]	-10.2°	**2.64** 2.89^{in}	-46.4°	**2.80** 2.89^{in}	-65.2°	**2.67** 2.75^{out}
32 **A**	SOSWEC[e]	[CpFe(CO)PPh_3- $CH(SCH_2CH_2S)$]	-11.0°	**2.63** 2.85^{in}	-54.3°	**2.78** 2.97^{in}	-63.5°	**2.65** 2.66^{out}
33 **A**	QUNSUN	[CpFe(CO)PPh_3- Sb(O(R)Ar)O(R')Ar']	-11.0°	**2.55** 2.92^{in}	-50.0°	**2.75** 2.99^{in}	-64.9°	**2.65** 2.67^{out}
34 **A**	SITPIU[e]	[CpRu(Cl)$PPh_3P(OMe)_3$]	-11.6°	**2.61** 2.50^{in}	-71.0°	**2.73** -	-48.4°	**2.64** 2.67^{out}
35 **A**	SIMSAI	[Cp*Re(NO)PPh_3- $COCH_2CORe(CO)_4$]	-11.6°	**2.61** 2.65^{in}	-65.1°	**2.85** -	-58.0°	**2.75** 2.57^{out}
36 **A**	ZEPTOD	[CpFe(CO)PPh_3- $Sb(O(R)Ar)_2$]	-11.9°	**2.57** 2.64^{in}	-57.0°	**2.74** -	-59.2°	**2.61** 2.69^{out}
37 **A**	VOWTUW [2][e]	[CpFe(CO)PPh_3- $COC(=CH_2)O$-CH_2Ph]	-12.1°	**2.56** 2.60^{in}	-73.2°	**2.80** -	-55.0°	**2.72** 2.49^{out}
38 **A**	ZEPVAR	[CpFe(CO)PPh_3- $Sb(O(R)Ar)_2$]	-12.2°	**2.72** 2.88^{in}	-51.6°	**2.56** 2.72^{in}	-58.4°	**2.52** 2.71^{out}
39 **A**	ZAFFUH[g]	[Cp*Ru(CO)PPh_3- $P(C_6H_{11})_2CH_2$- $CH_2OMe]BPh_4$	-12.5°	**2.54** 2.47^{in}	-100.1° [g]	**2.81** 2.71[g]	-45.3°	**2.79** 2.61^{out}
40 **A**	FOYFUU	[Cp*Re(NO)PPh_3- $COCH_2CO$-$Mn(CO)_4$]	-12.7°	**2.58** 2.64^{in}	-65.9°	**2.81** -	-57.2°	**2.73** 2.56^{out}
41 **A**	XOXROS[e]	[CpFe(CO)PPh_3- C_3H_5] C_3H_5 = cyclopropyl	-13.1°	**2.59** 2.60^{in}	-66.5°	**2.76** -	-54.3°	**2.62** 2.58^{out}
42 **A**	CIBJUS	[CpFe(CO)PPh_3- $(C_5H_4)Mn(CO)_3$]	-13.4°	**2.50** 2.72^{in}	-76.5°	**2.85** -	-61.3°	**2.87** 2.59^{out}
43 **A**	YOTBIS	[CpFe(CO)PPh_3- $CO_2Sn^nBu_4$]	-13.6°	**2.61** 2.78^{in}	-53.5°	**2.70** 2.89^{in}	-57.4°	**2.62** 2.78^{out}
44 **A**	KITVAK	[CpFe(CO)PPh_3COCRR']	-14.0°	**2.54** 2.64^{in}	-48.3°	**2.67** 2.79^{in}	-61.0°	**2.52** 2.62^{out}
45 **A**	FIHTEV[e]	[CpFe(CO)PPh_3- COCH(SPh)CHMeOH]	-14.0°	**2.67** 2.80^{in}	-63.8°	**2.72** -	-54.6°	**2.68** 2.66^{out}
46 **A**	GIRYIP[2][e]	[CpFe(CO)$PPh_3CC_3F_5$]	-14.3°	**2.50** 2.81^{in}	-39.5°	**2.69** 2.62^{in}	-78.9°	**2.56** 2.51^{out}
47 **A**	CAHYIT[e]	[CpFe(CO)PPh_3- $C(=CHMe)CO_2Et$]-(*E*)	-14.4°	**2.60** 2.94^{in}	-44.0°	**2.68** 2.72^{in}	-64.4°	**2.58** 2.62^{out}
48 **A**	PIRDID[e]	[CpFe(CO)PPh_3- $COCH_2C(OH)RR'$]	-14.4°	**2.55** 2.60^{in}	-69.3°	**2.78** -	-58.3°	**2.73** 2.54^{out}
49 **A/B**	GEFJEG[e]	[CpRe(NO)$PPh_3P^tBu_2$]	-14.5°	**2.59** 2.94^{out}	-34.1°	**2.62** 2.54^{in}	84.8°	**2.70** 2.67^{out}
50 **A**	FECPCB10[e]	[CpFe(CO)PPh_3COPh]	-15.2°	**2.44** 2.54^{in}	-60.7°	**2.65** -	-51.2°	**2.19** 2.23^{out}
51 **A**	FIHTOF[1][e]	[CpFe(CO)PPh_3- COCH(SPh)CHPhOH]	-15.4°	**2.53** 2.66^{in}	-69.8°	**2.70** -	-57.7°	**2.78** 2.62^{out}
52 no H[d]	GADWEN01 [e]	[CpFe(CO)PPh_3COMe]	-15.5°		-76.9°		-57.9°	
53 **A**	SECHEN[e]	[CpFe(CO)PPh_3- CH_2SCH_2Ph]	-16.0°	**2.54** 2.75^{in}	-59.7°	**2.63** 2.98^{in}	-61.2°	**2.62** 2.58^{out}
54 **A**	SOZTAC[e]	[CpRe(NO)PPh_3- $NHMe_2$]OTf	-16.3°	**2.54** 2.86^{in}	-44.6°	**2.63** 2.77^{in}	-68.4°	**2.63** 2.68^{out}
55 **A**	SAYFIH[e]	[CpFe(CO)PPh_3- C(OR)=CPhR']	-16.5°	**2.53** 2.71^{in}	-61.1°	**2.80** -	-56.6°	**2.73** 2.68^{out}
56	BOBYEW	[CpRe(NO)PPh_3-	-16.7°	**2.51**	-50.1°	**2.75**	-69.7°	**2.63**

A		$CHPhCH_2Ph$]		2.77^{in}		-		2.52^{out}
57 **A/B**	VOWVAE	[$CpFe(CO)PPh_3$- $COCMe(OCH_2Ph)$- $(CH_2)_4Me$]	-16.8°	**2.49** 2.67^{in}	-74.8°	**2.67** 2.88^{out}	-58.7°	**2.72** 2.45^{out}
58 no H[d]	RARXAJ	[$CpFe(CO)PPh_3CO$-3-py] py = pyridyl	-17.0°		-66.8°		-52.9°	
59 **A**	CICDUN	[$CpFe(CO)PPh_3$- CO(=CHMe)OMe]-(*Z*)	-17.3°	**2.61** 2.99^{in}	-46.8°	**2.70** 2.85^{in}	-68.0°	**2.54** 2.55^{out}
60 **A**	FEHTUH[e]	[$CpFe(CO)PPh_3$- $COCH_2C_3H_5$], C_3H_5 = cyclopropyl	-17.3°	**2.62** 2.75^{in}	-65.7°	**2.71** -	-54.1°	**2.65** 2.61^{out}
61 **A**	WEDMAT[e]	[$Cp^*Fe(CO)PPh_3$- $C(O)CH_2CH_2Ph$]	-17.6°	**2.57** 2.70^{in}	-51.4°	**2.69** 2.98^{in}	-55.9°	**2.54** 2.60^{out}
62 no H[d]	WAJYUB	[$CpFe(CO)PPh_3$- COCHPhCHMeOH]	-17.7°		-64.7°		-57.1°	
63 **A**	SELHIA[e]	[$CpRu(CO)PPh_3$- $C(=C(CN)_2)C(Ph)=C(CF_3)_2$]	-17.8°	**2.63** 2.92^{in}	-48.2°	**2.70** 2.87^{in}	-62.0°	**2.65** 2.58^{out}
64 **A**	HAPSIA	[$CpFe(CO)PPh_3$- $COCH_2CH_2C(CN)^iPrAr$]	-18.0°	**2.60** 2.55^{in}	-74.3°	**2.73** -	-41.9°	**2.78** 2.81^{out}
65 **A**	FIHTOF[2][e]	[$CpFe(CO)PPh_3$- COCH(SPh)CHPhOH]	-18.2°	**2.54** 2.68^{in}	-70.0°	**2.76** -	-53.6°	**2.80** 2.68^{out}
66 **A**	FIHTIZ[1][e]	[$CpFe(CO)PPh_3$- COCH(SPh)CHMeOH]	-19.7°	**2.66** 2.96^{in}	-54.4°	**2.63** -	-56.6°	**2.60** 2.68^{out}
67 **A**	CALWAN	[$CpFe(CO)PPh_3$- COCHMeEt]	-20.1°	**2.63** 2.80^{in}	-65.7°	**2.67** -	-53.3°	**2.63** 2.59^{out}
68 no H[d]	HASKOB[e]	[$CpRe(NO)PPh_3$- $NH=CPh_2$]OTf	-20.4°		-57.6°		-56.9°	
69 no H[d]	SENVOW	[$Cp^*Re(NO)PPh_3$- CONHCHMe-1-Np], Np = naphthyl	-20.7°		-51.6°		-62.3°	
70 no H[d]	CUYVIB10[e]	[$CpRe(NO)PPh_3$-PPh_2]	-20.7°		-43.3°		-76.2°	
71 **A**	BIQQEX[e]	[$CpRe(NO)PPh_3$- $SO_2CH_2CH(NR_2)COOEt$]	-20.9°	**2.66** 2.96^{in}	-58.8°	**2.64** -	-61.4°	**2.66** 2.67^{out}
72 **A**	LAFVAP	[$CpRu(CO)PPh_3OHEt]BF_4$	-21.0°	**2.48** 2.67^{in}	-62.3°	**2.66** -	-57.4°	**2.71** 2.66^{out}
73 **A/B**	CODZEB	[$CpRu(CO)PPh_3$- C(SMe)=CPhC- (SMe)=$C(CN)_2$]-(*Z*)	-21.4°	**2.58** 2.63^{in}	-72.2°	**2.69** 2.91^{out}	-49.0°	**2.66** 2.66^{out}
74 **A**	FIHTIZ[2][e]	[$CpFe(CO)PPh_3$- COCH(SPh)CHMeOH]	-21.9°	**2.60** 2.83^{in}	-63.5°	**2.67** -	-56.3°	**2.63** 2.57^{out}
75 **A**	DUHXOT	[$CpFe(CO)PPh_3$- COCH=CHMe]-(*E*)	-22.1°	**2.59** 2.82^{in}	-65.6°	**2.69** -	-52.7°	**2.64** 2.67^{out}
76 **A**	MCXCFE	[$CpFe(CO)PPh_3CO_2C_{10}H_{19}$] $C_{10}H_{19}$ = menthyl	-22.4°	**2.60** 2.89^{in}	-44.6°	**2.64** 2.94^{in}	-61.1°	**2.52** 2.59^{out}
77 **A**	DICFAW10	[$CpRe(NO)PPh_3$- $COCHMeCH_2Ph$][h]	-22.4°	**2.55** 2.72^{in}	-60.7°	**2.71** -	-54.9°	**2.70** 2.73^{out}
78 **A**	KOZPUK[e]	[$CpRu(CO)PPh_3$- CR(=CRPh)]	-22.5°	**2.49** 2.85^{in}	-41.5°	**2.58** 2.61^{in}	-65.5°	**2.62** 2.81^{out}
79 **A**	RAZCEA	[$CpFe(CO)PPh_3$- $COCH_2SMe$]	-23.4°	**2.62** 2.77^{in}	-57.7°	**2.69** -	-53.3°	**2.71** 2.78^{out}
80 no H[d]	GIBTUG[e]	[$CpFe(CO)PPh_3$- $COCH_2CRR'$]	-23.6°		-64.6°		-56.0°	
81 **A**	ZIQGIP[e]	[$CpFe(CO)PPh_3$- $CO_2CH_2CH_2W(CO)_3Cp$]	-24.0°	**2.56** 2.81^{in}	-65.9°	**2.70** -	-58.2°	**2.72** 2.59^{out}
82 **A**	BOZRUD(1)	[$CpFe(CO)PPh_3$- $C(=CH_2)PPh_3]BF_4$	-24.2°	**2.54** 2.77^{in}	-61.6°	**2.65** -	-53.3°	**2.59** 2.59^{out}
83 **A**	SELHEW[e]	[$CpRu(CO)PPh_3$- CR=CPhR']	-24.3°	**2.57** 2.99^{in}	-42.2°	**2.60** 2.64^{in}	-66.8°	**2.61** 2.79^{out}
84	KEHPUI[e,i]	[$CpFe(CO)PPh_3$-	-24.5°	**2.53**	-82.3°	**2.74**	-57.5°	**2.87**

A		N(O)^{t}Bu]BF_4		2.76^{in}		2.85^{in}		2.56^{out}
85 **A**	VADCEI[e]	[CpRu(CO)PPh_3-C(Me)=C(Me)R]	-24.8°	**2.54** 2.89^{in}	-41.7°	**2.66** 2.71^{in}	-64.5°	**2.58** 2.69^{out}
86 **A**	FELFOR[e]	[CpFe(CO)PPh_3-COCH=CHMe]-(*Z*)	-24.9°	**2.58** 2.80^{in}	-61.6°	**2.63** -[t]	-54.6°	**2.60** 2.61^{out}
87 **A/B**	SOGXOB	[CpFe(CO)PPh_3-$COCH_2OMe$]	-25.3°	**2.58** 2.82^{in}	-60.0°	**2.58** 2.98^{out}	-53.1°	**2.56** 2.59^{out}
88 **A**	FEBMAA[e]	[CpFe(CO)PPh_3-C(=CH_2)$OZrCp_2Cl$]	-25.7°	**2.72** 2.70^{in}	-51.9°	**2.54** 2.91^{in}	-44.6°	**2.49** 2.84^{out}
89 no H[d]	TAMGUJ[e]	[CpRe(NO)PPh_3-SMe_2]OTf	-26.1°		-47.6°		-61.9°	
90 **A**	WIZCOY	[CpRu(CO)PPh_3-CH(CN)SO_2Ph]	-26.9°	**2.57** 2.83^{in}	-63.9°	**2.67** -	-55.7°	**2.68** 2.65^{out}
91 **A/B**	NIDCIM01	[CpRu(Cl)PPh_3PHPh_2]	-28.0°	**2.55** 2.76^{in}	-62.1°	**2.59** 2.99^{out}	-49.5°	**2.63** 2.73^{out}
92 **A/B**	VIVTEZ	[CpFe(CO)PPh_3-$COCH_2PPh_2$]	-28.5°	**2.51** 2.54^{in}	-72.9°	**2.63** 2.83^{out}	-47.1°	**2.69** 2.53^{out}
93 **A/B**	GAKJEH[e]	[CpFe(CO)PPh_3-COCHMeCH(OCO-Ph)$(CH_2)_2CH$=CH_2]	-29.0°	**2.54** 2.86^{in}	-58.0°	**2.55** 2.93^{out}	-52.6°	**2.56** 2.69^{out}
94 no H[d]	RARXEN	[CpFe(CO)PPh_3COCRR']	-29.1°		-51.9°		-54.1°	
95 **A/B**	FUVPIV[e]	[CpRu(CO)PPh_3-C(CO_2Me)=$CHCO_2Me$]-(*Z*)	-29.9°	**2.45** 2.82^{out}	-47.0°	**2.52** 2.67^{in}	-61.2°	**2.59** 2.80^{out}
96 **A**	JIDLUD[e]	[CpFe(CO)$PPh_3CO_2SnPh_3$]	-30.7°	**2.57** 2.85^{in}	-58.2°	**2.65** -	50.0°	**2.60** 2.75^{out}
97 **A/B**	BOZRUD(2)[e, j]	[CpFe(CO)PPh_3-C(=CH_2)PPh_3]BF_4	-31.2°	**2.65** 2.93^{in}	-78.7°	**2.78** 2.76^{out}	-46.5°	**2.77** 2.67^{out}
98 **B**	DAWDUA	[CpFe(CO)PPh_3-$COCH_2CH_2CHMeOH$]	-31.4°	**2.50** 2.82^{out}	-72.2°	**2.58** 2.86^{out}	-55.4°	**2.82** 2.67^{out}
99 no H[d]	ZINXOJ[1][e]	[CpRe(NO)PPh_3-S(CH_2CH=CH_2)$_2$]SbF_6	-32.1°		-63.7°		-44.8°	
100 **A/B**	SECHIR	[CpFe(CO)PPh_3CH_2OMe]	-32.5°	**2.51** 2.85^{in}	-66.4°	**2.60** 2.79^{out}	-55.4°	**2.66** 2.54^{out}
101 **A**	SELHOG	[CpRu(CO)PPh_3-C(=C($CN)_2$)C(Me)=C($CF_3)_2$]	-32.9°	**2.57** 2.59^{in}	-56.4°	**2.60** -	-36.3°	**2.58** 2.84^{out}
102 no H[d]	ZINXOJ[2]	[CpRe(NO)PPh_3-S(CH_2CH=CH_2)$_2$] SbF_6	-34.6°		-62.3°		-38.8°	
103 **B**	HAXLIB[e]	[CpRe(NO)PPh_3-CR(=NHR')]OTf	-35.1°	**2.33** 2.57^{out}	-51.3°	**2.80** -	-68.5°	**2.72** 2.55^{out}
104 no H[d]	YEJDEW[e]	[CpRe(NO)PPh_3NR_2]	-35.5°		-35.7°		-54.2°	
105 no H[d]	HASKUH	[CpRe(NO)PPh_3-N(Me)=CHPh]OTf	-35.7°		-55.8°		-62.5°	
106 no H[d]	LEFYOK[e]	[CpRe(NO)PPh_3NRR']OTf	-36.4°		-57.6°		-57.1°	
107 no H[d]	BIDYAO[e]	[CpFe(CO)PPh_3-C(=CMe_2)CO_2Et]	-37.0°		-44.0°		-55.6°	
108 **A**	NORMEM	[CpFe(CO)PPh_3-C(=CH_2)CH_2SO_2Ph]	-37.4°	**2.50** 2.82^{in}	-43.8°	**2.57** 2.89^{in}	-47.6°	**2.58** -
109 **A/B**	ZOFCUS	[CpRu(CO)PPh_3-C(=CPhCH_2CH_2O]	-37.6°	**2.52** 2.82^{in}	-51.5°	**2.55** 2.97^{out}	-48.7°	**2.57** 2.84^{out}
110 **A/B**	UCULAG[e]	[CpRu(CO)PPh_3PPh_2-CHCO^{t}Bu]	-38.1°	**2.55** 2.89^{out}	-46.5°	**2.58** 2.90^{in}	-53.9°	**2.44** 2.82^{out}
111 **B**	ICUJIZ	[CpRe(NO)PPh_3-$PMeR_2$]OTf	-39.0°	**2.52** 2.89^{out}	-57.1°	**2.58** 2.79^{out}	-56.0°	**2.61** 2.73^{out}
112 **A/B**	ZEVGUE	[CpRu(CO)PPh_3-C(SeR)=CPhSeR]	-40.2°	**2.54** 2.89^{in}	-55.5°	**2.61** 2.89^{out}	-49.8°	**2.63** 2.86^{out}
113	QUNTAU	[CpFe(CO)PPh_3-	-40.6°	**2.44**	-57.9°	**2.57**	-50.4°	**2.66**

B		Sb(O(R)Ar)O(R')Ar']		2.72^{out}		2.90^{out}		2.77^{out}
114 **B**	POZYOS[e]	[CpFe(CO)PPh_3CRR']	-40.8°	**2.51** 2.83^{out}	-52.2°	**2.56** 2.83^{out}	-56.4°	**2.60** 2.77^{out}
115 **B**	LADFEB(2)[f]	[CpFe(CO)PPh_3-$CO_2Re(CO)_4PPh_3$]	-43.0°	**2.48** 2.82^{out}	-61.8°	**2.54** 2.81^{out}	-43.4°	**2.68** 2.88^{out}
116 **B**	NOCQIF	[CpFe(CO)PPh_3-$COCH_2C_6H_4$-*o*-Me]	-43.2°	**2.56** 2.82^{out}	-46.4°	**2.57** 2.97^{out}	-56.7°	**2.55** 2.77^{out}
117 no H[d]	VUHBOP	[CpRe(NO)PPh_3-1-quinoline]OTf	-43.3°		-53.9°		-51.8°	
118 no H[d]	TAMHEU	[CpRe(NO)PPh_3-$SOMe_2$]BF_4	-44.1°		-56.0°		-46.1°	
119 no H[d]	VEJYEO10	[CpRe(NO)PPh_3-2-quinoline]OTf	-47.2°		-47.8°		-61.3°	

[a]Brackets [] indicate independent molecules and parentheses () different ligands in the same molecule.
[b]Long formula were abbreviated by using R, R' etc. Formula will not exceed three lines.
[c]Variant **A** refers to $^{in}C_oH$-$^{in}C_o$ distances and variant **B** to $^{in}C_oH$-$^{out}C_o$ distances for **Ph1** and **Ph2**, respectively.
[d]No or not all hydrogen atoms located in structure.
[e]Structure in Cambridge file inverted to have **Ph1** up, **Ph2** on the left side, and **Ph3** on the right side for all compounds, looking along the P-M axis.
[f]Re-PPh_3group.
[g]Only case in which torsion angle M-P-C_i-C_o exceeds 90°, which changes in and out.
[h]Wrongly designated as CpFe(CO) compound in ref. X.
[i]Strange atom to ring 2.
[j]C-PPh_3 moiety.

Table S2. Sextuple phenyl embraces in the $Cp^{(*)}M\text{-}PPh_3$ complexes (M = Fe, Ru or Re) of Table 1: P...P distance and half the sum of the pertinent M-P…P and P…P-M angles

Entry **variant**	CSD symbol	Formula	Sextuple phenyl embrace	
			P...P distance / Å	M-P...P and P...P-M
15 **A**	VOWTUW[1]	$[CpFe(CO)PPh_3COC(=CH_2)\text{-}OCH_2Ph]$	7.69[a]	166.8°
20 **A**	LADFEB(1)	$[CpFe(CO)PPh_3CO_2Re(CO)_4\text{-}PPh_3]$	7.37[b]	160.2°
24 **A**	LAPJIV(2)	$[Cp^*Re(NO)PPh_3COCH_2\text{-}Re(CO)_4PPh_3]$	7.30[c]	170.0°
45 **A**	FIHTEV	$[CpFe(CO)PPh_3\text{-}COCH(SPh)CHMeOH]$	6.89	172.6°
65 **A**	FIHTOF[2]	$[CpFe(CO)PPh_3\text{-}COCH(SPh)CHPhOH]$	7.63[d]	150.4°
82 **A**	BOZRUD(1)	$[CpFe(CO)PPh_3\text{-}C(=CH_2)PPh_3]BF_4$	7.08[e]	171.8°
90 **A**	WIZCOY	$[CpRu(CO)PPh_3\text{-}CH(CN)SO_2Ph]$	6.94	175.7°
95 **A/B**	FUVPIV	$[CpRu(CO)PPh_3\text{-}C(CO_2Me)=CHCO_2Me]\text{-}(Z)$	7.11	170.8
97 **A/B**	BOZRUD(2)	$[CpFe(CO)PPh_3\text{-}C(=CH_2)PPh_3]BF_4$	6.33[f]	179.0°[g]
108 **A**	NORMEM	$[CpFe(CO)PPh_3\text{-}C(=CH_2)CH_2SO_2Ph]$	7.50	169.8°
115 **B**	LADFEB(2)	$[CpFe(CO)PPh_3\text{-}CO_2Re(CO)_4PPh_3]$	7.37[h]	160.2°
116 **B**	NOCQIF	$[CpFe(CO)PPh_3\text{-}COCH_2C_6H_4\text{-}o\text{-}Me]$	6.87	176.2°

[a] With VOWTUW[1]. [b] With LADFEB(2). [c] With LAPJIV(2). [d] With FIHTOF[1]. [e] With BOZRUD(1). [f] With BOZRUD(2).

[g] Half the sum of the pertinent C-P...P and P…P-C angles. [h] With LADFEB(2).