From a PGeP Pincer-Type Germylene to Metal Complexes Featuring Chelating (Ir) and Tripodal (Ir) PGeP Germyl and Bridging (Mn₂) and Chelating (Ru) PGeP Germylene Ligands

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Figure S1. ¹H (top, 400.1 MHz), ¹³C{¹H} (center, 100.6 MHz), and ³¹P{¹H} (bottom, 162.0 MHz) NMR spectra (CD₂Cl₂, 293 K) of [Ir{ κ^2 Ge,P-GeCl(NCH₂P^tBu₂)₂C₆H₄}(η^4 -cod)] (**2**).



Figure S2. ¹H (top, 300.1 MHz), ¹³C{¹H} (center, 100.6 MHz), and ³¹P{¹H} (bottom, 162.0 MHz) NMR spectra (C_6D_6 , 293 K) of [Ir{ κ^3P , Ge, P-GeCl(NCH₂P^tBu₂)₂C₆H₄}(CO)₂] (**3**).



Figure S3. ¹H (top, 300.1 MHz, C_6D_6 ,), ¹³C{¹H} (center, 100.6 MHz, CD_2CI_2), and ³¹P{¹H} (bottom, 162.0 MHz, CD_2CI_2) NMR spectra (293 K) of [Mn{ μ - $\kappa^{3}P$, *Ge*, *P*-Ge(NCH₂P^tBu₂)₂C₆H₄)(CO)₈] (**4**).



Figure S4. ¹H (top, 400.1 MHz), ¹³C{¹H} (center, 100.6 MHz), and ³¹P{¹H} (bottom, 162.0 MHz) NMR spectra (C₆D₆, 293 K) of [RuHCl(CO){ κ^2 Ge,P-Ge(NCH₂P^tBu₂)₂C₆H₄}(P^tPr₃)] (**5**).

	1	2	3 (C ₇ H ₈) _{0.75}	4 (C ₇ H ₈)	5
formula	$C_{24}H_{44}GeN_2P_2$	$C_{32}H_{56}CIGeIrN_2P_2$	$C_{26}H_{44}CIGeIrN_2O_2P_2$ $\cdot(C_7H_8)_{0.75}$	$C_{32}H_{44}GeMn_2N_2O_8P_2$ $\cdot C_7H_8$	$C_{34}H_{66}CIGeN_2OP_3Ru$
fw	495.14	830.96	847.95	921.23	820.90
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	C2/c	<i>P</i> 21/c	<i>P</i> 21/n	<i>P</i> –1	P21/c
<i>a</i> , Å	19.373(3)	14.5267(1)	26.1512(8)	11.2224(3)	8.5316(3)
b, Å	13.288(1)	18.0079(2)	10.0811(2)	12.3774(5)	18.5242(6)
<i>c</i> , Å	14.152(2)	13.3482(1)	26.2975(8)	16.3412(6)	24.9795(8)
lpha, deg	90	90	90	98.265(3)	90
β , deg	133.29(3)	93.090(1)	90.749(3)	109.005(3)	94.748(3)
γ, deg	90	90	90	99.290(3)	90
V, Å ³	2652(1)	3486.75(5)	6932.3(3)	2070.6(1)	3934.2(2)
Z	4	4	8	2	4
<i>F</i> (000)	1056	1672	3388	952	1720
D_{calcd} , g cm ⁻³	1.240	1.583	1.625	1.478	1.386
μ , mm ⁻¹ (Cu K α)	2.788	10.078	10.200	6.903	6.031
cryst size, mm	0.13 x 0.11 x 0.05	0.19 x 0.13 x 0.07	0.12 x 0.10 x 0.05	0.10 x 0.06 x 0.05	0.09 x 0.03 x 0.01
<i>Т</i> , К	138(2)	150(2)	150(2)	141(2)	154(2)
θ range, deg	4.57 to 69.43	3.05 to 69.66	3.36 to 69.87	3.70 to 69.58	2.98 to 69.96
min./max. <i>h</i> , <i>k</i> , <i>l</i>	–23/18, –15/14, –17/16	–14/17, –21/21, –16/15	-31/29, -9/12, -26/31	–13/9, –15/13, –18/19	-4/10, -22/22, -30/29
no. collected refins	5685	18914	38524	16902	18384
no. unique reflns	2372	6480	12885	7600	7228
no. refins with $l > 2\sigma(l)$	1945	6111	11148	6879	4842
no. params/restraints	138 /0	399/6	738/67	500/0	409/0
GOF (on F ²)	1.316	1.081	1.017	1.086	1.141
R_1 (on F, $l > 2s(l)$)	0.042	0.021	0.037	0.037	0.058
wR_2 (on F^2 , all data)	0.162	0.051	0.102	0.116	0.241
min./max. Δho , e Å ⁻³	-1.213/0.654	-1.025/0.673	-2.093/1.381	-0.552/1.171	-2.611/1.837
CCDC deposition no.	1829992	1829993	1829994	1829995	1829996

Table S1. Crystal, Measurement, and Refinement Data for the Compounds Studied by X-Ray Diffraction