

The Chloromethylgermyl Complexes $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_n\text{GeR}_2\text{CH}_2\text{Cl}$ [$\text{M} = \text{Fe}$ ($n = 2$), Mo , W ($n = 3$)]: Rearrangements, Transformations to 1-Germa-3-metallacyclobutanes $(\eta^5\text{-C}_5\text{H}_4)\text{M}(\text{CO})_n\text{CH}_2\text{GeR}_2$, and their Ring-Opening Polymerizations

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The reactions between the transition metal–carbonylate salts $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_n]^- \text{Na}^+$ ($\text{M} = \text{Fe}$ ($n = 2$), Mo , W ($n = 3$)) and $\text{ClCH}_2\text{GeR}_2\text{Cl}$ result in the high-yield formation of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_n\text{GeR}_2\text{CH}_2\text{Cl}$ ($\text{M} = \text{Fe}$, $\text{R} = \text{Me}$ (**1**), $n\text{-Bu}$ (**2**); $\text{M} = \text{Mo}$, $\text{R} = \text{Me}$ (**3**), $\text{R} = n\text{-Bu}$ (**4**); $\text{M} = \text{W}$, $\text{R} = \text{Me}$ (**5**), $\text{R} = n\text{-Bu}$ (**6**)). Complexes **1**, **2**, **5**, and **6** are transformed into the isomers $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_n\text{CH}_2\text{GeR}_2\text{Cl}$ (**1a**, **2a**, **5a**, and **6a**) thermally and/or photochemically. Treatment of either type of complex and the Mo complexes **3** and **4** with lithium diisopropylamide results in the formation of the metallacycles $(\eta^5\text{-C}_5\text{H}_4)\text{M}(\text{CO})_n\text{CH}_2\text{GeR}_2$ (**7–12**). The metallacycles of Mo and W (**9** and **11**) are crystalline complexes, and single-crystal X-ray analysis reveals a degree of ring strain. However, these complexes cannot be ring-opened, in contrast to the corresponding Fe complexes (**7** and **8**), which readily form new polymeric materials $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{CH}_2\text{GeR}_2]_n$.

Introduction

Ring-opening of well-defined metallacycles can lead to attractive materials with potential applications as catalysts,¹ ion-exchange resins,² polymeric support materials,³ precursors for ceramic materials,⁴ conducting polymers,^{5,6} and chemical sensors.⁶ There are limited reports on the synthesis and reactivity of germametallacyclobutanes.⁷ *ansa*-Dimethylgermyldicyclopentadienyl ligands of Zr, Hf, and Ti yield

tetrahedral complexes with little ring strain in the metallacycle portion of the structure, and no specific metallacyclobutane chemistry has been reported.⁷ However, they are useful catalysts for the polymerization of olefins.⁸ Although, 1-sila-3-metallacyclobutanes, $\text{Cp}_2\text{MCH}_2\text{SiMe}_2\text{CH}_2$, ($\text{M} = \text{Ti}$, Zr , Hf)^{1a} are known for their ring expansion chemistry, such chemistry is not reported for the related germa^{7a} and stanna^{7b} derivatives. On the other hand, 1-germa- and stannaferrocenophanes have been studied and shown to readily ring open to form interesting high molecular weight polymers.⁹

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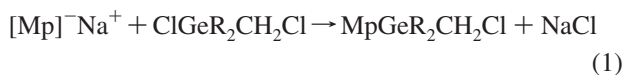
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We recently reported a series of 1-sila-3-ferracycles $(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{ER}_2\text{SiR}_2'$ ($\text{ER}_2 = \text{CH}_2$, SiR_2' ; $\text{R}' = \text{Me}$, $n\text{-Bu}$) that under certain conditions ring-opened to organometallic polymers.¹⁰ We now report the synthesis, characterization, rearrangements, and ring-opening polymerization of 1-germa-3-metallacyclobutanes, $(\eta^5\text{-C}_5\text{H}_4)\text{M}(\text{CO})_n\text{CH}_2\text{GeR}_2$ [$\text{M} = \text{Mo}$, W ($n = 3$); Fe ($n = 2$) and $\text{R} = \text{Me}$, Bu].

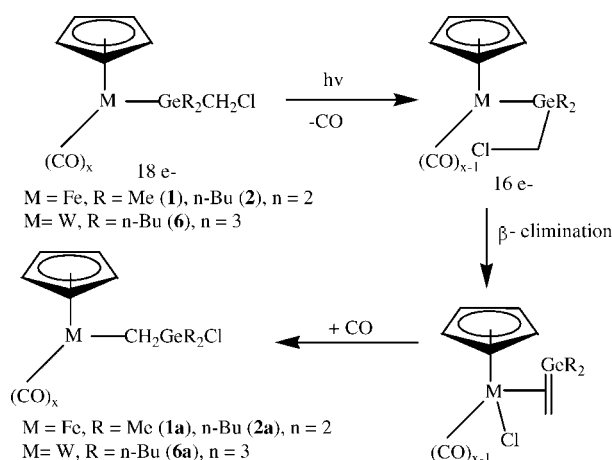
Results and Discussion

Using standard salt-elimination chemistry the synthesis of a series of dialkyl(chloromethyl)germyl metal complexes, $\text{MpGeR}_2\text{CH}_2\text{Cl}$, was accomplished in moderate yields as outlined in eq 1, $\text{Mp} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ [$\text{R} = \text{Me}$ (**1**), $n\text{-Bu}$ (**2**)] ($\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3$ [$\text{R} = \text{Me}$ (**3**), $n\text{-Bu}$ (**4**)] ($\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3$ [$\text{R} = \text{Me}$ (**5**), Bu (**6**)]).



The photolysis of benzene solutions of complexes $\text{MpGeR}_2\text{CH}_2\text{Cl}$ (**1**, **2**, and **6**) in sealed Pyrex NMR tubes for 14–24 h resulted in quantitative rearrangement to the isomeric complexes $\text{MpCH}_2\text{GeR}_2\text{Cl}$ [$\text{M} = \text{Fe}$, $\text{R} = \text{Me}$ (**1a**), $n\text{-Bu}$ (**2a**) and $\text{M} = \text{W}$, $\text{R} = n\text{-Bu}$ (**6a**)] containing a direct M–C bond. Benzene solutions of the iron complexes **1** and **2** also rearranged thermally to **1a** and **2a**, reminiscent of the thermal rearrangement of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiMe}_2\text{CH}_2\text{Cl}$ to $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{SiMe}_2\text{Cl}$.^{10,11} The iron isomers **1a** and **2a** were easily distinguished by the ^{13}C resonances of the methylene group, -16.8 ppm (**1a**, $\text{Fe-CH}_2\text{Ge}$), -20.6 ppm (**2a**, $\text{Fe-CH}_2\text{Ge}$) versus those of their parent complexes, 37.6 ppm (**1**, Fe-GeCH_2), 35.2 ppm (**2**, Fe-GeCH_2). Infrared spectroscopy was also useful to distinguish the two sets of isomers, and the carbonyl stretching frequencies for the Fp–Ge complex **1** are $\sim 10\text{ cm}^{-1}$ lower than the carbonyl stretching frequencies of Fp–C complex **1a**.¹² It is possible that the mechanism of the photochemical rearrangement may involve the initial decarbonylation to generate a $16e^-$ coordinatively unsaturated complex followed by β -elimination of chlorine to the metal center to generate a transient germene complex. The recoordination of CO drives the migration of chlorine to the germanium, Scheme 1, to effect the rearrangement process. Presumably the initial formation of the M–Ge complexes is associated with the greater kinetic lability of the Ge–Cl bond versus the C–Cl bond. However, the greater bond energy of the Ge–Cl versus C–Cl ($E_{\text{Ge-Cl}} = 83.1\text{ kcal/mol}$; $E_{\text{C-Cl}} = 68.3\text{ kcal/mol}$ ¹⁴) is in large measure the driving force for the formation of the thermodynamically stable product. The $E_{\text{Fe-Ge}}$ and $E_{\text{W-Ge}}$ data are not available to complete this

Scheme 1



analysis, but they cannot be more stable by $\sim 14.8\text{ kcal/mol}$ than the respective Fe–C and W–C bond energies ($E_{\text{Fe-C}} = 68.0\text{ kcal/mol}$,¹⁵ $E_{\text{W-C}} = 60.8\text{ kcal/mol}$).¹⁶ However, it is of interest that the Mo derivative, $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{GeMe}_2\text{CH}_2\text{Cl}$, did not rearrange either thermally or photochemically, presumably due to the higher Mo–Ge bond energy as compared to the Mo–C bond, as indicated by available data ($E_{\text{Mo-Ge}} = 51.5\text{ kcal/mol}$, $E_{\text{Mo-C}} = 33.2\text{ kcal/mol}$,^{14,17} $\Delta E = 18.3\text{ kcal/mol}$).

Treatment of complexes **1–6**, **1a**, **2a**, and **6a** containing M–Ge or M–C bonds with 1 equiv of lithium diisopropylamide, LDA, resulted in the initial formation of the corresponding 1-alkylgerma-3-metallacyclobutanes in high yield ($\sim 80\%$), Scheme 2, pathway A. In all cases the initial proof for the formation of the metallacyclobutanes was the observation of the ring methylene resonance in the ^{13}C NMR spectra at between ca. -50 and -65 ppm.

Isolation of the cyclobutanes was dependent upon the metal involved. In the case of the Mo and W complexes, **9–12**, these metallacyclobutanes were isolated as stable crystalline materials. The dimethylgerma iron complex **7** was short-lived and transformed to a polymer **7a**, $M_w = 2.5 \times 10^3$, $M_n = 2.2 \times 10^3$, (M_w/M_n) = 1.13 (Scheme 2, B).

The corresponding butylgermyl iron complex **8** was stable enough for isolation and purification by column chromatography; however, it also undergoes a ring-opening polymerization if it is kept for a prolonged time ($\sim$ a month) even at low temperature (0°C), resulting in the formation of polymer **8a**, $M_w = 5.4 \times 10^3$, $M_n = 2.5 \times 10^3$, PDI (M_w/M_n) = 2.1. This differs from our results with the silicon analogue di-*n*-butylsila-ferracyclobutane, $(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{CH}_2\text{SiBu}_2$, which was found to be very stable.^{10a} TGA analysis of the polymers **7a** and **8a** showed an onset of weight loss between 200 and 300°C , resulting in $\sim 45\%$ residual mass at 650°C .

X-ray Crystal Structures of 9 and 11. The molecular structures of **9** and **11** are shown in Figure 1. The two metallacycles are isostructural and crystallize in the triclinic space group $P\bar{1}$, and the asymmetric unit contains two molecules for each of the metallacycles with little variations in the bond lengths and angles. They exhibit almost planar cyclobutane rings, and the ligands are disposed in a distorted four-legged

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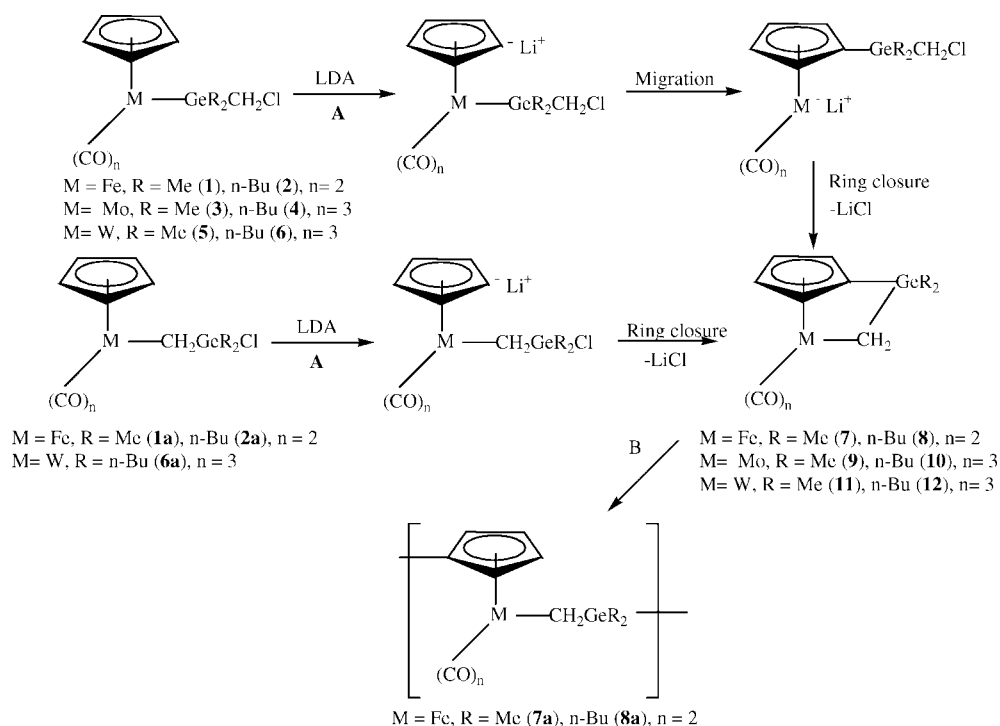
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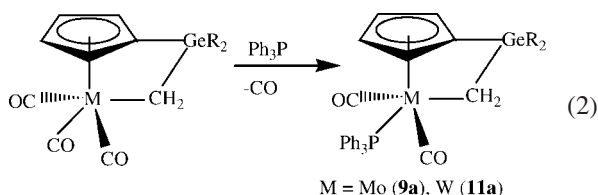
Scheme 2



piano stool fashion as observed for analogous tricarbonyl cyclopentadienyl group 6 metal complexes.¹⁸ The angles between adjacent atoms in the ring vary from 74.3° to 94.3 (4°) in **9** and 74.1° to 96.3 (4°) in **11** and are also typical for these types of structures (Table 2).¹⁸ The internal angles of the four-membered ring differ significantly from the values of normal tetrahedral angles, indicating that the cyclic portion of the molecules composed of $\text{M}-\text{C}-\text{Ge}-\text{C}$ possesses a significant strain and causes the cyclobutane ring to be puckered with folding angles of 15.5° (**9**, molecule 1), 9.8° (**9**, molecule 2) and 9.9° (**11**, molecule 1), 16° (**11**, molecule 2). Despite the ring strain, to date these metallacycles have not exhibited a propensity for ring-opening polymerization.

Metallacycle Reactivity. The Mo metallacycle (**9**) was treated with a range of reagents including a radical initiator (AIBN), anionic and base species ($n\text{-BuLi}$, LDA, Et_3N), and transition metal complexes such as $(\text{PPh}_3)_4\text{Pd}$ in attempts to observe ring-opened polymerization. None of these experiments were successful.

The thermal reaction of **9** and **11** with Ph_3P in THF resulted in the formation of the simple phosphine-substituted products $(\eta^5\text{-C}_5\text{H}_4)\text{Mo}(\text{CO})_2(\text{Ph}_3\text{P})\text{CH}_2\text{GeMe}_2$ (**9a**) and $(\eta^5\text{-C}_5\text{H}_4)\text{W}(\text{CO})_2(\text{Ph}_3\text{P})\text{CH}_2\text{GeMe}_2$ (**11a**) (eq 2).



Infrared and ^{13}C NMR spectral values indicated that **9a** [1920 (vs), 1843 cm^{-1} (s); -47.2 (d, CH_2 , $^2J_{\text{P-C}} = 7.6$ Hz); 228.6 (d, CO , $^2J_{\text{P-C}} = 16.5$ Hz)] and **11a** [1918 (vs), 1847 cm^{-1} (s); -57.6 (d, CH_2 , $^2J_{\text{P-C}} = 7.3$ Hz); 228.6 (d, CO , $^2J_{\text{P-C}} = 16.0$ Hz)] adopt the trans-isomeric form. The ^{13}C NMR spectral data of compound **9a** are similar to those of *trans*-(η^5 -

$\text{C}_5\text{H}_4\text{Mo}(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{CH}_2\text{GeMe}_2$ [233.9 (d, CO , $^2J_{\text{P-C}} = 33.8$ Hz); -47.2 (d, CH_2 , $^2J_{\text{P-C}} = 8.4$ Hz)].¹⁹ In addition to that, other molybdenum complexes, $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{L})\text{R}$ ($\text{L} = \text{P}(\text{OR}_3)_3$, PR_3 ; $\text{R} = \text{H}$, Hal , Me , PhCH_2 , etc.),²⁰ revealed the increase of trans-isomer percentage on increasing the steric bulk around the metal atom; for example, $\text{L} = \text{Ph}_3\text{P}$, $\text{R} = \text{Me}$, PhCH_2 forms >99% trans-isomer. Similarly, W complexes $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{Ph}_3\text{P})\text{X}$ ($\text{X} = \text{alkyl}$)²¹ are reported to adopt a trans-isomeric form on increasing the steric bulk around the metal atom.

No fluxional behavior for these compounds in solution state has been seen in the NMR spectroscopy, which is authenticated by the presence of only one doublet in the methylene and carbonyl region.

Experimental Procedures

All syntheses were performed using standard Schlenk techniques under nitrogen atmospheres. The required glassware was oven-dried at 100 °C for a period of 12 h, assembled hot and cooled under vacuum, and purged with nitrogen. Reagent grade tetrahydrofuran (THF) was dried and distilled from sodium-benzophenone. Benzene, hexanes, and toluene were dried and distilled from Na wire. The following reagents were purchased from Aldrich and used as received: bromobenzene, bromochloromethane, diisopropylamine, and $n\text{-BuLi}$ (as a 1.6 M solution in hexanes). Dimethyldichlorogermane and di- n -butyldichlorogermane were purchased from Gelest and used as received. The dimers $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2$ and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Mo}]_2$ were purchased from Strem Chemical; $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{W}]_2$ was purchased from Acros Organics. Lithium diisopropylamide (LDA) was freshly prepared from (1.6 M) $n\text{-BuLi}$ and diisopropyl amine. Solution NMR spectra were recorded on a

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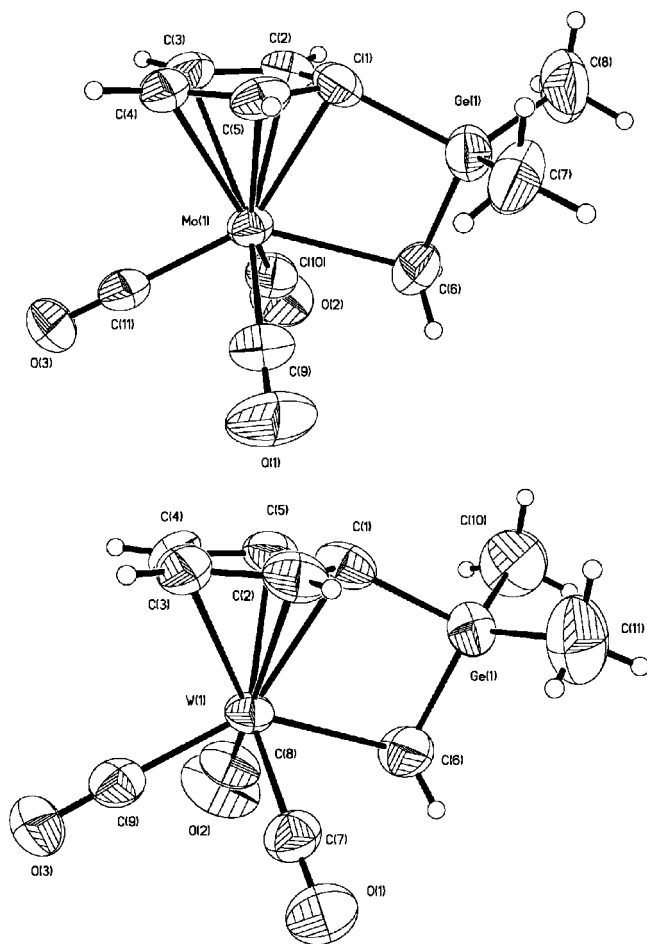


Figure 1. ORTEP diagram of the molecular structures of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_2\text{GeMe}_2$ (9) and $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{CH}_2\text{GeMe}_2$ (11). Thermal ellipsoids are drawn at the 50% probability level (only one molecule of each compound is shown).

Bruker 300 MHz spectrometer using CDCl_3 or C_6D_6 as solvent and reported as ppm; infrared spectra were recorded on an ATI Mattson Infinity Series FTIR; elemental analyses were performed by Galbraith Laboratories. Gel permeation chromatography (GPC) analysis of the molecular weight distribution of the polymers was performed on a high-performance liquid chromatography (HPLC) instrument comprised of a Spectra-Physics Spectra System P1500 gradient pump, UV2000 detector, and Winner for Windows software. A Waters 7.8×300 mm Styragel column packed with $5 \mu\text{m}$ particles of mixed pore size and highly cross-linked styrene-divinylbenzene copolymer particles maintained at 24°C was used for the analysis. The eluting solvent was HPLC grade THF at a flow rate of 1.0 mL/min . The retention times were calibrated against known polystyrene standards at molecular weights of 4000, 18 700, 44 000, 97 000, and 212 400.

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{GeMe}_2\text{CH}_2\text{Cl}$ (1). To 60 mL of a THF solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^- \text{Na}^+$ (prepared from 1.40 g (4.0 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$) was added, via syringe, 1.5 g (8.0 mmol) of $\text{ClCH}_2\text{GeMe}_2\text{Cl}$ ²² in 10 mL of THF at -78°C . The solution was initially stirred at low temperature, warmed to room temperature, and further stirred overnight. The solvent was removed under vacuum, the residue was extracted with 40 mL of hexane and filtered through Celite, and the solvent was removed under vacuum. The residue was redissolved in 30 mL of hexane and again filtered through Celite. Removal of the solvent afforded (2.0 g, 6.0 mmol, 77% yield) $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{GeMe}_2\text{CH}_2\text{Cl}$ (1)

Table 1. Summary of X-ray Crystallographic Data of 9 and 11

	9	11
empirical formula	$\text{C}_{11}\text{H}_{12}\text{GeMoO}_3$	$\text{C}_{11}\text{H}_{12}\text{GeWO}_3$
formula weight	360.74	448.65
temperature (K)	296(2)	296(2)
$\lambda(\text{Mo K}\alpha)$ (Å)	0.17073	0.17073
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimens		
a (Å)	6.8366(7)	6.822(2)
b (Å)	13.3860(15)	13.361(4)
c (Å)	14.6784(16)	14.685(4)
α (deg)	82.52(2)	82.50
β (deg)	79.88(2)	79.76
γ (deg)	81.76(2)	81.87
volume (Å ³)	1301.2(2)	1296.4(6)
Z	4	4
calcd density (Mg/m ³)	1.841	2.299
cryst size (mm)	$0.40 \times 0.20 \times 0.06$	$0.20 \times 0.20 \times 0.06$
refinement method	full-matrix least-squares on F^2	
final R (R_w)	$R_1 = 0.057$	$R_1 = 0.044$
	$wR_2 = 0.1200$	$wR_2 = 0.108$

as a dark red viscous material. Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{FeO}_2\text{GeCl}$: C, 36.49, H, 3.98. Found: C, 37.29, H, 4.04. ^1H NMR (C_6D_6): 0.59 (s, 6H, Me), 3.06 (s, 2H, CH_2), 4.01 (s, 5H, C_5H_5). ^{13}C NMR (C_6D_6): 3.93 (Me), 37.6 (CH_2), 83.0 (C_5H_5), 215.9 (CO). IR (ν CO, cm^{-1} , hexanes): 2001, 1952.

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{GeBu}_2\text{CH}_2\text{Cl}$ (2). As above $\text{FpGeBu}_2\text{CH}_2\text{Cl}$ (2) was obtained as a red viscous material from the reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^- \text{Na}^+$ (prepared from 2.0 g (5.6 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$) and 2.9 g (11.0 mmol) of $\text{ClCH}_2\text{GeBu}_2\text{Cl}$;¹⁷ yield 3.8 g, 9.2 mmol, 84%. Anal. Calcd for $\text{C}_{16}\text{H}_{25}\text{FeO}_2\text{GeCl}$ (mol wt 413.28): C, 46.50; H, 6.10. Found: C, 47.05; H, 6.25. ^1H NMR (C_6D_6): 0.96 (m, 6H, Bu), 1.21–1.50 (m, 12H, Bu), 3.20 (s, 2H, CH_2), 4.14 (s, 5H, C_5H_5). ^{13}C NMR (C_6D_6): 13.9, 20.4, 26.8, 28.7 (Bu), 35.2 (CH_2), 82.5 (C_5H_5), 215.7 (CO). IR (ν CO, cm^{-1} , THF): 1999, 1951.

$(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{GeMe}_2\text{CH}_2\text{Cl}$ (3). In a manner similar to that described above $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{GeMe}_2\text{CH}_2\text{Cl}$ (3) was obtained as a pale pink solid from the reaction between $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]^- \text{Na}^+$ (prepared from 0.88 g (1.80 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$) and 0.70 g (3.60 mmol) of $\text{ClCH}_2\text{GeMe}_2\text{Cl}$; yield (1.2 g, 3.0 mmol, 90%), mp 78°C . Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{MoO}_3\text{GeCl}$: C, 33.26; H, 3.30. Found: C, 33.22; H, 3.42. ^1H NMR (C_6D_6): 0.69 (s, 6H, Me), 3.17 (s, 2H, CH_2), 4.47 (s, 5H, C_5H_5). ^{13}C NMR (C_6D_6): 3.18 (Me), 36.8 (CH_2), 89.9 (C_5H_5), 225.8, 231.0 (CO). IR (ν CO, cm^{-1} , THF): 1999, 1926, 1901.

$(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{GeBu}_2\text{CH}_2\text{Cl}$ (4). The reaction between $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]^- \text{Na}^+$ (prepared from 2.0 g (4.10 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$) and 2.90 g (10.0 mmol) of $\text{ClCH}_2\text{GeBu}_2\text{Cl}$ afforded (4.0 g, 8.30 mmol, 83%) $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{GeBu}_2\text{CH}_2\text{Cl}$ (5) as a pale pink oil. Anal. Calcd for $\text{C}_{17}\text{H}_{25}\text{MoO}_3\text{GeCl}$: C, 42.42; H, 5.23. Found: C, 42.26; H, 5.19. ^1H NMR (C_6D_6): 0.93 (m, 6H, Bu), 1.45 (m, 12H, Bu), 3.36 (s, 2H, CH_2), 4.66 (s, 5H, C_5H_5). ^{13}C NMR (C_6D_6): 13.4, 20.4, 26.3, 28.5 (Bu), 35.0 (CH_2), 89.3 (C_5H_5), 225.7, 230.9 (CO). IR (ν CO, cm^{-1} , hexanes): 2005, 1936, 1913.

$(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{GeMe}_2\text{CH}_2\text{Cl}$ (5). As above, the reaction between $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]^- \text{Na}^+$ (prepared from 1.0 g (1.50 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$) and 0.56 g (3.0 mmol) of $\text{ClCH}_2\text{GeMe}_2\text{Cl}$ afforded (1.2 g, 2.47 mmol, 82.7%) of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{GeMe}_2\text{CH}_2\text{Cl}$ (3) as a yellow solid, mp 86°C . Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{WO}_3\text{GeCl}$: C, 27.23; H, 2.70. Found: C, 27.01; H, 2.65. ^1H NMR (C_6D_6): 0.72 (s, 6H, Me), 3.20 (s, 2H, CH_2), 4.47 (s, 5H, C_5H_5). ^{13}C NMR (C_6D_6): 2.36 (Me), 36.1 (CH_2), 82.6 (C_5H_5), 215.6, 219.3 (CO). IR (ν CO, cm^{-1} , hexanes): 2005, 1930, 1909.

$(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{GeBu}_2\text{CH}_2\text{Cl}$ (6). The reaction between $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]^- \text{Na}^+$ (prepared from 1.0 g (1.50 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$) and 0.81 g (3.0 mmol) of $\text{ClCH}_2\text{GeBu}_2\text{Cl}$ afforded

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **9** and **11**

Complex 9					
Mo—C(6)	2.360(9)	C(6)—Ge(1)	1.928(10)	Ge(1)—C(1)	1.970(9)
C(1)—Mo(1)	2.336(8)	Ge(1)—C(7)	1.933(11)	Ge(1)—C(8)	1.933(11)
C(1)—Mo(1)—C(6)	74.3(3)			Mo(1)—C(1)—Ge(1)	94.9(3)
C(1)—Ge(1)—C(6)	93.3(4)			Ge(1)—C(6)—Mo(1)	95.3(4)
Complex 11					
W(1)—C(6)	2.337(11)	C(6)—Ge(1)	1.940(11)	Ge(1)—C(1)	1.962(12)
C(1)—W(1)	2.334(10)	Ge(1)—C(10)	1.960(12)	Ge(1)—C(11)	1.941(14)
C(1)—W(1)—C(6)	74.4(3)			W(1)—C(1)—Ge(1)	95.8(4)
C(1)—Ge(1)—C(6)	92.8(4)			Ge(1)—C(6)—W(1)	96.3(4)

(1.44 g, 2.50 mmol, 85.0%) of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{GeBu}_2\text{CH}_2\text{Cl}$ (**6**) as a yellow oil. Anal. Calcd for $\text{C}_{17}\text{H}_{25}\text{WO}_3\text{GeCl}$: C, 35.87; H, 4.43. Found: C, 36.21; H, 4.32. ^1H NMR (C_6D_6): 0.94 (m, 6H, Bu), 1.44 (m, 12H, Bu), 3.40 (s, 2H, CH_2), 4.66 (s, 5H, C_5H_5). ^{13}C NMR (C_6D_6): 13.9, 19.9, 26.8, 29.1 (Bu), 34.8 (CH_2), 88.5 (C_5H_5), 216.1, 219.7 (CO). IR (ν CO, cm^{-1} , hexanes): 2003, 1928, 1907.

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{GeMe}_2\text{Cl}$ (1a**).** A solution of 100 mg of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{GeMe}_2\text{CH}_2\text{Cl}$ in 1 mL of C_6D_6 was degassed and sealed in an NMR tube. The NMR tube was placed in an oil bath at a temperature of 90–100 °C, and the progress of the reaction was followed by ^{13}C NMR. After 16 h the reaction was completed and the spectroscopic data indicated the quantitative formation of the rearranged product, 91% yield (0.9 g, 2.7 mmol). The photolysis of $\text{FpGeMe}_2\text{CH}_2\text{Cl}$ in a sealed NMR tube for 48 h also afforded the rearranged compound in an 80% yield along with some decomposition. Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{FeO}_2\text{GeCl}$: C, 36.49; H, 3.98. Found: C, 36.81; H, 3.84. ^1H NMR (C_6D_6): 0.65 (s, 6H, Me), 0.23 (s, 2H, CH_2), 4.04 (s, 5H, C_5H_5). ^{13}C NMR (C_6D_6): -16.8 (CH_2), 6.6 (Me), 84.9 (C_5H_5), 216.7 (CO). IR (ν CO, cm^{-1} , hexanes): 2017, 1965.

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{GeBu}_2\text{Cl}$ (2a**).** Compound **2a** was obtained in the same manner as **1a** as a red oil in a 95% yield. ^1H NMR (C_6D_6): 0.26 (s, 2H, CH_2), 0.92 (t, 6H, Bu), 1.16–1.60 (m, 12H, Bu), 4.19 (s, 5H, C_5H_5). ^{13}C NMR (C_6D_6): -20.6 (CH_2), 13.9, 21.7, 26.3, 26.9 (Bu), 85.2 (C_5H_5), 215.0 (CO). IR (ν CO, cm^{-1} , THF): 2015, 1963. Elemental analysis could not be performed due to continuous decomposition of the compound, which was used immediately upon formation.

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{CH}_2\text{GeBu}_2\text{Cl}$ (6a**).** A solution of 100 mg of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{GeBu}_2\text{CH}_2\text{Cl}$ (**6**) in 1 mL of C_6D_6 was degassed and sealed in an NMR tube. The photochemical (350 nm) treatment of this solution resulted in the quantitative formation of the rearranged product (**6a**). ^1H NMR (C_6D_6): 0.57 (s, 2H, CH_2), 0.95 (m, 6H, Bu), 1.44 (m, 12H, Bu), 4.57 (s, 5H, C_5H_5). ^{13}C NMR (C_6D_6): -34.8 (CH_2), 13.9, 22.5, 26.3, 26.9 (Bu), 88.5 (C_5H_5), 218.1, 229.4 (CO). IR (ν CO, cm^{-1} , hexanes): 2021, 1937, 1926. As with **2a**, elemental analysis was unsuccessful, and the material was used immediately upon formation.

Synthesis of $(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{CH}_2\text{GeMe}_2$ (7**).** In a 50 mL round-bottomed Schlenk flask was placed 0.6 g (1.8 mmol) of either $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{GeMe}_2\text{CH}_2\text{Cl}$ (**1**) or $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{GeMe}_2\text{Cl}$ (**1a**) in 10 mL of THF. To this solution at -25 °C was added 1.5 mL (1.9 mmol) of freshly prepared LDA in the same solvent via cannula. The color of the reaction solution immediately changed from red to dark brown. The solution was stirred for 30 min at low temperature and for 2 h at room temperature, and the formation of **7** was monitored by ^{13}C NMR spectroscopy. After that, the solvent was removed from the reaction mixture under vacuum and the product was extracted with hexanes. The NMR spectral data indicated the formation of the metallacycle **7**. ^1H NMR (CDCl_3): -1.53 (2H, s, CH_2), 0.41 (3H, s, Me), 4.86 (t, J = 1.5 Hz, 2H, C_5H_4), 5.13 (t, J = 1.5 Hz, 2H, C_5H_4). ^{13}C NMR (CDCl_3): -52.6 (CH_2), -1.14, (Me), 82.7 (ipso), 85.6, 92.5 (C_5H_4), 217.9 (CO). IR (ν CO, cm^{-1} , hexanes): 1957, 2009. Purification and elemental analysis of **7** could not be done due to continuous ring-

opening behavior, which eventually led to the formation of **7a** in quantitative yield. The solution of **7** in THF transformed into **7a** at low temperature (0 °C) after ~24–48 h. The purification of the polymer **7a** was done by repeated precipitation of a THF solution into hexanes. The spectroscopic data indicated the formation of polymer **7a** in 70% yield. ^1H NMR (CDCl_3): 0.11 (2H, CH_2), 0.36 (6H, GeMe_2), 4.3–4.8 (4H, C_5H_4). ^{13}C NMR (CDCl_3): -22.1 (CH_2), 84.7 (ipso, C_5H_4), 87.8, 91.2 (C_5H_4), 217.7 (CO). IR (ν CO, cm^{-1} , THF): 1999, 1943. GPC in THF: M_w = 2563, M_n = 2263, PDI (M_w/M_n) = 1.13.

Synthesis of $(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{CH}_2\text{GeBu}_2$ (8**).** Complex **8** was synthesized as described above by treatment of either $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{GeBu}_2\text{CH}_2\text{Cl}$ or $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{GeBu}_2\text{Cl}$ with freshly prepared LDA. After removal of the solvent the red-brown residue was extracted with hexanes and filtered on Celite. Evaporation of the solvent yielded the pure stable germametallacycle (**8**) as a red oil (70% yield). Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{FeO}_2\text{Ge}$: C, 42.44; H, 6.63. Found: C, 42.10; H, 6.55. ^1H NMR (CDCl_3): -1.21 (s, 2H, CH_2), 0.97–1.4 (m, 18H, Bu), 4.56, 4.64 (m, 4H, C_5H_4). ^{13}C NMR (C_6D_6): -54.4 (CH_2), 13.9, 15.1, 26.5, 27.1 (Bu), 75.4, 86.4, 92.6 (C_5H_4), 218.5 (CO). IR (ν CO, cm^{-1} , hexanes): 1999, 1947. The germametallacycle was stored at low temperature (0 °C) for 30 days, and after this time the spectroscopic data indicated the transformation of the metallacycle into the corresponding polymer (**8a**). ^1H NMR (CDCl_3): 0.11 (s, 2H, CH_2), 0.95–1.40 (m, 18H, Bu), 4.67–4.81 (m, 4H, C_5H_4). ^{13}C NMR (CDCl_3): -26.1 (CH_2), 13.7, 16.3, 26.6, 27.5 (Bu), 83.0 (ipso), 88.7, 91.2 (C_5H_4), 217.8 (CO). IR (ν CO, cm^{-1} , THF): 1997, 1943. GPC in THF: M_w = 5452, M_n = 2526, PDI (M_w/M_n) = 2.1.

Synthesis of $(\eta^5\text{-C}_5\text{H}_4)\text{Mo}(\text{CO})_3\text{CH}_2\text{GeR}_2$ [R** = Me (**9**), **n**-Bu (**10**)] and $(\eta^5\text{-C}_5\text{H}_4)\text{W}(\text{CO})_3\text{CH}_2\text{GeR}_2$ [**R** = Me (**11**), **n**-Bu (**12**)].** The above compounds were synthesized in the same

manner, and the preparation of $(\eta^5\text{-C}_5\text{H}_4)\text{Mo}(\text{CO})_3\text{CH}_2\text{GeMe}_2$ (**9**) is described as a representative example. In a 50 mL round-bottomed Schlenk flask was placed 1.0 g (2.52 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{GeMe}_2\text{CH}_2\text{Cl}$ in 20 mL of THF. To this solution at -25 °C was added 1.5 mL (2.6 mmol) of freshly prepared LDA in the same solvent via cannula. The color of the reaction solution immediately changed from a light yellow to dark red. The solution was stirred for 30 min at low temperature and overnight at room temperature. After removal of the solvent, the brown residue was extracted with hexanes and filtered on Celite. Evaporation of the hexanes yielded a pink solid material along with some decomposed material. After recrystallization from hexanes, 0.72 g (80%) of light pink crystals were obtained. Spectroscopic data indicated the

formation of $(\eta^5\text{-C}_5\text{H}_4)\text{Mo}(\text{CO})_3\text{CH}_2\text{GeMe}_2$ with no evidence of a ring-opening polymerization. This metallacycle was stored under nitrogen for several days, and no decomposition was observed. Mp: 66 °C. Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{MoO}_3\text{Ge}$: C, 36.62; H, 3.35. Found: C, 36.45; H, 3.50. ^1H NMR (C_6D_6): -1.21 (s, 2H, CH_2), 0.16 (s, 6H, Me), 4.71–5.00 (m, 4H, C_5H_4). ^{13}C NMR (C_6D_6): -51.9 (CH_2), -1.20 (Me), 80.5, 94.3, 95.9 (C_5H_4), 228.2, 239.5 (CO). IR (ν CO, cm^{-1} , hexanes): 2018, 1945, 1934.

(η^5 -C₅H₄)Mo(CO)₃CH₂GeBu₂ (**10**): yellow oil, 0.7g (87%). Anal. Calcd for C₁₇H₂₄MoO₃Ge: C, 45.89; H, 5.44. Found: C, 45.78; H, 5.40. ¹H NMR (C₆D₆): δ -1.19 (s, 2H, CH₂), 0.84–0.91 (m, 12H, Bu), 1.31–1.36 (m, 6H, Bu), 4.77 (t, *J* = 1.8 Hz, 2H, C₅H₄), 5.11 (t, *J* = 1.8 Hz, 2H, C₅H₄). ¹³C NMR (C₆D₆): -54.2 (CH₂), 13.9, 15.1, 26.4, 26.8 (Bu), 79.5, 94.5, 96.5 (C₅H₄), 228.3, 239.5 (CO). IR (ν CO, cm⁻¹, hexanes): 2017, 1943, 1932.

(η^5 -C₅H₄)W(CO)₃CH₂GeMe₂ (**11**): yellow solid, mp 98 °C (82%). Anal. Calcd for C₁₁H₁₂WO₃Ge: C, 29.45; H, 2.70. Found: C, 29.32, 2.63. ¹H NMR (C₆D₆): 0.99 (s, 2H, CH₂), 0.12 (s, 6H, Me), 4.63, 5.07 (m, 4H, C₅H₄). ¹³C NMR (C₆D₆): -64.2 (CH₂), -1.20 (Me), 83.9, 92.1, 94.3 (C₅H₄), 217.6, 222.2 (CO). IR (ν CO, cm⁻¹, hexanes): 2015, 1936, 1926.

(η^5 -C₅H₄)W(CO)₃CH₂GeBu₂ (**12**): yellow oil (77%). Anal. Calcd for C₁₇H₂₄WO₃Ge: C, 38.32; H, 4.54. Found: C, 38.29; H, 4.30. ¹H NMR (CDCl₃): -0.93 (s, 2H, CH₂), 0.74–0.93 (m, 12H, Bu), 1.25–1.39 (m, 6H, Bu), 4.67 (t, *J* = 1.5 Hz, 2H, C₅H₄), 5.17 (t, *J* = 1.8 Hz, 2H, C₅H₄). ¹³C NMR (C₆D₆): -66.7 (CH₂), 12.5, 15.1, 26.3, 26.6 (Bu), 82.9, 92.3, 94.9 (C₅H₄), 217.7, 229.3 (CO). IR (ν CO, cm⁻¹, hexanes): 2014, 1935, 1924.

Synthesis of (η^5 -C₅H₄)Mo(CO)₂(Ph₃P)CH₂GeMe₂ (9a**) and (η^5 -C₅H₄)W(CO)₂(Ph₃P)CH₂GeMe₂ (**11a**).** To 0.5 mL of a THF solution of **9** or **11** (1.0 mmol) in a NMR tube was added (1.10 mmol) PPh₃, and the contents were degassed twice by freeze–thaw cycles. The solution was then heated at 100 °C for ~48 h. After completion of the reaction the solvent was removed under vacuum. The solid material obtained was extracted with hexanes and

recrystallized from a benzene/hexanes mixture to yield **9a** or **11a** as an orange solid compound in 70% yield.

(η^5 -C₅H₄)Mo(CO)₂(Ph₃P)CH₂GeMe₂ (**9a**): orange solid, mp 131–132 °C (72%). Anal. Calcd for C₂₈H₂₇MoO₂GeP: C, 56.45; H, 4.70. Found: C, 56.52; H, 4.57. ¹H NMR (C₆D₆): -0.30 (s, 2H, CH₂), 0.42 (s, 6H, Me), 4.40, 5.55 (m, 4H, C₅H₄), 7.10–7.90 (15H, Ph). ¹³C NMR (C₆D₆): -47.2 (d, CH₂, ²*J*_{P-C} = 7.6 Hz), 0.81 (Me), 89.6, 93.4, 94.9 (C₅H₄), 128.1, 130.9, 131.9, 132.8 (Ph), 228.6 (d, CO, ²*J*_{P-C} = 16.5 Hz). ³¹P NMR (C₆D₆): 42.7. IR (ν CO, cm⁻¹, THF): 1920(vs), 1843(s).

(η^5 -C₅H₄)W(CO)₂(Ph₃P)CH₂GeMe₂ (**11a**): orange solid, mp 145–148 °C (70%). Anal. Calcd for C₂₈H₂₇WO₂GeP: C, 49.20; H, 4.10. Found: C, 49.24; H, 3.98. ¹H NMR (C₆D₆): -0.26 (s, 2H, CH₂), 0.49 (s, 6H, Me), 4.43, 5.58 (m, 4H, C₅H₄), 7.12–7.87 (15H, Ph). ¹³C NMR (C₆D₆): -57.6 (d, CH₂, ²*J*_{P-C} = 7.3 Hz), -1.10 (Me), 81.6, 92.2, 94.2 (C₅H₄), 128.7, 132.3, 133.9, 138.2 (Ph), 228.6 (d, CO, ²*J*_{P-C} = 16.0 Hz). ³¹P NMR (C₆D₆): 42.7 (¹*J*_{W-P} = 262.0 Hz). IR (ν CO, cm⁻¹, THF): 1918 (vs), 1847 (s).

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Supporting Information Available: Crystallographic data in CIF format (CCDC no. 670931 (for **9**) and 670932 (for **11**)). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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