Construction of Heterobimetallics Bridged by (Oxyalkyl)phosphines: Syntheses of *trans*-$Me_2Ta(\mu\text{-}CH_2)(\mu\text{-}OCMe_2CH_2Ph_2P)_2PtMe$ and $(TMEDA)\overline{Ta(\mu\text{-}CH_2)(\mu\text{-}Me)(\mu\text{-}OCMe_2CH_2Ph_2P)_2Ni}$

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Precursors to potentially bridging (oxyalkyl)phosphine ligands, μ-$OCR_2(CH_2)_nPh_2P$ ($R = {}^tBu$, $n = 1$; $R = Me$, $n = 1, 2$), were synthesized through the addition of $LiCH_2PPh_2{\cdot}TMEDA$ and $LiPPh_2$ to ${}^tBu_2C{=}O$ and $Me_2\overline{CCH_2O}$. Treatment of $ZrCl_4$ with 2.0 equiv of $LiOC{}^tBu_2CH_2Ph_2P{\cdot}x$THF provided $(Ph_2PCH_2C{}^tBu_2O)_2ZrCl_2$ (**1**), which could be alkylated with MeLi to generate pseudo-O_h *trans*-$(Ph_2PCH_2C{}^tBu_2O)_2ZrMe_2$ (**2**) and with ${}^tBuCH_2Li$ to give pseudo-T_d $(Ph_2PCH_2C{}^tBu_2O)_2Zr(CH_2{}^tBu)_2$ (**3**). The fluxional, five-coordinate tris(alkoxide) $(Ph_2PCH_2C{}^tBu_2O)_2\overline{Zr(OC{}^tBu_2CH_2Ph_2P})Cl$ (**4**), prepared from **1** and $LiOC{}^tBu_2CH_2Ph_2P{\cdot}x$THF, was methylated to afford four-coordinate $(Ph_2PCH_2C{}^tBu_2O)_3ZrMe$ (**5**). No heterobimetallics were produced when **1**–**5** were exposed to several substitutionally labile late-metal complexes. The ^{t}Bu groups apparently place severe conformational contraints on the potential bridging ligands. Alcoholysis of $Zr(CH_2Ph)_4$ by $HOCMe_2(CH_2)_2Ph_2P$ provided $(Ph_2P(CH_2)_2CMe_2O)_2Zr(CH_2Ph)_2$ (**6**) and $(Ph_2P(CH_2)_2CMe_2O)_4Zr$ (**7**), which was shown to conproportionate with $Zr(CH_2Ph)_4$ to give **6**. Complex mixtures were obtained when **6** was utilized in the preparation of heterobimetallics. Metathesis of Me_3TaCl_2 with 2 equiv of $LiOCMe_2CH_2Ph_2P$ afforded $(PPh_2CH_2CMe_2O)_2TaMe_3$ (**8**). Treatment of $(COD)PtMe_2$ with **8** produced *trans*-$Me_2Ta(\mu\text{-}CH_2)(\mu\text{-}OCMe_2CH_2Ph_2P)_2PtMe$ (**10**, 21%) via thermolysis of an intermediate oligomer, $([-(Me)_3Ta(\mu\text{-}OCMe_2CH_2Ph_2P)Pt(Me)_2PPh_2CH_2CMe_2O-]_n)_{1/n}$ (**9**). Similarly, $(TMEDA)NiMe_2$ and **8** yielded $(TMEDA)\overline{Ta(\mu\text{-}CH_2)(\mu\text{-}Me)(\mu\text{-}OCMe_2CH_2Ph_2P)_2Ni}$ (**11**, 30%). During the formation of **10** and **11**, bimetallic Me/Me exchange reactions were prevalent, as shown via labeling experiments and isotopic shifts observed in the $^{195}Pt\{^1H\}$ NMR spectra of **10**-d_n, a mixture of isotopomers prepared from $(CD_3)_3TaCl_2$ (**8**-d_9). Plausible mechanisms rationalizing the generation of the μ-CH_2 and μ-CH_3 ligands of **10** and **11** are also discussed.

Introduction

In order to model the structure and reactivity of heterogeneous catalysts containing disparate metals, heterobimetallic complexes containing (oxyalkyl)phosphine bridging ligands have been prepared and investigated.[1-4] For example, $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_2(\mu_2\text{-}\eta^2\text{-}O{=}CMe)(\mu\text{-}Cl)RhCO$ ($Cp^* = \eta^5\text{-}C_5Me_5$) releases acetaldehyde[2,3] when protonated, akin to Rh/ZrO_2[5] and other C_2-oxygenate selective[6] Fischer–Tropsch catalysts.[7] *cis*-$Cp^*MeZr(\mu\text{-}O(CH_2)_nPh_2P)_2PtMe_2$ ($n = 1, 2$) exhibits intermolecular and intramolecular Me/Me exchange processes,[4,8-10] suggesting that the migration of alkyl groups on surfaces occurs with equal facility. In addition, the Zr–Rh bond of $Cp^*\overline{Zr(\mu\text{-}OCH_2Ph_2P)_2Rh}Me_2$ is exceedingly short (2.444 (1) Å), indicative of pronounced $Rh(d\pi){\rightarrow}Zr(d\pi)$ bonding (~50%) that supplements the σ bond.[3,11] Similar molecular interactions may provide the basis for strong metal–support interactions (SMSI)[12,13] observed in partially reduced metal oxide/late-metal catalysts.

Although the μ-OCH_2Ph_2P compounds proved to be interesting models of several heterogeneous systems, some limitations of the three-atom bridge became apparent. For example, the μ-OCH_2Ph_2P linkage in $Cp^*\overline{Zr(\mu\text{-}OCH_2Ph_2P)_2Rh}Me_2$ appears to prevent closer contact of the disparate metal centers.[3] Reasoning that flexible four-atom bridges would permit greater interaction between early and late metals, a brief survey of lengthier bridges was undertaken to obtain a more fundamental understanding of the factors governing the synthesis of (oxyalkyl)phosphine-bridged binuclears. With Zr and Ta as the early

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[†] Alfred P. Sloan Foundation Fellow, 1987–1989.

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metals, complexes containing $-OCR_2(CH_2)_nPh_2P$ (R = ${}^tBu$, $n = 1$; R = Me, n = 1, 2) were prepared and applied as reagents toward the construction of heterobimetallics. Alkyl substitution at C1 was considered necessary to circumvent oligomerization of the early-metal moieties via μ-alkoxide bridges. Reported herein are these studies, including the synthesis of Ta/Pt and Ta/Ni complexes containing μ-CH_2 and μ-CH_3 fragments; these hydrocarbon residues are believed to exist on the surface of Fischer–Tropsch catalysts.[14-18]

Results and Discussion

Bridging-Ligand Syntheses. Nucleophilic addition of $LiCH_2Ph_2P\cdot TMEDA$[19] to di-*tert*-butyl ketone provided $LiOC^tBu_2CH_2Ph_2P\cdot x THF$ (eq 1, 94%), a potential (oxyalkyl)phosphine bridging ligand with *tert*-butyl groups adjacent to oxygen. The lithium alkoxide typically

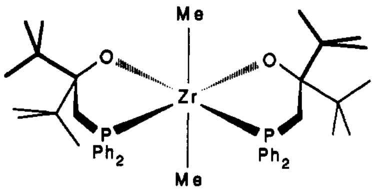
$$LiCH_2PPh_2\cdot TMEDA + {}^tBu_2C{=}O \xrightarrow[-TMEDA]{THF} LiOC^tBu_2CH_2Ph_2P\cdot xTHF \quad (1)$$

crystallized from hexane/THF with ~0.5 equiv of THF per lithium, but repeated recrystallizations from hexane resulted in material containing considerably less THF. Colorless $LiOC^tBu_2CH_2Ph_2P\cdot x THF$ is very soluble in Et_2O, THF, and aromatic hydrocarbons but only slightly soluble in hexane or pentane. Its ${}^{31}P\{^1H\}$ NMR spectrum consisted of a somewhat broad singlet at δ −17.07.

Ring opening of isobutylene oxide with $LiPPh_2$ or $LiCH_2PPh_2\cdot TMEDA$[19] followed by quenching and organic workup afforded the (hydroxyalkyl)phosphines $HOCMe_2CH_2Ph_2P$ (eq 2, 63%) and $HOCMe_2CH_2CH_2Ph_2P$ (eq 3, 44%), respectively. Dehydration of the alcohols frequently occurred to yield byproduct olefins, typically ~10–20%, that were conveniently removed via chromatography. Despite attempts to further purify $HOCMe_2CH_2Ph_2P$, it could only be isolated as a colorless oil. In contrast, $HOCMe_2CH_2CH_2Ph_2P$ slowly crystallized upon standing and could be recrystallized from hexane. Deprotonation of $HOCMe_2CH_2Ph_2P$ with lithium tetramethylpiperidide (LiTMP) in THF gave $LiOCMe_2CH_2Ph_2P$, which could be isolated solvent-free as a white powder in good yield (78%):

$$LiPPh_2 + Me_2\overline{CCH_2O} \xrightarrow[(2)\ H^+/H_2O/C_6H_6]{(1)\ THF} HOCMe_2CH_2Ph_2P \quad (2)$$

$$LiCH_2PPh_2\cdot TMEDA + Me_2\overline{CCH_2O} \xrightarrow[(2)\ H^+/H_2O/C_6H_6]{(1)\ THF,\ -TMEDA} HOCMe_2CH_2CH_2Ph_2P \quad (3)$$



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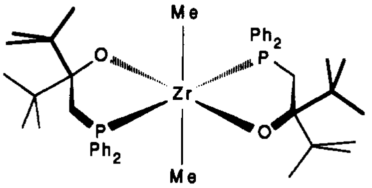

B

Figure 1. Possible structures for $(Ph_2\overline{PCH_2C^tBu_2O)_2Zr}Me_2$ (**2**).

$$HOCMe_2CH_2Ph_2P + LiTMP \xrightarrow[-TMPH]{THF} LiOCMe_2CH_2Ph_2P \quad (4)$$

Early-Metal Complexes of $-OC^tBu_2CH_2Ph_2P$. Zirconium was chosen as a suitable metal to survey the stability and utility of $-OC^tBu_2CH_2Ph_2P$, partly because of the precedent set in related studies of the comparably bulky ${}^tBu_3CO^-$ (tritox) ligand.[20] Treatment of $ZrCl_4$ with 2.0 equiv of $LiOC^tBu_2CH_2Ph_2P$ in Et_2O provided $(Ph_2\overline{PCH_2C^tBu_2O)_2Zr}Cl_2$ (**1**, eq 5) in 80% yield after precipitation from hexane. The monomeric dichloride **1** is very soluble in benzene and toluene but only slightly soluble in hexane, from which it can be recrystallized. In contrast to $(tritox)_2ZrCl_2$, which decomposes in benzene solution over a 24-h period at 25 °C, **1** is quite robust, withstanding thermolysis at 100 °C in benzene for several days.

$$ZrCl_4 + 2LiOC^tBu_2CH_2Ph_2P\cdot xTHF \xrightarrow[-2LiCl]{Et_2O} \underset{\mathbf{1}}{(Ph_2\overline{PCH_2C^tBu_2O)_2Zr}Cl_2} \quad (5)$$

Alkylation of $(Ph_2\overline{PCH_2C^tBu_2O)_2Zr}Cl_2$ (**1**) with 2 equiv of MeMgBr in Et_2O afforded the dimethyl derivative $(Ph_2\overline{PCH_2C^tBu_2O)_2Zr}Me_2$ (**2**, eq 6) in 90% yield. The ${}^1H$ NMR spectrum of **2** exhibited a triplet for the ZrMe

$$\underset{\mathbf{1}}{(Ph_2\overline{PCH_2C^tBu_2O)_2Zr}Cl_2} + 2MeMgBr \xrightarrow[-2MgBrCl]{Et_2O} \underset{\mathbf{2}}{(Ph_2\overline{PCH_2C^tBu_2O)_2Zr}Me_2} \quad (6)$$

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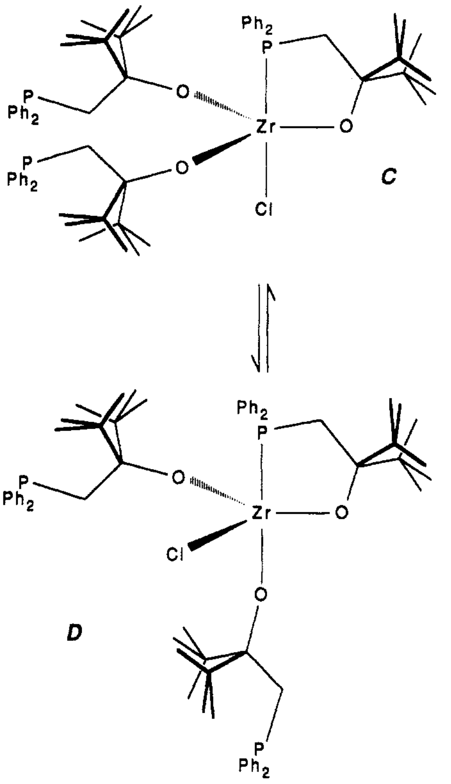

Figure 2. Possible structures for $(Ph_2PCH_2C^tBu_2O)_2Zr(OC^tBu_2CH_2Ph_2P)Cl$ (4).

groups (δ 0.81, $J = 4.2$ Hz), consistent with chelation of the (oxyalkyl)phosphine ligands.[21,22] The $^{31}P\{^1H\}$ spectrum consisted of a single resonance at δ −9.78, significantly downfield from the region in which ligands with free phosphine groups were observed, and ^1H and $^{13}C\{^1H\}$ NMR spectra supported the existence of a mirror plane. Assuming octahedral geometry, the data requires a trans arrangement of the two ZrMe groups, but the orientation of the chelates is ambiguous, with either of the structures in Figure 1 being possible. Structure A is tentatively preferred from electronic arguments, because it places the two alkoxides at 90° to one another, thereby maximizing π-donation.[22] On steric grounds, B lacks the cis diphenylphosphine stereochemistry and must be favored, although conformers that minimize Ph–Ph interactions are available to the octahedron of A.

The $^{31}P\{^1H\}$ NMR spectrum of dichloride 1 exhibited a single resonance at δ −2.78, also indicative of coordinated phosphines. As a consequence of the *gem*-dialkyl effect,[23] the formation of five-membered chelate rings[24] in both 1 and 2 is encouraged by the presence of the bulky *tert*-butyl groups. Chelation via phosphine binding necessitates a reduction of the Zr–O–C angles, which are nearly linear in tritox compounds,[20,21] thus reducing the ability of each oxygen to donate a second lone pair into an otherwise empty Zr orbital. Formally, $(Ph_2PCH_2C^tBu_2O)_2ZrCl_2$ (1) may be considered a thermally stable 16e complex, akin to Cp_2ZrCl_2, with a considerably less electrophilic Zr center than that of $(tritox)_2ZrCl_2$. The near-linear Zr–O–C angles of the latter (cf. $(tritox)_2ZrCl_3 \cdot Li(OEt_2)_2$) encourage the maximum $O(p\pi)$–$Zr(d\pi)$ donation, thereby inducing a pronounced instability ascribed to the heterolysis of the $^tBu_3C$–O bonds.[21]

Since the ultimate goal in this project involved the generation of potentially bridging (oxyalkyl)phosphines, the tendency toward chelation was clearly unproductive. Reasoning that the steric constraints in the above compounds were not sufficiently demanding to preclude binding of a rather bulky PPh_2R unit to the zirconium, additional crowding at the metal was sought via the introduction of neopentyl groups. Treatment of 1 with 2 equiv of $LiCH_2{}^tBu$ in benzene afforded white, crystalline $(Ph_2PCH_2C^tBu_2O)_2Zr(CH_2{}^tBu)_2$ (3, eq 7) in 80% yield.

$$\underset{1}{(Ph_2PCH_2C^tBu_2O)_2ZrCl_2} + LiCH_2{}^tBu \xrightarrow[-2LiCl]{C_6H_6} \underset{3}{(Ph_2PCH_2C^tBu_2O)_2Zr(CH_2{}^tBu)_2} \quad (7)$$

The $CH_2{}^tBu$ resonance in the ^1H NMR spectrum was a sharp singlet, and the unbound nature of the phosphines was corroborated by an upfield resonance in the $^{31}P\{^1H\}$ spectrum (δ −17.29).

Steric saturation was also achieved by the addition of a third bulky alkoxide group to the coordination sphere. Treatment of dichloride 1 with 1.0 equiv of $LiOC^tBu_2CH_2Ph_2P \cdot xTHF$ produced $(Ph_2PCH_2C^tBu_2O)_3ZrCl$ (4, eq 8), but the reaction required heating to ~65 °C for 6 h. Somewhat surprisingly, given the aforementioned precedent of ligand C–O bond degradation,[21] no decomposition of 4 was seen upon thermolysis in C_6D_6 at ~100 °C for >2 weeks, perhaps indicating that some phosphine coordination was still plausible (vide infra). Alternatively, the coordination of three alkoxides may be sufficient to lower the electrophilicity of the Zr center. It is interesting that both bis- and tris-$OC^tBu_2CH_2Ph_2P$ derivatives could be conveniently prepared via straightforward metathetical procedures. Controlling the stoichiometry of alkoxide[25] and amide[26] addition to $ZrCl_4$ has at times proven difficult.

$$\underset{1}{(Ph_2PCH_2C^tBu_2O)_2ZrCl_2} + LiOC^tBu_2CH_2Ph_2P \cdot xTHF \xrightarrow[-LiCl]{C_6H_6} \underset{4}{(Ph_2PCH_2C^tBu_2O)_3ZrCl} \quad (8)$$

At 20 °C, the $^{31}P\{^1H\}$ NMR spectrum of 4 consisted of a single, slightly broadened resonance at ~δ −10, and the proton spectrum displayed a single peak for the ligand *tert*-butyl groups. When a toluene-d_8 solution of 4 was cooled, the ^{31}P resonance gradually broadened into the base line ($T_C = -43$ °C, $\Delta G^\ddagger = 10.1$ (5) kcal/mol) and then emerged as two broad resonances at δ 2 and −15 in an approximate 1:2 ratio, consistent with one chelated and two pendent phosphine groups. It became apparent that these signals could be assigned to an averaged structure, since further cooling (−80 °C) resulted in a set of comparatively sharp resonances at δ 3.9 and −5.0 due to bound phosphines and a set at δ −11.3, −15.4, and −16.5 resulting

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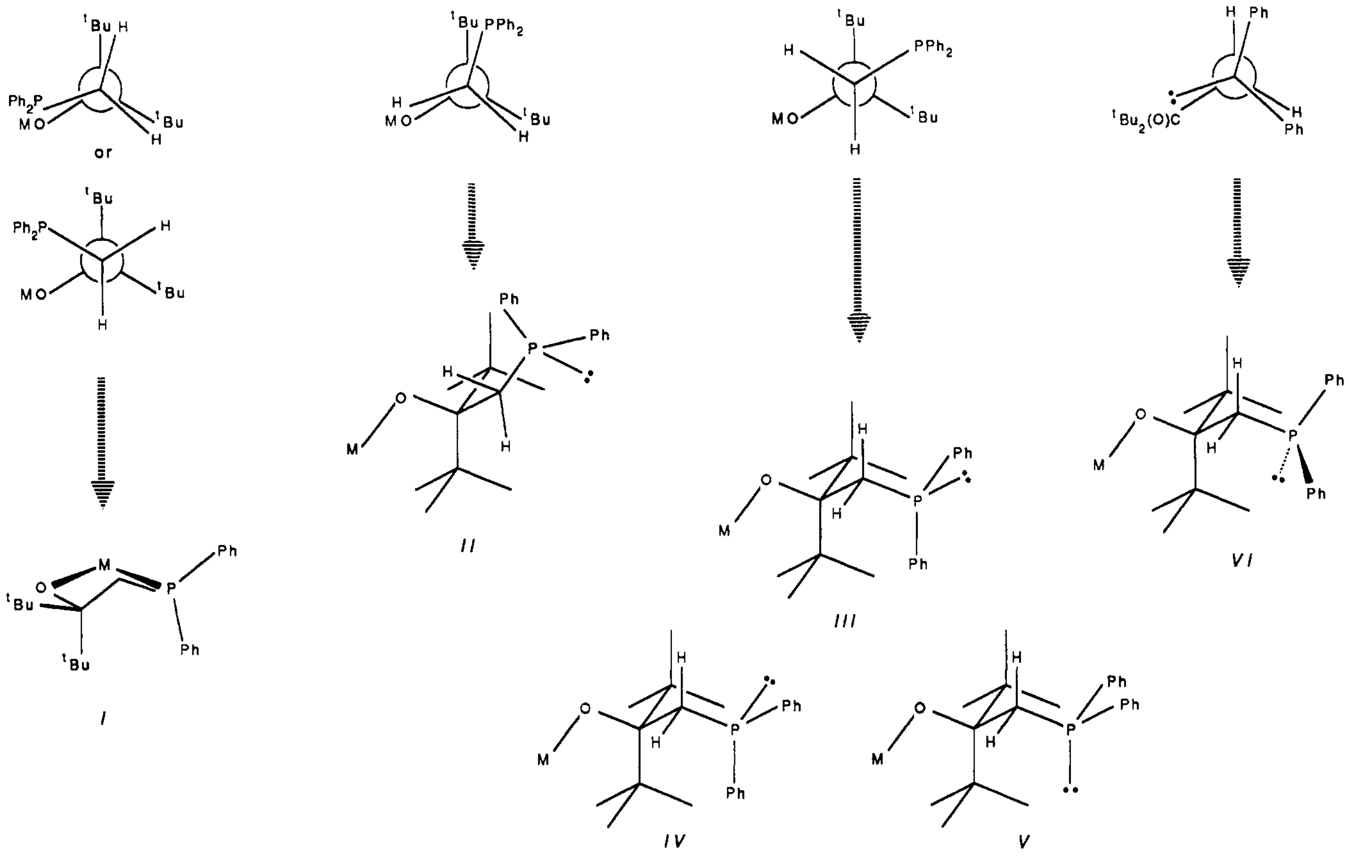

Figure 3. Conformers of MOC^{t}Bu$_2$CH$_2$Ph$_2$P based on the diamond lattice.

from unbound Ph$_2$RP units. At the lower temperature, a second dynamic process equilibrating separate isomers is apparently frozen out.[24,27] While the limited spectral data preclude definitive structural assignments, in combination with steric and electronic arguments, two limiting geometries are particularly appealing. Assuming a tbp conformation, a structure containing two pendent equatorial (oxyalkyl)phosphines and one chelated group with the alkoxide again equatorial (Figure 2, structure C) would maximize O(pπ)–Zr(dπ) bonding[28] and exhibit a 1:2 ratio of bound to unbound RPh$_2$P units. The remaining three resonances could correspond to a tbp structure in which the positions of one unbound RPh$_2$P group and the chloride were reversed (D). Note that the chemical shift at δ −5.0 would best correspond to a bound phosphine opposite an alkoxide (D), considering the arguments rationalizing the geometries of 1 and 2. Facile equilibration of C and D could occur via a turnstile process.

Alkylation of 4 with MeMgBr in Et$_2$O provided the methyl complex (Ph$_2$PCH$_2$C^{t}Bu$_2$O)$_3$ZrCH$_3$ (**5**, eq 9), which was isolated in 60% yield upon crystallization from diethyl ether. The methyl resonance in the ^{1}H NMR spectrum

$$\underset{\mathbf{4}}{(\mathrm{Ph_2PCH_2C^tBu_2O})_3\mathrm{ZrCl}} + \mathrm{MeMgBr} \xrightarrow[-\mathrm{MgBrCl}]{\mathrm{Et_2O}} \underset{\mathbf{5}}{(\mathrm{Ph_2PCH_2C^tBu_2O})_3\mathrm{ZrMe}} \quad (9)$$

appeared at δ 0.79 as a singlet, and the ^{31}P{^{1}H} NMR spectra of 5 indicated the phosphine groups to be pendent (δ −17.91). No change was observed upon cooling the sample to −80 °C. The tris-OC^{t}Bu$_2$CH$_2$Ph$_2$P compounds showed substantially lower solubility than the corresponding bis species, being only slightly soluble in Et$_2$O and virtually insoluble in aliphatic hydrocarbons.

Efforts to attach late metals to the phosphines of the above compounds were generally unsuccessful. Late-metal complexes containing easily displaced ligands (e.g., (COD)PtMe$_2$,[29] [(C$_2$H$_4$)$_2$RhCl]$_2$,[30] Ni(COD)$_2$,[31] (Et$_2$S)$_2$Pt(C$_2$O$_4$),[32] etc.) failed to react with any of the compounds discussed above, including those possessing free phosphines. Even the highly reactive, photochemically generated 14e species (Et$_3$P)$_2$Pt[32] did not react with (Ph$_2$PCH$_2$C^{t}Bu$_2$O)$_3$ZrCH$_3$ but preferentially attacked the CD$_2$Cl$_2$ solvent.

The reasons for the dramatic lack of reactivity of the phosphines in these complexes, especially those known to be unbound, are not obvious. It is possible that the large substituents on the ligand backbone place severe conformational constraints on the bridge. Figure 3 illustrates the potential problem with use of conformational arguments based on projection views and the diamond lattice. When the PPh$_2$ and MO functionalities are eclipsed, or if the interaction between phenyl and *tert*-butyl substituents is minimized by rotating into a staggered conformation such that PPh$_2$ and MO are gauche to each other, the formation of a chelate (I) is virtually assured. Alternatively, chelation may be attributed to the *gem*-dialkyl effect.[23] A different eclipsed geometry leads to a high-energy syn interaction between PPh$_2$ and ^{t}Bu groups (II), regardless of the Ph$_2$P orientation.

Chelation is prevented in a staggered configuration where the Ph$_2$P group is anti to MO, leading to consid-

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eration of three conformers differing in rotation about the P–CH_2 bond (i.e., the lowest energy rotamers indicated by the diamond lattice). Although the phosphorus lone pair in each is available for complexation, conformation III possesses two prominent 1,3-diaxial interactions (i.e., Ph/^{t}Bu) and rotamers IV and V each contain one of these destructive influences. In addition, the ^{t}Bu groups in IV and V eclipse a lone pair, thereby blocking the path of an electrophile. Rotation about the P–C bond such that the Ph substituents eclipse the methylene hydrogens places the phenyl groups anti to the $^tBu_2CO$ fragment (VI) but directs the lone pair between these bulky groups, hindering the formation of bridges to late-metal complexes. In other P–CH_2 rotamers of this type, a bulky phenyl group must reside between the ^{t}Bu moieties (not illustrated), a conformation that is clearly unfavorable on steric grounds. In conclusion, the most likely conformer that does not lead to chelation is VI, a geometry that *precludes* nucleophilic attack by the R_2P unit. Either other conformers are destabilized by severe steric interactions or the phosphine is similarly prevented from binding to another metal.

Early-Metal Complexes of $-OCMe_2(CH_2)_nPh_2P$ (n = 1, 2). Because of the problems encountered in trying to prepare heterobimetallic complexes containing the $-OC^tBu_2CH_2Ph_2P$ ligand, the *tert*-butyl groups of the difunctional ligand were replaced with less sterically demanding Me substituents. It was hoped that early-metal complexes containing more flexible (oxyalkyl)phosphines (e.g., $-OCMe_2CH_2Ph_2P$ and $-OCMe_2CH_2CH_2Ph_2P$) would be much less conformationally restricted and would readily form heterobimetallics.

In contrast to the clean metathetical reactions discussed in the previous section, various combinations of $LiOCMe_2CH_2Ph_2P$ and $ZrCl_4$ failed to yield any tractable products. Attempts to generate $(Ph_2PCH_2CMe_2O)_2ZrCl_2$ in situ at low temperatures and subsequently alkylate with MeMgBr to afford the dimethyl compound, presumed to be more stable, were also unsuccessful. The dichloride, if formed, must be dramatically less stable than $(Ph_2\overline{PCH_2C^tBu_2O})_2ZrCl_2$ (**1**). One possible explanation concerns elimination pathways available to alkoxides that possess γ-hydrogens. With ^{t}Bu groups present, the internal phosphine lone pair is directed away from the C–H bonds of the methylene and an attack by an external base at the CH_2 unit is blocked. This steric hindrance is greatly lessened when methyls replace ^{t}Bu groups, and Ph_2P: can now function as an internal base in aiding an elimination that has a large heterolytic component with respect to the C–O bond.

Alcoholysis reactions with metal alkyls provided an alternate entry into group 4 complexes. Although both alcohols $HOCMe_2(CH_2)_nPh_2P$ (n = 1, 2) were available, the crystalline nature of $HOCMe_2(CH_2)_2Ph_2P$ made it more convenient to use in these reactions. When $Zr(CH_2Ph)_4$[33] was treated with 2 equiv of $HOCMe_2(CH_2)_2Ph_2P$ in C_6D_6 at 25 °C, the ^{1}H NMR analysis initially showed a complex mixture of peaks, but after 5 h at 20 °C the mixture had conproportionated to a single product whose spectrum was consistent with the expected $(Ph_2PCH_2CH_2CMe_2O)_2Zr(Ch_2Ph)_2$ (**6**, eq 10). If 4 equiv of $HOCMe_2(CH_2)_2Ph_2P$

$$(CH_2Ph)_4Zr + 2HOCMe_2(CH_2)_2Ph_2P \xrightarrow{C_6D_6} \underset{\mathbf{6}}{(Ph_2P(CH_2)_2CMe_2O)_2Zr(CH_2Ph)_2} + 2C_7H_8 \quad (10)$$

was used, the initial spectrum showed the clean formation of the tetraalkoxide $(Ph_2P(CH_2)_2CMe_2O)_4Zr$ (**7**, eq 11).[34]

$$Zr(CH_2Ph)_4 + 4HOCMe_2(CH_2)_2Ph_2P \xrightarrow{C_6D_6} \underset{\mathbf{7}}{(Ph_2P(CH_2)_2CMe_2O)_4Zr} + 4C_7H_8 \quad (11)$$

$$\underset{\mathbf{7}}{(Ph_2P(CH_2)_2CMe_2O)_4Zr} + Zr(CH_2Ph)_4 \xrightarrow{C_6D_6} 2\underset{\mathbf{6}}{(Ph_2P(CH_2)_2CMe_2O)_2Zr(CH_2Ph)_2} \quad (12)$$

The ^{1}H NMR spectrum of **7** correlated with one of the major components in the initial mixture leading to **6**. In order to test the hypothesis that **7** was formed rapidly and then underwent conproportionation with the remaining $Zr(CH_2Ph)_4$, 1 equiv of $Zr(CH_2Ph)_4$ was added to a C_6D_6 solution of **7** (eq 12). The ^{1}H NMR spectrum was again initially complicated but after a few hours showed nearly quantitative formation of **6**. Evidence of similar conproportionations was obtained during the synthesis of $Cp^*MeZr(\mu\text{-}O(CH_2)_nPh_2P)_2PtMe_2$ (n = 1, 2).[4] Unfortunately, **6** reacted with late-metal substrates to give complex mixtures of products, but this general method continues to hold some promise as a synthetic strategy.

Treatment of Me_3TaCl_2[35] with 2 equiv of $LiOCMe_2CH_2Ph_2P$ in Et_2O at −78 °C afforded $(Ph_2PCH_2CMe_2O)_2Ta(CH_3)_3$ (**8**, eq 13) in ~60% yield as a pentane-soluble, light yellow oil. The ^{1}H NMR spectrum

$$Me_3TaCl_2 + 2LiOCMe_2CH_2Ph_2P \xrightarrow[-78\ ^\circ C]{Et_2O} \underset{\mathbf{8}}{(Ph_2PCH_2CMe_2O)_2TaMe_3} \quad (13)$$

of **8** displayed a singlet at δ 0.56, indicating equivalent Ta–CH_3 groups, probably a result of a rapidly rearranging five-coordinated structure.[23,27] The corresponding $^{31}P\{^1H\}$ spectrum consisted of a sharp resonance at δ −23.71, consistent with unbound phosphine groups. No sign of decomposition was observed after thermolysis in C_6D_6 at 105 °C for 1 month. This remarkably robust compound, with its pendent phosphines and more flexible chains, was deemed a likely candidate to form complexes with late metals.

Heterobimetallic Complexes Derived from $(PPh_2CH_2CMe_2O)_2Ta(CH_3)_3$ (8). Treatment of **8** with $(COD)PtMe_2$[29] in toluene (25 °C) led to the precipitation of a white, insoluble material, presumably having the empirical formula $Me_3Ta(\mu\text{-}OCMe_2CH_2Ph_2P)_2PtMe_2$. The liberation of COD was noted by ^{1}H NMR spectroscopy, and the elemental analysis is consistent with the above formulation. The insoluble nature of this material, even in polar solvents such as THF and CH_2Cl_2, suggested that it was a highly cross-linked oligomer (**9**) resulting from the random attachment of phosphine groups to platinum as shown in eq 14.

$$\underset{\mathbf{8}}{(PPh_2CH_2CMe_2O)_2TaMe_3} + (COD)PtMe_2 \xrightarrow[-COD]{C_7H_8,\ 25\ ^\circ C} \underset{\mathbf{9}}{(1/n)[-(Me)_3Ta(\mu\text{-}OCMe_2CH_2Ph_2P)Pt(Me)_2PPh_2CH_2CMe_2O-]_n} \quad (14)$$

Thermolysis of this insoluble material (**9**) in THF at 100 °C for 2–4 h resulted in the evolution of 1.1 (1) equiv of CH_4 (^{1}H NMR, IR), as measured by Toepler pump, and

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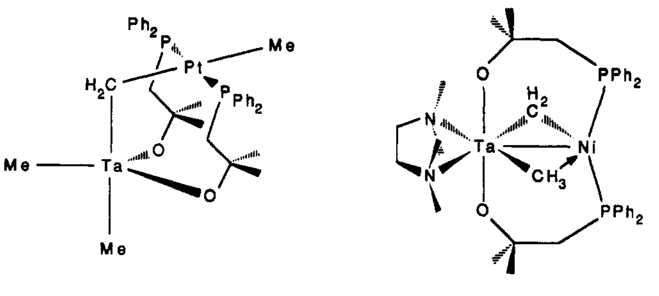

10 11

Figure 4. Plausible structures of *trans*-$Me_2Ta(\mu\text{-}CH_2)(\mu\text{-}OCMe_2CH_2Ph_2P)_2PtMe$ (10) and $(TMEDA)Ta(\mu\text{-}CH_2)(\mu\text{-}Me)(\mu\text{-}OCMe_2CH_2Ph_2P)_2Ni$ (11).

the formation of *trans*-$Me_2Ta(\mu\text{-}CH_2)(\mu\text{-}OCMe_2CH_2Ph_2P)_2PtMe$ (**10**, eq 15), which could be isolated from pentane in 21% yield as a yellow solid. Although the

$$\underset{\mathbf{9}}{(1/n)[\text{-}(Me)_3Ta(\mu\text{-}OCMe_2CH_2Ph_2P)\text{-}Pt(Me)_2PPh_2CH_2CMe_2O\text{-}]_n} \xrightarrow[2\text{-}4\ h]{THF,\ 100\ ^\circ C} \underset{\mathbf{10}}{trans\text{-}Me_2Ta(\mu\text{-}CH_2)(\mu\text{-}OCMe_2CH_2Ph_2P)_2PtMe} + CH_4 \qquad (15)$$

reaction proceeded in 70–80% yield by ^1H NMR spectroscopy, the high solubility of **10** hindered purification and isolation efforts. The isolated solid still contained ~5% unidentified impurities according to the ^1H NMR spectrum; the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were considerably cleaner.

Heterobimetallic *trans*-$Me_2Ta(\mu\text{-}CH_2)(\mu\text{-}OCMe_2CH_2Ph_2P)_2PtMe$ (**10**) was assigned a trans geometry about Pt on the basis of the large J_{PtP} value of 3050 Hz[36] and triplet resonances in the ^1H and $^{13}C\{^1H\}$ NMR spectra ascribed to $\mu\text{-}CH_2$ (^1H NMR δ 4.23, $J_{PH} = 8.6$ Hz, $J_{PtH} = 52$ Hz; $^{13}C\{^1H\}$ NMR δ 93.50, $J_{PC} = 4$ Hz, $J_{PtC} = 287$ Hz) and Pt–CH_3 (δ 0.25, $J_{PH} = 6.1$ Hz, $J_{PtH} = 54$ Hz; $^{13}C\{^1H\}$ NMR δ −0.06, $J_{PC} = 7.2$ Hz, $J_{PtC} = 474$ Hz) groups. Both signals were accompanied by ^{195}Pt satellites, and the $\mu\text{-}CH_2$ resonance falls into the expected chemical shift region of both homo- and heterobimetallic bridging methylene complexes.[37] Inequivalent Ta–CH_3 groups appeared at δ 0.64 and 1.18, and the bridging (oxyalkyl)phosphines displayed inequivalent Me substituents and diastereotopic methylenes. Variable-temperature NMR spectra taken up to 60 °C failed to reveal coalescence or broadening phenomena, in accord with a five-coordinate structure containing a rigid tridentate ligand that makes pseudorotation implausible (Figure 4). Equilibration of the axial and equatorial methyls would probably require dissociation of a Pt-bound phosphine. Although it is conceivable that the alkoxides are axial and the $\mu\text{-}CH_2$ and methyls equatorial, the former description is preferred on both steric and electronic grounds.[28]

The recently reported $(TMEDA)NiMe_2$[38] complex proved to be a valuable reagent for the construction of a related Ni/Ta heterobimetallic. Thermolysis (60 °C, 5 h) of a benzene solution containing $(Ph_2PCH_2CMe_2O)_2Ta(CH_3)_3$ (**8**) and $(TMEDA)NiMe_2$ provided $(TMEDA)Ta(\mu\text{-}CH_2)(\mu\text{-}Me)(\mu\text{-}OCMe_2CH_2Ph_2P)_2Ni$ (**11**, eq 16) in 30%

$$\underset{\mathbf{8}}{(Ph_2PCH_2CMe_2O)_2Ta(CH_3)_3} + (TMEDA)NiMe_2 \xrightarrow[60\ ^\circ C,\ 5\ h]{C_6H_6} CH_4 + C_2H_6 + \underset{\mathbf{11}}{(TMEDA)Ta(\mu\text{-}CH_2)(\mu\text{-}Me)(\mu\text{-}OCMe_2CH_2Ph_2P)_2Ni} \qquad (16)$$

yield. Upon completion of the reaction, Toepler pump measurements indicated that 1.1 (1) equiv of CH_4 and 0.9 (1) equiv of C_2H_6, identified via IR and NMR spectroscopy, had evolved. Inspection of the dark brown reaction mixture by ^1H NMR spectroscopy revealed that a considerable amount of TMEDA was present during the course of reaction, in part due to the pronounced thermal instability of $(TMEDA)NiMe_2$. In contrast to the case for **10**, the solubility of **11** in aliphatic hydrocarbons is low, and red crystals could be obtained from Et_2O.

The ^1H NMR spectrum of **11** revealed a triplet ($J_{PH} = 14$ Hz) at δ 5.71 for the $\mu\text{-}CH_2$ group and another triplet ($J_{PH} = 3.5$ Hz) at δ −0.39 for the $\mu\text{-}CH_3$, while inequivalent methyls and diastereotopic methylene units characterized the $\mu\text{-}OCMe_2CH_2Ph_2P$ ligands. Two discrete sets of TMEDA methyl groups are observed, consistent with a structure containing a mirror plane comprised of Ni, Ta, $\mu\text{-}CH_2$, $\mu\text{-}CH_3$, and the TMEDA backbone. Figure 4 illustrates this rigid molecule, formally depicting the intermetallic interaction as Ni^I/Ta^{IV}. An attractive alternative, predicated on viewing the $Ta{=}CH_2$ unit as an olefin, represents the metals as Ta^V and Ni^0, with the latter tetrahedrally coordinated by two $RPPh_2$ groups, $\mu\text{-}CH_3$, and the alkylidene. Note that the reaction of two coordinatively unsaturated molecules has resulted in a heterobimetallic in which both the early and late metals can be considered to have a full 18-electron count.

Bridging methylene complexes containing like metals are fairly common and have been the subject of an extensive review by Herrmann.[37] Heterobimetallic complexes in which the CH_2 unit bridges two disparate metal centers are relatively rare. Those reported have been prepared with use of the isolobal approach to heterobimetallic μ-CR and μ-CRR′ complexes pioneered by Stone.[39] This methodology is based on the premise that a M=CRR′ unit will react as an olefin. Bergman et al. synthesized $Cp_2(CH_3)Ta(\mu\text{-}CH_2)Pt(PMe_3)_2$ and paramagnetic $Cp_2Ta(\mu\text{-}CH_2)_2CoCp$ via the addition of $Cp_2(CH_3)Ta{=}CH_2$ to $(C_2H_4)Pt(PMe_3)_2$[40] and $CpCo(C_2H_4)_2$,[41] respectively. Thermolysis or photolysis of $Cp_2(CH_3)Ta(\mu\text{-}CH_2)Pt(PMe_3)_2$ led to the formation of $Cp_2Ta(\mu\text{-}CH_2)_2PtH(PMe_3)$,[40] and oxidation of $Cp_2Ta(\mu\text{-}CH_2)_2CoCp$ provided $[Cp_2Ta(\mu\text{-}CH_2)_2Co(NCMe)Cp]^+BF_4^-$.[41] Grubbs and coworkers prepared a series of heterobimetallic μ-methylene (e.g., $Ti(\mu\text{-}CH_2)M$, M = Rh, Ir, Pt, Au) and μ-methyl complexes[10,42,43] derived from reactions of the transiently generated methylene complex "$Cp_2Ti{=}CH_2$" with various late-metal compounds. For example, treatment of Cp_2

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Table I. Pertinent NMR Spectral Data (δ, J (Hz) for Representative Heterobimetallic μ-CH_2 and μ-CH_3 Complexes[a]

	δ_H	δ_C	$^1J_{CH}$	$^2J_{MH}$	$^1J_{MC}$
μ-CH_2 Compounds					
$Me_2Ta(\mu\text{-}CH_2)(\mu\text{-}OCMe_2CH_2Ph_2P)_2PtMe$ (**10**)	4.23	93.5	129	52	287
$(TMEDA)Ta(\mu\text{-}CH_2)(\mu\text{-}CH_3)(\mu\text{-}OCMe_2CH_2Ph_2P)_2Ni$ (**11**)	5.71	153.7	122	*b*	*b*
$Cp_2MeTa(\mu\text{-}CH_2)Pt(PMe_3)_2$[c]	4.09	103.6	*d*	21.3	466
$Cp_2Ta(\mu\text{-}CH_2)_2PtH(PMe_3)$[c]	5.17	95.0	*d*	31	352
	4.74	114.3	*d*	26	244
$Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Rh(COD)$[e]	7.48	186.5	128	0	20
$Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}CH_3)Rh(COD)$[f]	7.24	185.4	129	0	24
$Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Pt(Me)(SMe_2)$[e]	7.42	152.7	136	46.9	580
$Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Pt(Me)(PMe_2Ph)$[g]	8.09	179.2	136	39.3	409
$Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Me)Pt(Me)(PMe_2Ph)$[g]	7.92[h]	178.5	137	33.5	472
	7.42[i]	180.0	133	22.5	324
μ-CH_3 Compounds					
$(TMEDA)Ta(\mu\text{-}CH_2)(\mu\text{-}CH_3)(\mu\text{-}OCMe_2CH_2Ph_2P)_2Ni$ (**11**)	−0.39	40.7	115	*b*	*b*
20 °C[j]	−0.75				
−98 °C[j]	−3.00, 0.25[k]				
$Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}CH_3)Rh(COD)$[f] 25 °C	−3.13	49.7	114	0	29
−90 °C	−12.15 (t), 1.28 (d, J = 12.8 Hz)				
$Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Me)Pt(Me)(PMe_2Ph)$[g] 25 °C[h]	−3	47.6	115	*k*	381
−82 °C[h,l]	−12.4 (t), 1.20 (d)[k]				
25 °C[i]	−3	46.9	120	*k*	553
−82 °C[i,l]	−11.3 (t), 1.61 (d)[k]				

[a] In benzene-d_6 at 20 °C, referenced to Me_4Si (δ = 0) unless otherwise noted. [b] Not applicable. [c] Reference 40. [d] Not reported. [e] Reference 43. [f] Reference 10. [g] Reference 42. [h] PMe_2Ph trans to μ-CH_2. [i] Me trans to μ-CH_2. [j] In THF-d_8. [k] Indeterminate due to broadness. [l] In 3:1 Toluene-d_8/THF-d_8.

$TiCH_2CMe_2CH_2$ with $[(COD)RhCl]_2$ cleanly led to $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Rh(COD)$,[43] which was then methylated to generate $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}CH_3)Rh(COD)$.[10]

NMR spectral data pertaining to the μ-CH_2 bridge of *trans*-$Me_2Ta(\mu\text{-}CH_2)(\mu\text{-}OCMe_2CH_2Ph_2P)_2PtMe$ (**10**), $(TMEDA)Ta(\mu\text{-}CH_2)(\mu\text{-}Me)(\mu\text{-}OCMe_2CH_2Ph_2P)_2Ni$ (**11**), and comparable heterobimetallics are presented in Table I. Two extremes of bonding are typically considered for the μ-methylene ligand; one regards the bridge as a substituted alkyl with sp^3 hybridization (i.e., M–CH_2–M′, I), and the other treats M=CH_2 as an olefin (i.e., (η^2-M=CH_2)M′, II). The methylene CH coupling constants, usually considered a measure of hybridization, range from 122 to 137 Hz, but without a discernable pattern.[42,43] For example, the 122-Hz coupling constant for the Ta/Ni derivative (**11**) is less than the 129 Hz attributed to μ-CH_2 of the Ta/Pt complex (**10**), implicating greater sp^3 character in a case where less would be expected. The $^2J_{PtH}$ and $^1J_{PtC}$ values have been considered as alternative indicators,[43] but again a discrepancy arises. In **10**, the 287-Hz value for $^1J_{PtC}$ is substantially less than the related Pt–CH_3 coupling constant ($^1J_{PtC}$ = 474 Hz), suggesting a significant contribution from alkylidene resonance form II, but the $^2J_{PtH}$ value of 52 Hz is nearly identical with that of the Pt–CH_3 group ($^2J_{PtH}$ = 54 Hz). In the Ti/Pt complexes of Grubbs et al., the magnitudes of $^2J_{PtH}$ and $^1J_{PtC}$ tentatively corroborate the anticipated trans influence of Me > PR_3 > SR_2. When Me is trans to μ-CH_2 in $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Me)PtMe(PMe_2Ph)$, the alkylidene resonance form (II) appears to be of greater significance.[42]

The chemical shift data tend to cluster into two distinct groups. The Ta/Pt complexes exhibit proton shifts within δ 4.09–5.17, whereas the Ti/Pt(Rh) signals occur at markedly lower field (δ 7.24–8.09). Similarly, the carbon shifts of the former are in the δ 93.5–114.3 range, while the latter group again appears at lower field (δ 178.5–186.5). Two exceptions are found. The ^{13}C resonance for $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)PtMe(SMe_2)$ resides at δ 152.7, perhaps hinting at greater alkyl character in accord with the weak trans influence of SR_2. The Ta/Ni heterobimetallic has comparatively low field proton (δ 5.71) and carbon (δ 153.7) resonances in relation to those of the other Ta-containing molecules. These deviations may simply reflect the propensity of Ni to exist in lower formal oxidation states, hence favoing the alkylidene (II) resonance form. In terms of full resolution of the μ-CH_2 hybridization question, none of the data are particularly compelling; thus, both **10** and **11** must be considered intermediate cases in the absence of structural information.

The $^1J_{CH}$ value (115 Hz) for μ-CH_3 of $(TMEDA)Ta(\mu\text{-}CH_2)(\mu\text{-}Me)(\mu\text{-}OCMe_2CH_2Ph_2P)_2Ni$ (**11**) implicated a weak agostic interaction[44] between a C–H bond and the nickel center.[45] When a THF-d_8 solution of **11** was cooled, the μ-CH_3 resonance, which appeared at δ −0.75 at 20 °C, began to broaden considerably. Below −71 °C, a new signal at δ −3.00 emerged and continued to sharpen. As a consequence of a slow rotation of the μ-CH_3 group, this agostic C–H resonance is now distinct from the normal C–H bonds. Grubbs reported this phenomenon with $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}CH_3)Rh(COD)$ (Table I), where the time-averaged peak at δ −3.13 was replaced by two resonances at δ 1.28 (d) and δ −12.15 (t) with T_C = −40 °C (90 MHz, $\Delta G^\ddagger$ = 9.8 kcal/mol).[10] Unfortunately, even at −98 °C, the peaks in the spectrum of **11** were still too broad to be definitively assigned as the μ-CH_3 resonances by their $^2J_{HH}$ values. Another resonance appears at δ ~0.25, which is expected on the basis of the averaged chemical shift at room temperature, but other dynamic processes are also being slowed (e.g., phenyl group rotation), and the complexity of the spectrum increases dramatically. If both peaks correspond to μ-CH_3, $\Delta G^\ddagger \approx$ 8.8 (2) kcal/mol. Unfortunately, corroboration of the agostic interaction via IR studies could not be obtained. As expected,[10] hydrogen exchange between the μ-CH_2 and μ-CH_3 units was not evidenced by NMR spectroscopy.

The formation of *trans*-$Me_2Ta(\mu\text{-}CH_2)(\mu\text{-}$

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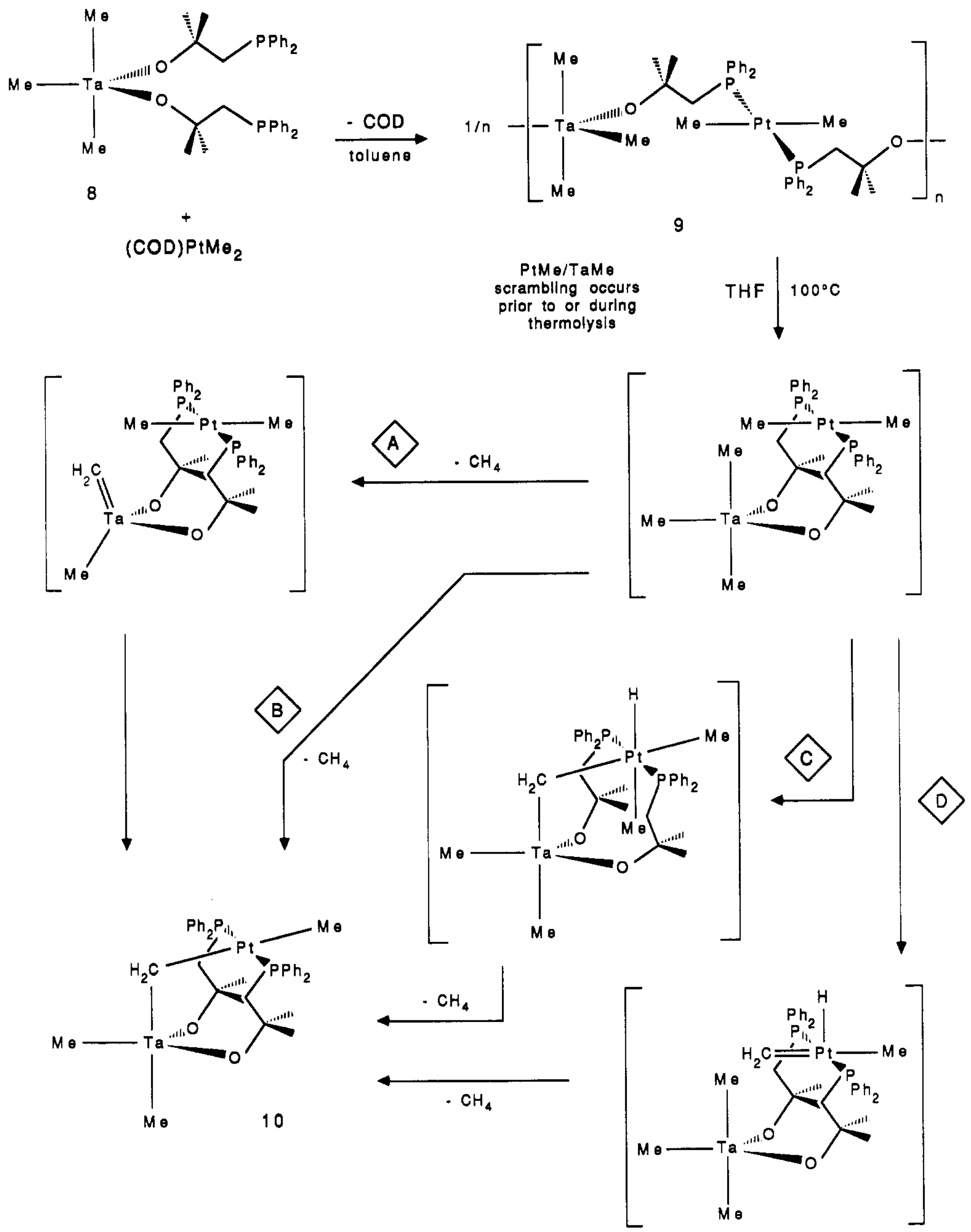
Scheme I. Possible Mechanisms for the Formation of *trans*-$Me_2Ta(\mu-CH_2)(\mu-OCMe_2CH_2Ph_2P)_2PtMe$ (10)



$OCMe_2CH_2Ph_2P)_2PtMe$ (10) and $(TMEDA)Ta(\mu-CH_2)(\mu-Me)(\mu-OCMe_2CH_2Ph_2P)_2Ni$ (11) both involve the breakdown of an alkyl. Scheme I illustrates plausible mechanisms for the generation of the Ta/Pt heterobimetallic. Phosphine substitution of COD in $(COD)PtMe_2$ affords the oligomer, $[-(Me)_3Ta(\mu-OCMe_2CH_2Ph_2P)Pt(Me)_2PPh_2CH_2CMe_2O-]_n$ (9), whose thermolysis generates *trans*-$Me_3Ta(\mu-OCMe_2CH_2Ph_2P)_2Pt(Me)_2$. Pathway A shows a Ta-based abstraction,[46] followed by a Pt-to-Ta Me migration or $H-CH_2Pt$ activation leading to **10**. In path B, a heterobimetallic H-abstraction affords **10**, while path C illustrates an oxidative addition of $TaCH_2-H$ to generate a Pt^{IV} dimethyl hydride. The subsequent reductive elimination of MeH yields **10**. Bergman has postulated a similar event in the production of $Cp_2Ta(\mu-CH_2)_2PtH(PMe_3)$ from $Cp_2(CH_3)Ta(\mu-CH_2)Pt(PMe_3)_2$.[40] If $(Ph_2PCH_2CMe_2O)_2Ta(CD_3)_3$ (**8**-d_9), prepared from $Cl_2Ta(CD_3)_3$, is the early-metal precursor, mechanism A is predicted to produce CD_4 and path B would give either CD_3H or CH_3D, depending on the origin of the abstracting methyl. In path C, only CH_3D should be produced. Recent decomposition studies of $(Me_2PCH_2CH_2PMe_2)PdMe_2$[47] suggest that a Pt-based α-elimination pathway leading to a $Pt{=}CH_2$ moiety and loss of CH_4 must also be considered (D). Following Ta-to-Pt Me migration or $H-CH_2Ta$ activation, **10** would be formed in a manner similar to that in mechanism A. In each instance, the μ-methylene bridge and accompanying methyl substituents would reflect the population of remaining CD_3 groups. Since **8** does not decompose upon prolonged thermolysis at >100 °C, abstraction pathway A must be disfavored.

Thermolysis of **9**-d_n, prepared from $(Ph_2PCH_2CMe_2O)_2Ta(CD_3)_3$ (**8**-d_9) and $(COD)Pt(CH_3)_2$, resulted in a mixture of labeled methanes (approximately 23% CD_4, 50% CD_3H, 2% CH_3D, and 25% CH_4 by MS),

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[46] Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502–1509.

[47] de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907–2917.

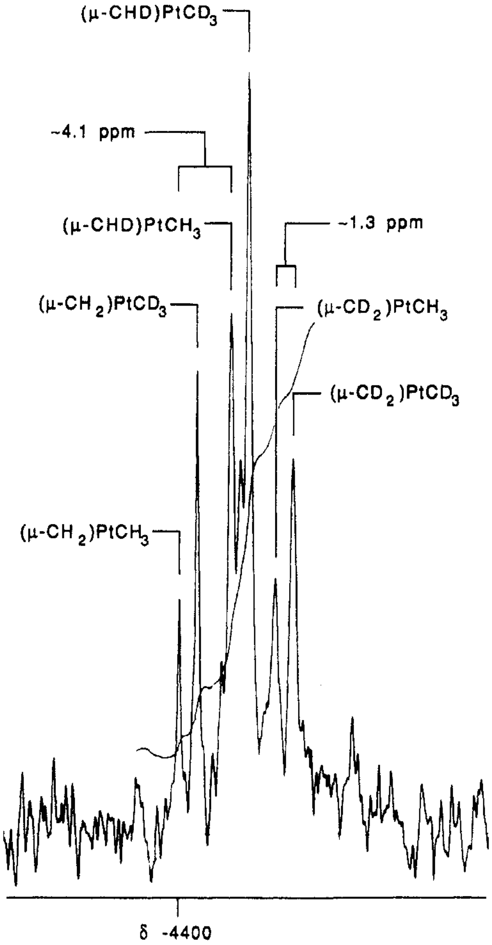

Figure 5. $^{195}Pt\{^1H\}$ NMR spectrum of several isotopmers of *trans*-$Me_2Ta(\mu\text{-methylene})(\mu\text{-}OCMe_2CH_2Ph_2P)_2PtMe$ (**10**-d_n), derived from $(Ph_2PCH_2CMe_2O)_2Ta(CD_3)_3$ (**8**-d_9) and (COD)Pt$(CH_3)_2$, showing only the central resonance of the triplet (J_{PtP} = 3050 Hz). Isotopic shifts of ~4.1 ppm/D correspond to deuteration of μ-methylene, while those of ~1.3 ppm/CD_3 (~0.4 ppm/D) refer to a terminal Pt-Me. Confirmation of the assignments was achieved by (1) spiking the above sample with **10** and (2) observing a ~9.7 ppm difference between **10** and **10**-d_{11}, prepared from **8**-d_9 and (COD)Pt$(CD_3)_2$.

and the Ta/Pt complex (**10**-d_n) that was formed had deuterium in the μ-CH_2, Pt-CH_3, and both Ta-CH_3 positions. Since a C-H(D) bond is broken in the process of forming the μ-methylene bridge, the ratio of CH_4 + CD_3H to CD_4 + CH_3D should reflect a primary isotope effect, regardless of the abstracting group.[48] Unfortunately, the results are not adequately explained by a purely statistical distribution of labeled Me groups. For example, although a preponderance of H-abstracted methanes is observed (3:1), the CH_4 to CH_3D ratio of 12.5:1 far exceeds the CD_3H to CD_4 ratio of 2:1. Me scrambling events[4,8-10] may be competing with the MeH-forming process, thereby complicating the overall reaction. The μ-CH_2 group of **10**-d_n contained ~50% D (^1H NMR), and $TaMe_2$/PtMe groups were comprised of a slightly higher percentage of deuterium. However, the latter were observed in a 1:1:1 ratio, again implicating Me scrambling, perhaps after the methane-forming step(s).

Figure 5 shows the $^{195}Pt\{^1H\}$ NMR spectrum of the sample described above. The spectrum, revealing only the central resonance of the ^{31}P triplet, exhibits at least six isotopomers of **10**-d_n, with the unlabeled material appearing at δ -4400. The larger isotopic shift[4,49] (~4.1 ppm/D) corresponds to deuteration of the μ-CH_2 position and the smaller (~1.3 ppm/CD_3; ~0.4 ppm/D) to the presence of terminal CH_3 and CD_3 groups on Pt. The nearly statistically deuterated μ-methylene position convincingly manifests the complexity of the overall reaction. The distribution of label in the methylene suggests that H/D exchange occurs only between μ-CH_2 and Ta-Me groups, since exchange with the platinum methyls would generate Pt-CHD_2 and Pt-CD_2H fragments that would easily be detected in the $^{195}Pt\{^1H\}$ NMR spectrum. Both Grubbs[10] and Bergman[40] have observed hydrogen exchanges between μ-CH_2 and CH_3/μ-CH_3 groups; thus, an intermediate akin to $[MeTa(\mu\text{-}CH_2)(\mu\text{-}CH_3)(\mu\text{-}OCMe_2CH_2Ph_2P)_2PtMe]$ might be expected to facilitate such an exchange. In a second experiment, the insoluble Ta/Pt precursor **9**-d_n was thermolyzed in the presence of unlabeled **10**. Intermolecular Me/Me exchanges were observed to occur on the time scale of the dissolution of **9**-d_n, since the $^{195}Pt\{^1H\}$ NMR was not a superposition of **10** and **10**-d_n but appeared to reflect a statistical mixture. As was shown in previous studies with Cp*MeZr$(\mu\text{-}OCH_2Ph_2P)_2PtMe_2$,[4] intermolecular and intrabimetallic Me exchanges can often be quite facile.[8-10]

The reaction between $(PPh_2CH_2CMe_2O)_2Ta(CD_3)_3$ (**8**-d_9) and (TMEDA)Ni$(CH_3)_2$ proved to be equally complicated. Even at room temperature in C_6D_6, CH_3 was seen to exchange into the Ta-Me positions of **8**-d_9 by ^1H NMR spectroscopy, consistent with intermolecular early-metal/late-metal alkyl exchanges occurring prior to the formation of **11**. The isotopic mixture of methanes (approximately 60% CD_4, 35% CH_3D, 5% CH_4, and <1% CD_3H by IR and MS methods) and ethanes (50% C_2D_6, 40% CH_3CD_3, and 10% C_2H_6 by MS) evolved during the course of the reaction contained a disproportionate amount of deuterium.[50] Furthermore, a significant amount of partially deuterated **8** remained after **11** was formed, again indicative of extensive Me scrambling. Although the labeling experiments fall short of providing mechanistic information pertinent to formation of the heterobimetallic, a plausible mechanism can be drawn from precedent. Scheme II invokes the reductive elimination of ethane from Ni after formation of a Ta-containing diphosphine chelate. The subsequent oxidative addition of a $TaCH_2$-H bond is followed by dinuclear reductive elimination of MeH. Finally, the Ta center is captured by TMEDA, completing the hypothesized pathway to (TMEDA)$Ta(\mu\text{-}CH_2)(\mu\text{-}Me)(\mu\text{-}OCMe_2CH_2Ph_2P)_2Ni$ (**11**). Ni^{II} dialkyls are prone to reductive elimination,[51] and the aforementioned results of Bergman et al.[40] support the oxidative-addition step. Similar dinuclear reductive-elimination steps have been postulated for the formation of Cp*$Zr(\mu\text{-}OCH_2Ph_2P)_2Rh(PPh_3)$ from Cp*MeZr$(\mu\text{-}OCH_2Ph_2P)_2$ and $HRh(PPh_3)_3$.[3]

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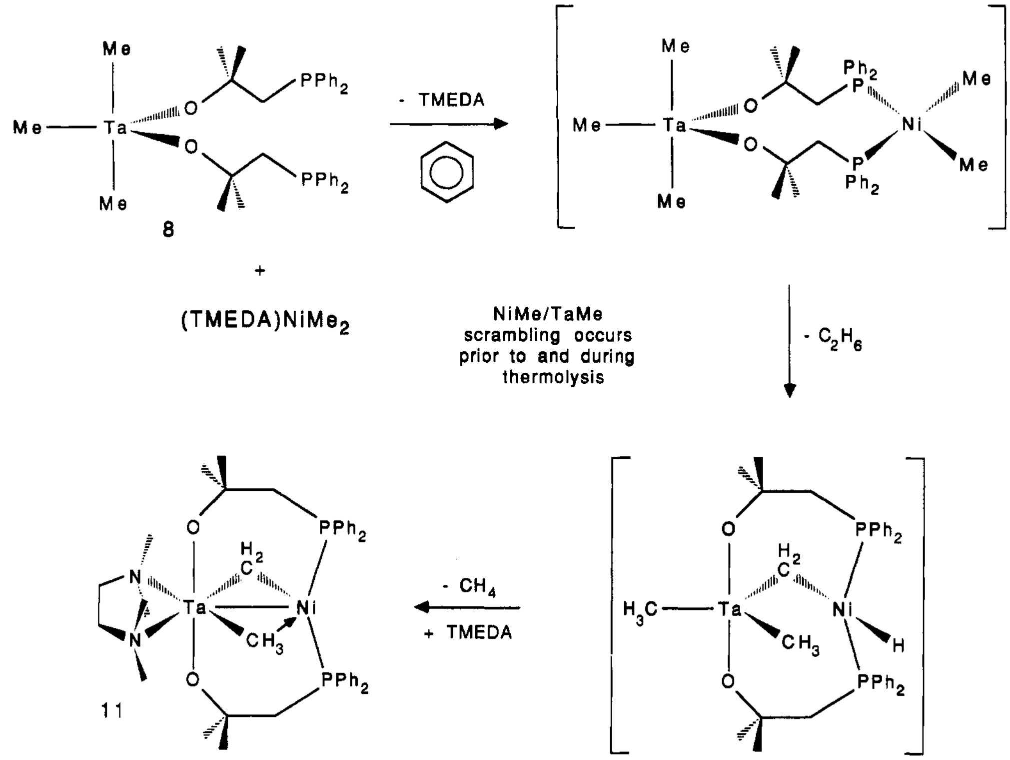
[48] If k_H/k_D = 1, a statistical distribution would be 30% CD_3H, 30% CD_4, 30% CH_3D, and 10% CH_4. Note that the observed mass spectral data are internally consistent with a ~60% deuterated sample.

(49) Jameson, C. J.; Osten, H. J. *Annu. Rep. NMR Spectrosc.* **1986**, *17*, 1-78. The isotope shifts of 4.1 ppm/D in μ-CH_2 versus 0.4 ppm/D in Pt-CH_3 do not correlate with the J_{PtH} values of 52 and 54 Hz, respectively, in contrast with trends observed for one-bond isotope shifts. Given the observation that *cis*-Cp*MeZr$(\mu\text{-}OCH_2Ph_2P)_2PtMe_2$[4] exhibits a 1.3 ppm/D shift, the differences in methylene and methyl shifts for **10** are substantial. The magnitude of an isotope shift reflects the degree of bond displacement and bond angle deformation upon isotope substitution. It is plausible that bond angle deformations play a large role in determining the isotope shifts for the μ-CH_2 group or that the potential energy surface that describes the methylene C-H bonds manifests substantial anharmonicity.

(50) According to the mass spectral data, both methane and ethane contain ~70% deuterium, consistent with substantial Me scrambling prior to or during the formation of 11.

(51) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181-8188 and references therein.

Scheme II. Possible Mechanism for the Formation of (TMEDA)Ta(μ-CH_2)(μ-Me)(μ-$OCMe_2CH_2Ph_2P$)$_2$Ni (11)



The reactivity of (TMEDA)Ta(μ-CH_2)(μ-Me)(μ-$OCMe_2CH_2Ph_2P$)$_2$Ni (11) and *trans*-Me_2Ta(μ-CH_2)(μ-$OCMe_2CH_2Ph_2P$)$_2$PtMe (10), while only briefly surveyed, proved disappointing. The Ta/Ni derivative (11) is considerably more thermally sensitive than 10, decomposing in several hours at 100 °C, while the latter shows no sign of decomposition. Both compounds decomposed under H_2, giving extremely complex mixtures and minor amounts of methane. Neither reacted with ethylene, even when heated to 100 °C.

Conclusions

Through the use of (oxyalkyl)phosphine ligands (i.e., $-OCR_2(CH_2)_nPh_2P$; R = ^{t}Bu, $n = 1$; R = Me, $n = 1, 2$) with substituents adjacent to oxygen, it has been possible to prepare monomeric early-metal compounds with various properties. With very bulky *tert*-butyl substituents, the heterodifunctional ligands seem to be conformationally restricted, thus favoring chelate formation. In cases where the steric constraints for chelation are prohibitive, the pendent phosphines are unreactive toward late metals because they are blocked from electrophilic attack. Fortunately, the use of methyl substituents provided much more reactive bridging groups. On the basis of the observations herein, the design and construction of more versatile bridging ligands should prove easier. When the size of the ligand substituents is modified, the length of the alkyl chain adjusted, and the number of bridging ligands varied, the designed synthesis of elaborate heterobimetallic species may be within reach via a combination of the metathesis, alcoholysis, and substitution reactions.

The tantalum derivative ($Ph_2PCH_2CMe_2O$)$_2$TaMe$_3$ (8) proved versatile in the construction of Pt and Ni heterobimetallics via substitution reactions, although the ultimate products, *trans*-Me_2Ta(μ-CH_2)(μ-$OCMe_2CH_2Ph_2P$)$_2$PtMe (10) and (TMEDA)Ta(μ-CH_2)(μ-Me)(μ-$OCMe_2$-CH_2Ph_2P)$_2$Ni (11), manifest additional, complicated transformations. The mechanisms responsible for these binuclear species are difficult to ascertain due to the presence of Me/Me scrambling pathways that negate the utility of labeling experiments. The observation of facile alkyl-exchange processes corroborates earlier findings that emphasize the importance of these oft-neglected reactions.[4,8-10] Regardless of their formation, the compounds are conceptually important since their μ-CH_2 and μ-CH_3 ligands are considered to model hydrocarbon fragments on bimetallic heterogeneous surfaces that catalyze Fischer–Tropsch and related reactions.[6,7,14-18]

Experimental Section

General Considerations. All manipulations were performed with use of standard glovebox, high-vacuum-line, or Schlenk-line techniques except where noted. Hydrocarbon solvents were purified by initial distillation from purple sodium/benzophenone ketyl followed by vacuum transfer from same. Small amounts of tetraglyme (2–5 mL/1200 mL) were added to hydrocarbons to solubilize the ketyl. CH_2Cl_2 was distilled from P_2O_5 and then vacuum-transferred from activated Linde 4-Å molecular sieves. Benzene-d_6 and CD_2Cl_2 were dried over activated Linde 4-Å sieves; THF-d_8 was dried over sodium/benzophenone ketyl. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was distilled from KOH prior to use. Di-*tert*-butyl ketone,[52] Ph_2PCH_2Li·TMEDA,[19] (COD)PtMe$_2$,[29] (TMEDA)NiMe$_2$,[38] Me_3TaCl_2,[25] and Zr(CH_2Ph)$_4$[33] were prepared via literature procedures. Isobutylene oxide was purchased from Comprehensive Research Chemical Co., Orange, CA.

NMR spectra were obtained on Varian XL-200 (^{1}H, ^{31}P{^{1}H}) and XL-400 (^{13}C{^{1}H}, ^{195}Pt{^{1}H}) and Bruker WM-300 (^{13}C{^{1}H}) spectrometers. ^{31}P spectra are referenced to external PCl_3 at δ 219.0 ppm downfield from H_3PO_4. ^{1}H and ^{13}C spectra are referenced to solvent resonances, and all coupling constants are reported in Hz. Infrared spectra, recorded on a Mattson FT-IR instrument, were used as fingerprints and are not reported. Mass spectra were obtained on a Finnigan 3300 instrument (EI for CH_4). Elemental analyses were performed by Oneida Research Services, Whitesboro, NY. Molecular weights were determined by freez-

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(52) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, pp 142–144.

ing-point depression in benzene.

Procedures. 1. LiOC^{t}Bu$_2$CH$_2$Ph$_2$P·xTHF. To a solution of Ph$_2$PCH$_2$Li·TMEDA (3.04 g, 9.15 mmol) in 35 mL of THF was slowly added 1.65 mL of di-*tert*-butyl ketone (1.36 g, 9.56 mmol) via syringe. Most of the yellow color of the solution was discharged immediately, and the nearly colorless solution was stirred at 25 °C for 1 h. THF was removed, and the resulting solid was triturated once in 40 mL of hexane. Hexane (~30 mL) was added, and the solid was collected by filtration, washed with 2 × 3 mL of hexane, and dried in vacuo to yield a white, microcrystalline product (3.31 g, 94%). ^{1}H NMR (C$_6$D$_6$): δ 1.23 (^{t}Bu, s, 18 H), 1.35 (THF, m), 2.93 (PCH$_2$, "d", J = 9, 2 H), 3.52 (THF, m), 6.95–7.15 (Ph, m, 6 H), 7.68 (Ph, "t", J = 7, 4 H). ^{31}P{^{1}H} NMR: δ -17.07 (br s). ^{13}C{^{1}H} NMR: δ 30.63 (C(*C*H$_3$)$_3$, s), 39.08 (*C*(CH$_3$)$_3$, s), 43.76 (P*C*H$_2$, s), 82.48 (O*C*^{t}Bu$_2$, s), 128.57 (Ph, s), 128.67 (Ph, s), 134.06 (ortho Ph, d, J = 10), 140.40 (ipso Ph, s). Anal. Calcd for C$_{22}$H$_{30}$LiOP·0.25THF: C, 75.39; H, 8.80. Found: C, 75.83; H, 8.70.

2. HOCMe$_2$CH$_2$Ph$_2$P. To a flask containing 1.96 g of LiPPh$_2$ (10.2 mmol) in 50 mL of THF was added 0.85 mL of isobutylene oxide (0.74 g, 10.2 mmol) under argon counterflow at 0 °C. As the epoxide was added, the bright yellow color of the solution was slowly discharged. After 1.5 h, the solution volume was reduced to ~15 mL; then 20–30 mL of benzene was added, followed by 10 mL of aqueous NH$_4$Cl. The mixture was opened to the air, stirred for 5 min, and transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with 3 × 40 mL of benzene. The combined organics were dried over MgSO$_4$ and evaporated under reduced pressure to a colorless oil. This crude product was often contaminated with ~10% of an impurity tentatively identified as Me$_2$C=CHPPh$_2$, resulting from elimination of H$_2$O from HOCMe$_2$CH$_2$Ph$_2$P. Flash chromatography through a silica column with CH$_2$Cl$_2$ efficiently removed this impurity (R_f 0.8), and the product (R_f 0.3) was isolated as a colorless oil (1.66 g, 63%). ^{1}H NMR (C$_6$D$_6$): δ 1.20 (CH$_3$, d, J = 1.4, 6 H), 1.80 (OH, br, 1 H), 2.29 (PCH$_2$, d, J = 3.5, 2 H), 6.99–7.12 (Ph, m, 6 H), 7.46 (Ph, tm, J = 7.5, 4 H). ^{31}P{^{1}H} NMR: δ -24.30 (s). ^{13}C{^{1}H} NMR: δ 31.13 (CH$_3$, d, J = 7.1), 45.32 (PCH$_2$, d, J = 14.3), 70.68 (OCMe$_2$, d, J = 14.7), 128.60 (Ph, s), 128.68, (Ph, s), 133.33 (ortho Ph, d, J = 19.5), 140.27 (ipso Ph, s).

3. LiOCMe$_2$CH$_2$Ph$_2$P. To a thoroughly degassed solution of HOCMe$_2$CH$_2$Ph$_2$P (1.68 g, 6.50 mmol) in 25 mL THF at -78 °C was slowly added solid lithium tetramethylpiperidide (0.96 g, 6.5 mmol) from a side arm over a 30-min period. The light yellow solution was stirred for 15 min at -78 °C and then 3 h at 25 °C. The solution was reduced to ~5 mL; then 10 mL of hexane was added to precipitate a white solid. THF was removed completely by repeatedly taking the mixture to dryness and adding more hexane. An off-white solid was collected by filtering a 10-mL hexane slurry. The solid was washed with 3 × 10 mL of hexane and dried in vacuo to afford a white powder (1.33 g, 78%). ^{1}H NMR (C$_6$D$_6$): δ 1.42 (CH$_3$, s, 6 H), 2.41 (PCH$_2$, d, J = 5.1, 2 H), 7.04–7.10 (Ph, m, 6 H), 7.57 (Ph, tm, J = 4, 4 H). ^{31}P{^{1}H} NMR: δ -21.03 (br s). ^{13}C{^{1}H} NMR: δ 37.05 (CH$_3$, d, J = 5), 47.31 (PCH$_2$, br s), 69.54 (OCMe$_2$, d, J = 12.2), 128.49 (Ph, s), 128.58 (Ph, s), 133.48 (ortho Ph, d, J = 18), 139.82 (ipso Ph, s). Anal. Calcd for C$_{16}$H$_{18}$LiOP: C, 72.73; H, 6.87. Found: C, 72.44; H, 6.54.

4. HOCMe$_2$CH$_2$CH$_2$Ph$_2$P. Procedure 2 was followed with use of 4.05 g of Ph$_2$PCH$_2$Li·TMEDA (12.5 mmol) in 80 mL of THF and 1.05 mL of isobutylene oxide (0.91 g, 12.5 mmol). Chromatography of the crude product (procedure 2) afforded a light yellow oil, which crystallized upon standing. These white crystals were washed with 2 × 5 mL of hexane and air-dried (1.5 g, 44%). The analytical sample was recrystallized from hexane and dried in vacuo. ^{1}H NMR (C$_6$D$_6$): δ 0.94 (CH$_3$, s, 6 H), 1.11 (OH, s, 1 H), 1.53 (CH$_2$, m, 2 H), 2.13 (PCH$_2$, m, 2 H), 7.05–7.13 (Ph, m, 6 H), 7.48 (Ph, td, J = 7.4, 1.5, 4 H). ^{31}P{^{1}H} NMR: δ -15.42 (s). ^{13}C{^{1}H} NMR: δ 23.04 (CH$_2$, d, J = 13), 29.21 (C(CH$_3$)$_2$, s), 40.19 (PCH$_2$, d, J = 16.5), 70.30 (OCMe$_2$, d, J = 11.5), 128.64 (Ph, s), 128.70 (Ph, s), 133.15 (ortho Ph, d, J = 19), 139.87 (ipso Ph, d, J = 14.5). Anal. Calcd for C$_{17}$H$_{21}$OP: C, 74.98; H, 7.77. Found: C, 74.97; H, 7.35.

5. (Ph$_2$PCH$_2$C^{t}Bu$_2$O)$_2$ZrCl$_2$ (1). To a flask containing 0.680 g of ZrCl$_4$ (2.91 mmol) and 2.242 g of LiOC^{t}Bu$_2$CH$_2$Ph$_2$P·xTHF (5.83 mmol) was added 60 mL of Et$_2$O at -78 °C. The slurry was warmed slowly to 25 °C over a 2–4-h period. After a total of 5 h, Et$_2$O was replaced with 50 mL of toluene and the resulting solution stirred for ~1 h further. LiCl was filtered off and washed once with 5 mL of toluene. The solution volume was reduced to ~5 mL, and 20 mL of hexane was added to complete precipitation of the product, which was collected by filtration and washed with hexane to yield a white solid (1.96 g, 80%). ^{1}H NMR (C$_6$D$_6$): δ 1.21 (^{t}Bu, s, 36 H), 3.04 (PCH$_2$, "d", J = 9.5, 4 H), 6.9–7.04 (Ph, m, 12 H), 7.76 (Ph, "tm", J = 7.5, 8 H). ^{31}P{^{1}H} NMR: δ -2.78 (s). ^{13}C{^{1}H} NMR: δ 30.65 (C(*C*H$_3$)$_3$, s), 38.14 (PCH$_2$, s), 43.95 (*C*(CH$_3$)$_3$, s), 99.11 (OC^{t}Bu$_2$, d, J = 9), 128.58 (Ph, s), 128.64 (Ph, s), 133.94 (ortho Ph, d, J = 12), 138.09 (ipso Ph, d, J = 5). M_r: found, 790; calcd, 845. Anal. Calcd for C$_{44}$H$_{60}$Cl$_2$O$_2$P$_2$Zr: C, 62.54; H, 7.16. Found: C, 62.85; H, 7.20.

6. (Ph$_2$PCH$_2$C^{t}Bu$_2$O)$_2$Zr(CH$_3$)$_2$ (2). To a solution of 0.435 g of 1 (0.514 mmol) in 20 mL of Et$_2$O at -78 °C was added 0.38 mL of 2.8 M CH$_3$MgBr solution (1.06 mmol) in diethyl ether. The solution was stirred 40 min at -78 °C, the cold bath removed, and the mixture warmed to 25 °C and stirred 1 h. The reaction mixture was filtered, and the collected solids were washed with 4 × 5 mL of Et$_2$O. The filtrate was reduced to ~8–10 mL and cooled to -78 °C, giving colorless crystals of the product, which were collected by cold filtration and dried in vacuo (0.373 g, 90%). ^{1}H NMR: δ 0.81 (ZrMe$_2$, t, J_{PH} = 4.2, 6 H), 1.26 (^{t}Bu, s, 36 H), 3.02 (PCH$_2$, d, J = 8.6, 4 H), 6.95–7.10 (Ph, m, 12 H), 7.68 (Ph, "td", J = 7.5, 1.6, 8 H). ^{31}P{^{1}H} NMR: δ -9.78 (s). ^{13}C{^{1}H} NMR: δ 30.39 (C(*C*H$_3$)$_3$, s), 36.26 (PCH$_2$, s), 40.11 (ZrCH$_3$, t, J = 10), 43.60 (*C*(CH$_3$)$_3$, s), 95.17 (OC^{t}Bu$_2$, d, J = 10), 128.58 (Ph, s), 128.69 (Ph, s), 133.57 (ortho Ph, d, J = 14.5), 140.24 (ipso Ph, s). Anal. Calcd for C$_{46}$H$_{66}$O$_2$P$_2$Zr: C, 68.70; H, 8.27. Found: C, 69.55; H, 8.35.

7. (Ph$_2$PCH$_2$C^{t}Bu$_2$O)$_2$Zr(CH$_2$^{t}Bu)$_2$ (3). To a flask containing 460 mg of 1 (0.54 mmol) and 85 mg of LiCH$_2$^{t}Bu (1.1 mmol) was added 20 mL of benzene. After the mixture was stirred at 25 °C for 45 min, benzene was replaced with 20 mL of hexane and LiCl was filtered and washed once with 10 mL of hexane. The hexane solution was reduced to 10 mL and cooled to -78 °C, and the resulting colorless crystals were collected by cold filtration. Further reduction of this filtrate afforded a second crop of crystals. The total yield was 395 mg (80%). ^{1}H NMR: δ 1.27 (CH$_2$C(*C*H$_3$)$_3$, s, 18 H), 1.35 (^{t}Bu, s, 36 H), 1.52 (C*H$_2$*C(CH$_3$)$_3$, s, 4 H), 3.17 (PCH$_2$, d, J = 6.7, 4 H), 7.05–7.13 (Ph, m, 12 H), 7.73 (Ph, tm, J = 7.0, 8 H). ^{31}P{^{1}H} NMR: δ -17.29 (s). ^{13}C{^{1}H} NMR: δ 30.96 (C(*C*H$_3$)$_3$, d, J = 4.6), 35.30 (CH$_2$C(CH$_3$)$_3$, s), 35.97 (CH$_2$^{t}Bu, s), 38.36 (PCH$_2$, d, J = 16.8), 43.26 (*C*(CH$_3$)$_3$, s), 95.80 (OC^{t}Bu$_2$, s), 128.65 (Ph, s), 128.75 (Ph, s), 133.60 (ortho Ph, d, J = 17.0), 141.92 (ipso Ph, s). Anal. Calcd for C$_{54}$H$_{82}$O$_2$P$_2$Zr: C, 70.78; H, 9.02. Found: C, 70.68; H, 8.94.

8. (Ph$_2$PCH$_2$C^{t}Bu$_2$O)$_3$ZrCl (4). Into a Pyrex bomb reactor containing 300 mg of 1 (0.355 mmol) and 136 mg of LiOC^{t}Bu$_2$CH$_2$Ph$_2$P·xTHF (0.354 mmol) was distilled 15 mL of benzene. The solution was heated at 65 °C for 6 h and then cooled to 25 °C, precipitating LiCl. The solution was then transferred into a flask, filtered, and reduced in volume, and 10 mL of hexane was added to precipitate 4 as a white solid. After the mixture was stirred 5 min, the solid was collected by filtration, washed with ~2 mL of hexane, and dried in vacuo (286 mg, 70%). ^{1}H NMR (C$_6$D$_6$): δ 1.37 (^{t}Bu, s, 27 H), 3.23 (PCH$_2$, d, J = 7.3, 6 H), 6.97–7.11 (Ph, m, 18 H), 7.82 (Ph, td, J = 7.7, 1.3, 12 H). ^{31}P{^{1}H} NMR: (C$_6$D$_6$, 20 °C): δ -10.12 (s). ^{31}P{^{1}H} NMR (C$_7$D$_8$, -80 °C): -16.5 (s), -15.4 (s), -11.3 (s), -5.0 (s), 3.9 (s). ^{13}C{^{1}H} NMR: δ 31.37 (C(*C*H$_3$)$_3$, d, J = 4.6), 37.97 (PCH$_2$, d, J = 17), 43.25 (*C*(CH$_3$)$_3$, s), 98.04 (OC^{t}Bu$_2$, d, J = 15), 128.72 (Ph, d, J = 8), 128.84 (Ph, s), 133.80 (ortho Ph, d, J = 17), 140.43 (ipso Ph, d, J = 7.1). Anal. Calcd for C$_{66}$H$_{90}$ClO$_3$P$_3$Zr: C, 68.87; H, 7.88. Found: C, 69.07; H, 7.89.

9. (Ph$_2$PCH$_2$C^{t}Bu$_2$O)$_3$ZrCH$_3$ (5). To a flask containing a solution of 420 mg of 4 (0.365 mmol) in 15 mL of Et$_2$O was syringed in 0.15 mL of 2.8 M CH$_3$MgBr (0.42 mmol) in Et$_2$O under argon counterflow at -78 °C. The reaction mixture was warmed slowly to 25 °C and left to stir for 12 h. The solution was filtered, and the collected white solid was washed with 10 × 10 mL of Et$_2$O. The filtrate was cooled to -78 °C and filtered to collect a colorless microcrystalline solid, which was dried in vacuo (247 mg, 60%). ^{1}H NMR (C$_6$D$_6$): δ 0.79 (ZrCH$_3$, s, 3 H), 1.37 (^{t}Bu, s, 27 H), 3.10

($\mathrm{PCH_2}$, d, J = 5.7, 6 H), 6.85–7.10 (Ph, m, 18 H), 7.70 (Ph, td, J = 7.5, 1.5, 12 H). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ −17.91 (s). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: δ 31.00 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$, d, J = 5.7), 32.56 ($\mathrm{ZrCH_3}$, s), 38.31 ($\mathrm{PCH_2}$, d, J = 24), 43.08 ($\mathit{C}\mathrm{(CH_3)_3}$, d, J = 15), 94.55 ($\mathrm{OC^tBu_2}$, s), 128.54 (Ph, d, J = 9.5), 128.69 (Ph, d, J = 12), 133.62 (ortho Ph, d, J = 20), 142.17 (ipso Ph, d, J = 17). Anal. Calcd for $\mathrm{C_{67}H_{93}O_3P_3Zr}$: C, 71.18; H, 8.29. Found: C, 70.80; H, 7.93.

10. $\mathbf{(Ph_2PCH_2CMe_2O)_2Ta(CH_3)_3}$ (8). To a flask containing 395 mg of $\mathrm{LiOCMe_2CH_2Ph_2P}$ (1.49 mmol) and 222 mg of $\mathrm{TaMe_3Cl_2}$ (0.75 mmol) was added 20 mL of $\mathrm{Et_2O}$ at −78 °C. The mixture was stirred for several hours while being slowly warmed to 25 °C, giving a light yellow solution and a gray precipitate. $\mathrm{Et_2O}$ was replaced with 10 mL of pentane, and the solution was filtered. The solids were extracted with 2 × 3 mL of pentane, and the filtrate was evaporated in vacuo to provide **8** as a light yellow oil (~270 mg, 50%). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.56 ($\mathrm{TaCH_3}$, s, 9 H), 1.54 ($\mathrm{C(CH_3)_2}$, s, 12 H), 2.75 ($\mathrm{PCH_2}$, d, J = 2.8, 4 H), 7.04–7.07 (Ph, m, 12 H), 7.52 (Ph, td, J = 7.5, 1.5, 8 H). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ −23.71 (s). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: δ 31.35 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$, d, J = 7.3), 45.49 ($\mathrm{PCH_2}$, d, J = 17.4), 51.31 ($\mathrm{TaCH_3}$, s), 82.66 ($\mathrm{OCMe_2}$, d, J = 17), 128.48 (Ph, s), 128.58 (Ph, s), 133.48 (ortho Ph, d, J = 17), 140.55 (ipso Ph, d, J = 14.7). Anal. Calcd for $\mathrm{C_{35}H_{45}O_2P_2Ta}$: C, 56.76; H. 6.12. Found: C, 55.83; H, 5.87.

11. *trans*-$\mathbf{Me_2Ta(\mu\text{-}CH_2)(\mu\text{-}OCMe_2CH_2Ph_2P)_2PtMe}$ (10). To a solution containing 262 mg of **8** (0.35 mmol) in 10 mL of toluene was added 116 mg of $\mathrm{(COD)PtMe_2}$ (0.35 mmol) with stirring. After 30–45 min, a finely divided white solid precipitated from the solution. The solution was stirred for several hours at 25 °C; then the toluene was replaced with THF and the solution filtered. The collected solid was washed twice with THF and dried in vacuo. The yield of the solid was typically ~75%, based on $[\mathrm{Me_3Ta(\mu\text{-}OCMe_2CH_2Ph_2P)_2PtMe_2}]_n$ (**9**). The solid was placed in a small Pyrex bomb reactor, and ~15 mL of THF was transferred in. The reaction mixture was heated to 100 °C for 4 h or until no insoluble material remained. The resulting yellow-brown solution was transferred to a flask and reduced to dryness. Residual THF was removed by repeated cycles of addition and removal of pentane. A 5-mL solution in pentane was filtered, and the collected solids were extracted with 6 × 3 mL of pentane. The filtrate was concentrated, cooled and filtered to yield **10** as a yellow microcrystalline solid (80 mg, 21%, based on **8**). ^{1}H NMR (20 °C, $\mathrm{C_6D_6}$): δ 0.25 ($\mathrm{PtCH_3}$, t, J_{PH}= 6.1, J_{PtH} = 54; 3 H), 0.64 ($\mathrm{TaCH_3}$, s, 3 H), 0.96 ($\mathrm{OC(CH_3)Me}$, s, 6 H), 1.18 ($\mathrm{TaCH_3}$, s, 3 H), 1.51 ($\mathrm{OCMe(CH_3)}$, s, 6 H), 2.23 ($\mathrm{PCH_2}$, dt, J_{HH} = 14, J_{PH} = 3, J_{PtH} = 65, 2 H), 3.47 ($\mathrm{PCH_2}$, dt, J_{HH} = 14, J_{PH} = 6.4, J_{PtH} not resolved, 2 H), 4.23 (μ-$\mathrm{CH_2}$, t, J_{PH} = 8.6, J_{PtH} = 52, 2 H), 6.89–7.15 (Ph, m, 12 H), 7.62 (Ph, m, 4 H), 7.88 (Ph, "dd", J = 12, 5, 4 H). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ 12.65 (s, J_{PtP} = 3050). $^{195}\mathrm{Pt}\{^1\mathrm{H}\}$ NMR: δ −4400 (t, J_{PtP} = 3050). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: δ −0.06 ($\mathrm{PtCH_3}$, t, J_{PC} = 7.2, J_{PtC} = 474), 30.77 ($\mathrm{OC(}\mathit{C}\mathrm{H_3)Me}$, s), 34.66 ($\mathrm{OCMe(}\mathit{C}\mathrm{H_3)}$, t, J = 4.0), 37.85 ($\mathrm{PCH_2}$, t, J_{PC} = 17.8, J_{PtC} = 20), 44.67 ($\mathrm{TaCH_3}$, s), 53.32 ($\mathrm{TaCH_3}$, s), 79.61 ($\mathrm{OCMe_2}$, s), 93.50 (μ-$\mathrm{CH_2}$, t, J_{PC} = 4, J_{PtC} = 287, J_{CH} = 129), 128.03 (para Ph, s), 128.09 (meta Ph, s), 128.15 (meta Ph, s), 128.20 (para Ph, s), 129.39 (ortho Ph, s), 130.40 (ortho Ph, s), 132.72 (ipso Ph, t, J_{PC} = 5.6, J_{PtC} = 22), 135.80 (ipso Ph, t, J_{PC} = 6.3, J_{PtC} = 22). Anal. Calcd for $\mathrm{C_{36}H_{47}O_2P_2PtTa}$: C, 45.53; H, 4.99. Found: C, 46.60; H, 4.66.

12. $\mathbf{(TMEDA)\overline{Ta(\mu\text{-}CH_2)(\mu\text{-}CH_3)(\mu\text{-}OCMe_2CH_2Ph_2P)_2Ni}}$ (11). To a solution of **8** (880 mg, 1.20 mmol) in 10 mL of $\mathrm{C_6H_6}$ was added 242 mg of $\mathrm{(TMEDA)Ni(CH_3)_2}$ (1.18 mmol). The solution was heated to 60 °C in a Pyrex bomb reactor for 5 h. Addition of hexane to the brown solution precipitated a red-brown solid, which was washed with 3 × 5 mL of hexane and dried in vacuo. A small second crop was obtained from the filtrate. The total yield was 330 mg (30%). The analytical sample was recrystallized from $\mathrm{Et_2O}$. ^{1}H NMR ($\mathrm{C_6D_6}$): δ −0.39 (μ-$\mathrm{CH_3}$, t, J = 3.5, 3 H), 0.78 ($\mathrm{OC(CH_3)Me}$, s, 6 H), 1.16 ($\mathrm{OCMe(CH_3)}$, s, 6 H), 1.92 ($\mathrm{NCH_2}$, m, 4 H), 2.10 ($\mathrm{PCH_2}$, d, J = 12, 2 H), 2.21 ($\mathrm{N(CH_3)_2}$, s, 6 H), 2.52 ($\mathrm{N(CH_3)_2}$, s, 6 H), 2.61 ($\mathrm{PCH_2}$, d, J = 12, 2 H), 5.71 (μ-$\mathrm{CH_2}$, t, J = 14, 2 H), 7.00–7.11 (Ph, m, 6 H), 7.26 (Ph, t, J = 7.5, 6 H), 7.90 (Ph, m, 4 H), 8.41 (Ph, m, 4 H). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ 25.13 (s). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: δ 31.34 ($\mathrm{C(}\mathit{C}\mathrm{H_3)Me}$, s), 35.18 ($\mathrm{CMe(}\mathit{C}\mathrm{H_3)}$, s), 35.89 ($\mathrm{PCH_2}$, t, J = 15), 40.65 (μ-$\mathrm{CH_3}$, t, J = 7, J_{CH} = 115), 49.94 ($\mathrm{N(CH_3)_2}$, s), 51.92 ($\mathrm{N(CH_3)_2}$, s), 58.83 ($\mathrm{NCH_2}$, s), 79.52 ($\mathrm{OCMe_2}$, t, J = 3.5), 127.12 (meta Ph, s), 127.66 (para Ph, s), 127.70 (para Ph, s), 128.16 (meta Ph, s), 133.14 (ortho Ph, t, J = 8), 134.33 (ortho Ph, t, J = 9), 141.57 (ipso Ph, s), 144.60 (ipso Ph, t, J = 3), 153.68 (μ-$\mathrm{CH_2}$, t, J = 8, J_{CH} = 122). Anal. Calcd for $\mathrm{C_{40}H_{57}N_2O_2P_2NiTa}$: C, 53.41; H. 6.39; N, 3.11. Found: C, 53.11; H, 5.99; N, 2.56.

13. NMR-Tube Reactions. Five-millimeter NMR tubes were sealed onto 14/20 ground-glass joints, charged with reagents in the drybox, and brought out on needle valve adapters. The samples were freeze–pump–thaw degassed (−196 °C) and sealed off with a torch.

a. $\mathbf{(Ph_2PCH_2CH_2CMe_2O)_2Zr(CH_2Ph)}$ (6). To an NMR tube containing 16 mg of $\mathrm{Zr(CH_2Ph)_4}$ (0.035 mmol) and 19 mg of $\mathrm{HOCMe_2CH_2CH_2Ph_2P}$ (0.070 mmol) was added 0.4 mL of $\mathrm{C_6D_6}$. After 5 h, no starting material remained and **6** had formed cleanly. ^{1}H NMR: δ 1.15 ($\mathrm{C(CH_3)_2}$, s, 12 H), 1.44 ($\mathrm{CH_2Ph}$, s, 4 H), 1.63 ($\mathrm{CH_2CMe_2}$, m, 4 H), 2.14 ($\mathrm{PCH_2}$, m, 4 H), 6.90 ($\mathrm{CH_2}\mathit{Ph}$, d, J = 7.5), 7.05–7.15 (Ph, m), 7.50 (Ph, dt, J = 1.9, 8). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ −14.57 (s).

b. $\mathbf{(Ph_2PCH_2CH_2CMe_2O)_4Zr}$ (7). To an NMR tube containing 12 mg of $\mathrm{Zr(CH_2Ph)_4}$ (0.026 mmol) and 30 mg of $\mathrm{HOCMe_2CH_2CH_2Ph_2P}$ (0.11 mmol) was added 0.5 mL of $\mathrm{C_6D_6}$. After 1 h **7** had formed cleanly. ^{1}H NMR: δ 1.23 ($\mathrm{C(CH_3)_2}$, s, 24 H), 1.73 ($\mathrm{CH_2CMe_2}$, m, 8 H), 2.31 ($\mathrm{PCH_2}$, m, 8 H), 7.05–7.16 (Ph, m, 24 H), 7.55 (Ph, dt, J = 1.8, 7.5, 16 H). When an additional 13 mg of $\mathrm{Zr(CH_2Ph)_4}$ (0.029 mmol) was added to the tube, **6** formed after ~3 h.

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