introduced. This model of the structure converged with $R = 0.0665$ and $R_w = 0.0733$ with a data to parameter ratio of 7.9. The high-temperature factors of the benzene carbon atoms suggest either some positional disorder or partial occupancy or both, but this was not investigated further. A final difference Fourier synthesis revealed no peaks higher than those previously assigned to hydrogen atoms, and the weighting scheme appeared reasonable.

In these refinements anomalous disperson effects for Ni and Fe were included in the calculation of F_c using the values of Cromer and Liberman.[33] The atomic scattering factors were those of Cromer and Mann.[34] Final positional parameters for **2** are given in Table III. Tables of anisotropic temperature factors and positional parameters of calculated hydrogen atoms and a list of observed and calculated structure factor amplitudes are also available.[35]

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Registry No. **1a**, 96897-79-9; **1b**, 96897-80-2; **1c**, 96897-81-3; **2**, 96913-28-9; $\mathbf{2}^+PF_6^-$, 96913-31-4; $\mathbf{2}^+Br^-$, 96913-32-5; **3**, 96913-29-0; $Ni(\eta\text{-}C_5H_5)_2$, 1271-28-9; $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$, 12154-95-9; $Co(\eta\text{-}C_5H_5)(CO)_2$, 12078-25-0; $(\eta\text{-}Ph_4C_4)CoCp$, 1278-02-0; $Co_3(\mu\text{-}CPh)_2(\eta\text{-}C_5H_5)_3$, 72271-50-2; $[Fe_2(CO)(\mu\text{-}C_4H_2Ph_2)(\eta\text{-}C_5H_5)_2]$, 96928-54-0; $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma{:}\eta^3\text{-}ClO)C_2Ph(H)\}(\eta\text{-}C_5H_5)_2]$, 83691-33-2; $PhC{\equiv}CPh$, 501-65-5; Fe, 7439-89-6; Ni, 7440-02-0.

Supplementary Material Available: Listings of anisostropic temperature factors (Table S1), positional and thermal parameters for calculated hydrogen atoms (Table S2), and observed and calculated structure factors (Table S3) (10 pages). Ordering information is given on any current masthead page.

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Early/Late Metal Binuclear Complexes Bridged by μ-OCH$_2$Ph$_2$P: Structure of $(\eta^5\text{-}C_5Me_5)Zr(\mu\text{-}OCH_2Ph_2P)_3NiCO{\cdot}C_7H_8$

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Methodology enabling the linkage of Ni and Zr via μ-OCH$_2$Ph$_2$P bridges has been explored. Treatment of $(COD)_2Ni$ with 4 equiv of $HOCH_2Ph_2P$ provided $(HOCH_2Ph_2P)_4Ni$ (**1**), which, upon stoichiometric addition of Cp^*ZrMe_3 ($Cp^* = \eta^5\text{-}C_5Me_5$), was converted to $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiPPh_2CH_2OH$ (**2**) with the concomitant formation of CH_4. Heterobimetallic **2** was derivatized with PMe_3, $P(OMe)_3$, and CO to obtain $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiPMe_3$ (**3**), $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiP(OMe)_3$ (**4**), and $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiCO$ (**5**), respectively, in good yield. An X-ray structure determination of $\mathbf{5}{\cdot}C_7H_8$ exhibited the expected pseudo-Td coordination about Zr and Ni. Crystal data: monoclinic, $P2_1/n$, $a = 14.189$ (3) Å, $b = 27.603$ (4) Å, $c = 13.448$ (3) Å, $\beta = 97.240$ (10)°, $Z = 4$, and $T = 25$ °C. Standard refinement procedures yielded an R of 0.061 from 5866 data where $|F_o| \geq 3\sigma(F_o)$. Examination of the bridging unit suggests that the μ-OCH$_2$Ph$_2$P ligand should serve to bring two disparate metal centers together for the activation of small molecules.

Introduction

In examining the composition of heterogeneous catalysts which make[1] or break[2] carbon–carbon bonds, it becomes evident that the combination of electron rich and electron poor metals is quite common. Typical Fischer–Tropsch (e.g., Co, Fe, Ru/TiO$_2$, Al$_2$O$_3$, SiO$_2$)[1,3] and reforming (e.g., Pt/Re/Al$_2$O$_3$)[2,4] catalysts exemplify such heterogeneous materials. Although it is clear that an important role of the support is to keep the electron-rich metal dispersed, these cocatalysts may play a more direct role[5] in the forming or breaking of C–C bonds, given the fact that certain zeolites (e.g., ZSM-5) possess the ability to catalyze the formation of hydrocarbons from methanol.[6]

In order to more fully understand the relationship between disparate metal centers, homogeneous analogues[7] to these heterogeneous species need to be constructed. In this manner, the potential cooperative reactivity of two widely different (early–late) metals[8–16] may be more clearly

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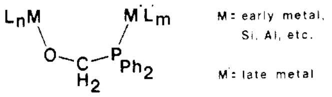
Table I. Selected Interatomic Distances (Å) and Bond Angles (deg) for $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiCO \bullet C_7H_8$ ($5 \bullet C_7H_8$)[a]

		Bond Lengths			
Ni-P1	2.190 (2)	Ni···Zr	4.049 (1)	Zr-C8	2.519 (7)
Ni-P2	2.186 (2)	Ni-C4	1.735 (7)	Zr-C9	2.521 (8)
Ni-P3	2.205 (2)	C4-O4	1.161 79)	C5-C51	1.535 (14)
P1-C1	1.857 (7)	C1-O1	1.426 (8)	C6-C61	1.469 (15)
P2-C2	1.853 (7)	C2-O2	1.409 (7)	C7-C71	1.523 (18)
P3-C3	1.849 (6)	C3-O3	1.405 (8)	C8-C81	1.519 (15)
P1-C111	1.828 (6)	Zr-O1	1.925 (5)	C9-C91	1.512 (15)
P1-C121	1.839 (7)	Zr-O2	1.936 (4)	C5-C6	1.383 (13)
P2-C211	1.826 (7)	Zr-O3	1.921 (5)	C6-C7	1.411 (12)
P2-C221	1.851 (6)	Zr-C5	2.511 (7)	C7-C8	1.337 (13)
P3-C311	1.816 (6)	Zr-C6	2.519 (8)	C8-C9	1.413 (12)
P3-C321	1.831 (6)	Zr-C7	2.512 (9)	C9-C5	1.346 (12)
Zr-R	2.226 (14)				
		Bond Angles			
P1-Ni-P2	110.6 (1)	Ni-P2-C2	120.1 (2)	Zr-O3-C3	155.1 (4)
P2-Ni-P3	109.7 (1)	Ni-P3-C3	119.5 (2)	O1-Zr-O2	107.2 (2)
P3-Ni-P1	109.5 (1)	P3-C3-O3	111.7 (4)	O2-Zr-O3	105.5 (2)
P1-Ni-C4	108.4 (3)	P2-C2-O2	112.1 (4)	O1-Zr-O3	105.5 (2)
P2-Ni-C4	105.3 (2)	P1-C1-O1	110.8 (4)	R-Zr-O1	111.7 (4)
P3-Ni-C4	113.2 (2)	Zr-O1-C1	153.7 (4)	R-Zr-O2	111.8 (4)
Ni-C4-O4	175.8 (7)	Zr-O2-C2	151.2 (4)	R-Zr-O3	114.6 (4)
Ni-P1-C1	120.4 (2)				

[a] R = Cp* ring centroid.

observed. In an approach designed with these goals in mind, a ligand system was sought in which the two metal centers would be proximate, yet not intimately bound (i.e., no M-M′ bonds, no monatomic bridges). Since the bridging ligand must be compatible with both electron-rich and electron-poor metals, the initial studies described herein involve the utilization of the (alkoxymethyl)diphenylphosphine bridge (μ-OCH_2Ph_2P).[17]



An alkoxy early metal linkage (a possible model of an oxide)[18] and a phosphine late metal bond should both be robust enough to withstand conditions necessary to affect small molecule reactivity between cooperative metal centers. In the initial efforts reported here, the methodology required to link an early (Zr) and a late metal (Ni) with the alkoxyalkylphosphine has been explored. Structural studies indicate that this bridging ligand will adequately serve to keep disparate metals at a distance suitable for binuclear small molecule activation.

Synthetic Studies

The formation of the alkoxyalkylphosphine bridge between Ni and Zr was envisioned to occur in a sequential manner. First, the phosphine–Ni linkage would be formed via a substitution reaction.[19] Completion of the bridge would then be accomplished via the alcoholysis of a zirconium–alkyl bond[20] by the hydroxy portion of the bound phosphine.

Treatment of bis(1,5-cyclooctadiene)nickel ($(COD)_2Ni$) with 4 equiv of $HOCH_2Ph_2P$ afforded the bright yellow tetraphosphine complex $(HOCH_2Ph_2P)_4Ni$ (1) in 81% yield according to eq 1. Stoichiometric addition of

$$(COD)_2Ni + 4HOCH_2Ph_2P \rightarrow \underset{1}{(HOCH_2Ph_2P)_4Ni} + 2COD \quad (1)$$

Cp^*ZrMe_3 ($Cp^* = \eta^5\text{-}C_5Me_5$)[21] to 1 resulted in the formation (82% yield) of $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiPPh_2CH_2OH$ (2) concomitant with 3 equiv of CH_4 (eq 2). Since the

$$Cp^*ZrMe_3 + 1 \rightarrow \underset{2}{Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiPPh_2CH_2OH} + 3CH_4 \quad (2)$$

extreme solubility of 2 hampered purification, derivatization of this new heterobimetallic complex was accomplished via exposure to excess PMe_3, $P(OMe)_3$, and CO to form $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiPMe_3$ (3), $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiP(OMe)_3$ (4), and $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiCO$ (5) in 85%, 52%, and 76% yields, respectively, according to eq 3. The PMe_3 derivative 3 was

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$$2 + L \rightarrow Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiL + PPh_2CH_2OH \quad (3)$$
$$\begin{gathered} \mathbf{3}, L = PMe_3 \\ \mathbf{4}, L = P(OMe)_3 \\ \mathbf{5}, L = CO \end{gathered}$$

isolated as a precipitate but the phosphite (**4**) and carbonyl (**5**, $\nu(C{\equiv}O)$ 1905 cm^{-1}) derivatives are yellow, crystalline complexes. Compounds **2**–**5** appear to possess similar stabilities in solution as well as the solid state, despite the wide range of cone angles (PPh_2CH_2OH (138°) > PMe_3 (118°) > $P(OMe)_3$ (107°) > CO (90°?))[22] attributed to their terminal ligands.

Curiously, compounds **1**, **2**, **3**, and **5**, whether isolated as powders or as crystalline materials, all contained variable amounts of occluded solvent molecules; ^1H NMR analysis of each batch of product revealed free solvent resonances. Since direct binding of solvent was not indicated, it is presumed that the solvent molecules occupy lattice spaces created by the irregular shapes of the heterobimetallic species. Since further reactivity studies of these molecules proved to be unsuccessful, an X-ray crystallographic characterization of **5** was undertaken to more fully understand the geometry of the alkoxyalkylphosphine bridging unit.[23]

Molecular Structure of $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiCO$ (5)

Slow crystallization of a diethyl ether solvate of **5** from toluene afforded a single crystal of $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiCO\cdot C_7H_8$ (**5**$\cdot C_7H_8$), a toluene solvate. Figure 1 depicts the molecular structure of **5**, with all the phenyl carbons except those attached to phosphorus removed for clarity. Structure solution proved to be routine; no disorder problems were encountered, including the refinement of the toluene molecule (not pictured).

Both metal centers may be described as being tetrahedrally coordinated (Table I). The P–Ni–P angles average 109.9 (6)° and the P–Ni–C4 angles average 109 (4)°, clearly indicating the approximate Td geometry about the Ni. The O–Zr–O (106 (1)° average) and R–Zr–O angles (113 (2)° average, R = Cp* ring centroid) suggest that the environment about the Zr is also pseudo-Td. Typical Zr–O (1.927 (8) Å average)[20] and somewhat short Zr–C (2.516 (5) Å average)[24] distances are observed; the Ni–P bond lengths (2.194 (10) Å average) are representative of phenylphosphine Ni(0) complexes.[25-27] Normal carbonyl bond lengths (Ni–C4 = 1.735 (7) Å; C4–O4 = 1.161 (9) Å) are manifested in accord with the IR stretch of 1905 cm^{-1}. Although the geometry of the complex could accommodate a Ni→Zr dative bond, the 4.049 (1) Å Ni–Zr distance is much greater than the sum of the covalent radii of the metals (2.60 Å).

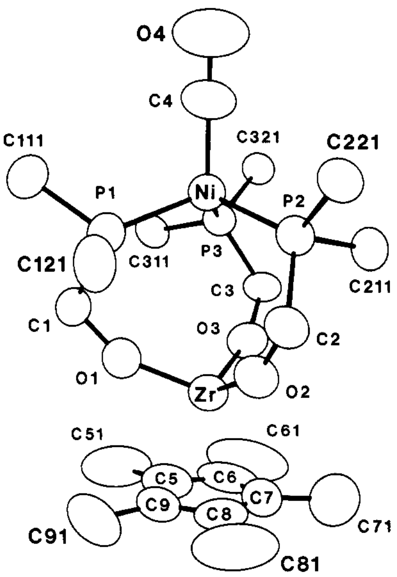

Figure 1. Molecular structure of $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiCO$ (**5**) with the phenyl carbons (except those attached to phosphorus) removed for clarity.

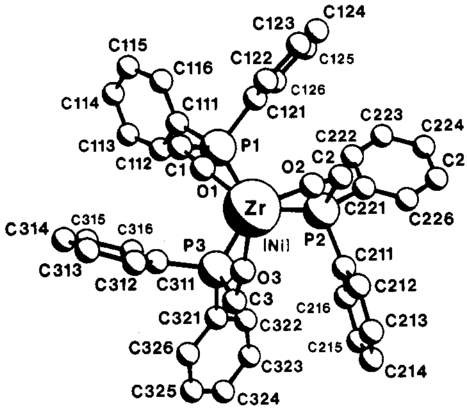

Figure 2. View of $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiCO$ (**5**) down the Zr–Ni axis. The Cp* carbons are removed for clarity.

The somewhat obtuse C–O–Zr (153 (2)° average) angles, concomitant with the 1.927 (8) Å Zr–O distances, intimate that the oxygen atoms are substantial π-donors to the Lewis acidic Zr;[20] alternatively, the steric properties of the alkoxyalkylphosphine ligands may require greater linearity in the C–O–Zr angles. As Figure 2 indicates, the bridging ligands adopt a threefold (C_3) symmetry as viewed down the Ni–Zr axis. Apparently the staggered disposition of the phenyls are a consequence of their steric interactions; the bridging atoms are thereby compelled to twist about the Ni–Zr axis. Similar 1,1,1-tris((diphenylphosphino)methyl)ethane,[28] np$_3$ (tris(2-(diphenylphosphino)ethyl)amine),[29] and tetraphos-2 (tris(2-(diphenylphosphino)ethyl)phosphine)[30] complexes also appear to display this C_3 twist in their coordination to Ni(0,[27] I, II[28-30]) complexes. It is clear that the $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3$ unit functions as

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an excellent tripod ligand for tetrahedral Ni(0). Sacconi's pseudo-Td (np$_3$)NiCO (ν(C$\equiv$O) 1880 cm^{-1}) complex[25] is directly analogous to 5; its Ni–P distances (2.215 (9) Å average), P–Ni–P angles (112.7 (10)° average), and the twisted geometry of the np$_3$ ligand parallel the features of 5.

Discussion

The procedures utilized in the preparation of the Ni/Zr complexes above have established a methodology by which a number of new heterobimetallic complexes may be synthesized. In order to observe bimetallic chemistry from complexes **2–5**, cleavage of at least one of the μ-OCH$_2$Ph$_2$P from the complexes was viewed as a necessity. All attempts to *cleanly* sever the bridging ligand from the coordination sphere of either metal failed. Treatments of **3** and **5** with nucleophilic R$^-$ equivalents were ineffective at displacing the alkoxy portion of the bridge from Zr.[31] Electrophilic attack of **3** and **5** with a variety of reagents (RX, HX, etc.) also led to complex mixtures of products. Although many such substrates might be expected to oxidatively add to the Ni(0) center, thus freeing one phosphine, the observed product mixtures discouraged further study. Clearly, two severe problems hindered these efforts: the displacement of alkoxides from Zr is difficult, in part due to the strength of the Zr–O linkage, and the noted lability of phosphines attached to Ni render such complexes susceptible to a myriad of decomposition modes.[19] In this case, the Ni–P bonds are not robust enough to withstand the conditions necessary to affect cooperative reactivity.

The geometry of the alkoxyalkylphosphine ligands of **5** signifies that this bridge will perform the desired role; the intermetallic distance of 4.049 (1) Å lends credence to the proposed cooperative bimetallic activation of small molecules such as CO. With use of procedures similar to those above, complexes of Zr or Ta and Pd, Pt, Rh, or Ir, containing one or two μ-OCH$_2$Ph$_2$P bridges, are now being prepared and surveyed for bimetallic small molecule reactivity.

Experimental Section

General Considerations. All manipulations were performed by using either glovebox, high vacuum line, or Schlenk line techniques. All 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. Benzene-d_6 was dried over activated 4-Å molecular sieves. (Hydroxymethyl)diphenylphosphine[17] (^{31}P{^{1}H} NMR (C$_6$D$_6$) δ -11.84), (COD)$_2$Ni[19] and Cp*ZrMe$_3$[21] were prepared via literature procedures.

^{1}H NMR spectra were obtained by using Varian EM-390 and CFT-20 spectrometers. ^{31}P{^{1}H} spectra were recorded on a JEOL FX90Q instrument and referenced to an external sample of PCl$_3$ at +219.0 ppm. Infrared spectra were obtained by using a Perkin-Elmer 357 spectrophotometer. Analyses were performed by Analytische Labortorien, Germany.

In almost all of the complexes synthesized according to the procedures below, *solvent molecules were found to be occluded* in either powder or crystalline samples. The amount of solvent varied from process to process and was routinely monitored via ^{1}H NMR after the sample was subjected to vacuum (10^{-3} torr) for 30–45 min. In all cases, no evidence of solvent binding was detected.

Table II. Fractional Coordinates and Thermal Parameters[a] (Non-Hydrogen Atoms) for Cp*Zr(μ-OCH$_2$Ph$_2$P)$_3$NiCO • C$_7$H$_8$ (5 • C$_7$H$_8$)

atom[b]	x	y	z	B(eqv), Å^2
Zr	0.2258 (0)	0.0789 (0)	0.1631 (1)	5.8 (1)*
Ni	0.4307 (1)	0.1784 (0)	0.2447 (1)	4.3 (1)*
P(1)	0.3443 (1)	0.1694 (1)	0.3673 (1)	4.7 (1)*
P(2)	0.4966 (1)	0.1097 (1)	0.2110 (1)	4.5 (1)*
P(3)	0.3407 (1)	0.2050 (1)	0.1101 (1)	4.3 (1)*
O(1)	0.1944 (3)	0.1212 (2)	0.2679 (3)	6.1 (2)*
O(2)	0.3463 (3)	0.0487 (2)	0.2106 (4)	6.0 (2)*
O(3)	0.2509 (3)	0.1209 (2)	0.0556 (3)	5.9 (2)*
O(4)	0.5902 (4)	0.2402 (2)	0.3147 (5)	9.4 (4)*
C(1)	0.2143 (5)	0.1588 (2)	0.3401 (5)	5.3 (3)*
C(2)	0.4440 (4)	0.0516 (2)	0.2455 (5)	5.1 (3)*
C(3)	0.2907 (5)	0.1613 (2)	0.0132 (5)	5.0 (3)*
C(4)	0.5246 (5)	0.2169 (3)	0.2848 (6)	6.1 (4)*
C(111)	0.3345 (4)	0.2196 (2)	0.4539 (4)	4.9 (3)*
C(112)	0.3561 (6)	0.2658 (3)	0.4257 (5)	6.6 (4)*
C(113)	0.3402 (7)	0.3067 (3)	0.4844 (6)	7.6 (5)*
C(114)	0.3056 (6)	0.2998 (3)	0.5727 (7)	7.4 (4)*
C(115)	0.2832 (6)	0.2548 (3)	0.6011 (6)	7.7 (5)*
C(116)	0.2983 (5)	0.2135 (3)	0.5423(6)	6.8 (4)*
C(121)	0.3823 (5)	0.1199 (2)	0.4549 (5)	5.6 (3)*
C(122)	0.3343 (7)	0.0778 (3)	0.4551 (6)	7.0 (4)*
C(123)	0.3710 (8)	0.0400 (4)	0.5161 (7)	9.5 (6)*
C(124)	0.4536 (9)	0.0474 (4)	0.5715 (7)	9.3 (6)*
C(125)	0.5065 (8)	0.0904 (4)	0.5769 (7)	9.8 (6)*
C(126)	0.4669 (6)	0.1257 (3)	0.5154 (6)	6.9 (4)*
C(211)	0.5106 (4)	0.1005 (2)	0.0792 (5)	5.0 (3)*
C(212)	0.4627 (5)	0.0657 (3)	0.0171 (5)	5.9 (4)*
C(213)	0.4704 (6)	0.0642 (3)	−0.0817 (6)	6.8 (4)*
C(214)	0.5257 (7)	0.0955 (4)	−0.1243 (6)	8.1 (5)*
C(215)	0.5771 (6)	0.1305 (3)	−0.0655 (6)	7.9 (5)*
C(216)	0.5700 (5)	0.1325 (3)	0.0351 (6)	6.5 (4)*
C(211)	0.6177 (4)	0.0957 (2)	0.2724 (5)	4.9 (3)*
C(222)	0.6480 (5)	0.1156 (3)	0.3638 (6)	6.4 (4)*
C(223)	0.7315 (6)	0.1015 (3)	0.4181 (6)	7.7 (5)*
C(224)	0.7885 (5)	0.0679 (3)	0.3803 (7)	7.6 (5)*
C(225)	0.7609 (6)	0.0500 (3)	0.2889 (7)	8.0 (5)*
C(226)	0.6739 (5)	0.0629 (3)	0.2352 (6)	6.3 (4)*
C(311)	0.2356 (4)	0.2386 (2)	0.1330 (4)	4.6 (3)*
C(312)	0.1445 (5)	0.2212 (3)	0.1122 (6)	6.1 (4)*
C(313)	0.0688 (5)	0.2469 (3)	0.1436 (6)	7.1 (4)*
C(314)	0.0816 (5)	0.2901 (4)	0.1913 (6)	7.7 (5)*
C(326)	0.3336 (5)	0.2698 (2)	−0.0533 (5)	5.6 (3)*
C(315)	0.1717 (6)	0.3088 (3)	0.2093 (6)	7.6 (5)*
C(316)	0.2492 (5)	0.2832 (3)	0.1800 (5)	6.1 (4)*
C(321)	0.3916 (4)	0.2456 (2)	0.0234 (4)	4.4 (3)*
C(322)	0.4886 (5)	0.2503 (3)	0.0277 (6)	6.3 (4)*
C(323)	0.5296 (5)	0.2760 (3)	−0.0438 (7)	7.4 (4)*
C(324)	0.4710 (6)	0.2982 (3)	−0.1211 (6)	7.5 (4)*
C(325)	0.3728 (56)	0.2958 (3)	−0.1247 (6)	6.9 (4)*
C(5)	0.0546 (5)	0.0542 (3)	0.1268 (7)	6.9 (4)*
C(6)	0.0953 ()6	0.0424 (3)	0.0418 (6)	7.1 (4)*
C(7)	0.1609 (6)	0.0049 (3)	0.0696 (7)	7.3 (4)*
C(8)	0.1596 (6)	−0.0057 (3)	0.1664 (7)	6.8 (4)*
C(9)	0.0916 (6)	0.0251 (3)	0.2020 (6)	6.9 (4)*
C(51)	−0.0207 (7)	0.0931 (4)	0.1380 (12)	11.4 (8)*
C(61)	0.0679 (11)	0.0660 (6)	−0.0555 (9)	12.5 (8)*
C(71)	0.2227 (11)	−0.0186 (5)	−0.0016 (12)	13.0 (8)*
C(81)	0.2146 (8)	−0.0443 (4)	0.2300 (13)	12.0 (8)*
C(91)	0.0705 (9)	0.0231 (5)	0.3093 (9)	11.1 (7)*
R	0.1124 (11)	0.0242 (5)	0.1213 (12)	13.0 (8)*
T(1)	0.8806 (10)	−0.1460 (4)	0.2665 (9)	11.7 (8)*
T(2)	0.8297 (9)	−0.1064 (5)	0.3105 (9)	13.1 (9)*
T(3)	0.8619 (9)	−0.0808 (4)	0.3824 (8)	11.5 (8)*
T(4)	0.9500 (11)	−0.0884 (5)	0.4174 (11)	14.5 (10)*
T(5)	1.0146 (10)	−0.1187 (5)	0.3928 (11)	14.7 (10)*
T(6)	0.9718 (12)	−0.1443 (7)	0.3107 (10)	16.5 (12)*
T(7)	0.7403 (10)	−0.1070 (7)	0.2677 (10)	14.7 (10)*

[a] From the anisotropic thermal parameters in the form exp$[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$, the B(equivalents)'s are derived: $B(\text{eqv}) = 4.0[V^2 \det(\beta_{ij})]^{1/3}$. [b] T(1–7) are the toluene carbons. R = Cp* ring centroid.

Procedures. 1. (HOCH$_2$Ph$_2$P)$_4$Ni (1). To a flask containing (COD)$_2$Ni (250 mg, 0.910 mmol) and HOCH$_2$Ph$_2$P (785 mg, 3.63 mmol) was distilled 15 mL of diethyl ether at -78 °C. The solution was allowed to warm to room temperature and was stirred for an additional 2.5 h. Upon removal of 5 mL of Et$_2$O, filtration, and one wash with 5 mL of cold Et$_2$O, (HOCH$_2$Ph$_2$P)$_4$Ni·0.6Et$_2$O

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[31] Chamberlain, L.; Keddington, J.; Rothwell, I. P. *Organometallics* **1982**, *1*, 1098.

(1) was isolated as a bright yellow powder in 81% yield (715 mg). Varying amounts of ether were occluded in the powder, depending on the batch (checked via ^1H NMR): ^1H NMR (C_6D_6) δ 3.91 (CH_2, br m, 8 H), 4.20 (OH, br s, 4 H), 6.88 (Ph, br m, 24 H), 7.31 (Ph, br m, 16 H); $^{31}P\{^1H\}$ NMR δ 20.9 (s). Anal. Calcd for $C_{52}H_{52}O_4P_4NiZr{\cdot}1.6(C_4H_{10}O)$: C, 67.48; H, 6.19; P, 12.57. Found: C, 67.16; H, 6.07; P, 12.14.

2. Cp*Zr(μ-OCH$_2$Ph$_2$P)$_3$NiPPh$_2$CH$_2$OH (2). To a slurry of $(HOCH_2Ph_2P)_4Ni{\cdot}0.8Et_2O$ (1) (430 mg, 0.438 mmol) in 15 mL of diethyl ether at 0 °C was slowly added Cp^*ZrMe_3 (119 mg, 0.439 mmol) over a 20-min period. The immediate evolution of CH_4 was noted as the solution turned orange. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. Removal of the Et_2O yielded 435 mg of $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiPPh_2CH_2OH{\cdot}0.8Et_2O$ (2) as a yellow-orange powder (82%, ether content measured via ^1H NMR): extreme solubility prevented further purification; $^{31}P\{^1H\}$ NMR indicated 94% purity. ^1H NMR (C_6D_6) δ 2.10 ($C_5(CH_3)$, s, 15 H), 3.73 (μ-PCH_2, s, 6 H), 4.60 ($HOCH_2Ph_2P$, "t", 2 H, $^3J_{HH}$ = 6, $^2J_{PH}$ = 6 Hz), 7.34 (Ph, m, 16 H), 6.92 (Ph, m, 24 H); ^{31}P NMR δ 28.2 ($HOCH_2Ph_2P$, q, ($^2J_{PP}$ = 17 Hz); 24.3 (μ-P, d); IR ν(O–H) 3530 cm^{-1} (w).

3. Cp*Zr(μ-OCH$_2$Ph$_2$P)$_3$NiPMe$_3$ (3). Into a flask containing 268 mg (0.221 mmol) of $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiPPh_2CH_2OH{\cdot}0.8Et_2O$ (2) and 10 mL of diethyl ether at −78 °C was distilled a large excess (2–3 mL, ca. 25 mmol) of PMe_3. The reaction mixture was allowed to warm to room temperature and stirred for an additional hour. During this time, the color of the solution changed from orange to yellow and a bright yellow precipitate formed. Upon removal of 3 mL of Et_2O, filtration, and one wash with cold Et_2O, 210 mg of $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiPMe_3{\cdot}1.4Et_2O$ (3) was obtained (85%, ether content measured via ^1H NMR). Upon standing for 3 weeks under a dry nitrogen atmosphere, the ether content was <10% (^1H NMR): ^1H NMR (C_6D_6) δ 2.17 ($C_5(CH_3)_5$, s, 15 H), 3.76 CH_2, s, 6 H), 1.14 (CH_3, d, 9 H, $^2J_{PH}$ = 5 Hz), 7.62 (Ph, m, 12 H), 7.02 (Ph, m, 18 H); $^{31}P\{^1H\}$ NMR δ −24.4 (PMe_3, q, $^2J_{PP}$ = 15 Hz), 29.8 (μ-P, d). Anal. Calcd for $C_{52}H_{60}O_3P_4NiZr$: C, 62.03; H, 6.01. Found: C, 62.15; H, 6.59.

4. Cp*Zr(μ-OCH$_2$Ph$_2$P)$_3$NiP(OMe)$_3$ (4). Into a flask containing 202 mg (0.172 mmol) of $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiPPh_2CH_2OH{\cdot}0.4Et_2O$ (2) and 5 mL of diethyl ether at −78 °C was condensed 0.29 mmol of $P(OMe)_3$ from a calibrated gas bulb. The reaction mixture was allowed to warm to room temperature and stirred for 6 h. During this time, fine yellow crystals deposited. Upon removal of 2 mL of ether, filtration, and one wash with 3 mL of cold ether, 95 mg of $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiP(OMe)_3$ (4) was obtained (52%). Although the $^{31}P\{^1H\}$ NMR indicated <0.3% P-containing impurities, the complex would not analyze: ^1H NMR (C_6D_6) δ 2.17 ($C_5(CH_3)_5$, s, 15 H), 3.79 (CH_2, s, 6 H), 3.16 (CH_3, d, 9 H, $^2J_{PH}$ = 10 Hz), 7.72 (Ph, m, 12 H), 7.03 (Ph, m, 18 H); $^{31}P\{^1H\}$ NMR δ 152.4 ($P(OCH_3)_3$, q, $^2J_{PP}$ = 15 Hz), 29.3 (μ-P, d).

5. Cp*Zr(μ-OCH$_2$Ph$_2$P)$_3$NiCO (5). A flask containing 410 mg (0.340 mmol) of $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiPPh_2CH_2OH{\cdot}0.8Et_2O$ (2) and 10 mL of diethyl ether at −78 °C was opened to a manifold (1 L) filled with 200 torr (ca. 11 mmol) of CO. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The color of the solution changed from orange to pale yellow, and a pale yellow precipitate formed. Upon removal of 3 mL of Et_2O, filtration, and one 5-mL wash with cold Et_2O, 278 mg of $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiCO{\cdot}1.6Et_2O$ (5) was obtained (76%, ether content measured by ^1H NMR). ^1H NMR (C_6D_6) 2.12 ($C_5(CH_3)_5$, s, 15 H), 3.73 (CH_2, s, 6 H), 6.90 (Ph, m, 18 H), 7.58 (Ph, m, 12 H); $^{31}P\{^1H\}$ NMR δ 33.0 (s); IR ν(C≡O) 1905 cm^{-1} (s). Anal. Calcd for $C_{50}H_{51}O_4P_3NiZr{\cdot}1.6(C_4H_{10}O)$: C, 62.87; H, 6.27. Found: C, 62.63; H, 6.06.

Single-Crystal X-ray Diffraction Analysis of 5. From slow evaporation of a toluene solution containing $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiCO{\cdot}0.8Et_2O$ (5), an irregularly shaped pale yellow crystal was judged suitable for X-ray study. ^1H NMR analysis of this batch of crystals revealed that toluene was now occluded in the lattice. This single crystal of $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiCO{\cdot}C_7H_8$ ($5{\cdot}C_7H_8$), roughly 0.25 mm in diameter, was sealed in a Lindemann capillary. Preliminary X-ray diffraction photographs displayed monoclinic symmetry. Precise lattice constants, determined from a least-squares fit of 15 diffractometer measured 2θ values at 25 °C were a = 14.189 (3) Å, b = 27.603 (4) Å, c = 13.448 (3) Å, and β = 97.240 (10)°. The cell volume is 5225.0 Å^3 with a calculated density of 1.336 g/cm^3. The space group was determined to be $P2_1/n$ and the asymmetric unit consisted of $C_{57}H_{59}O_4P_3NiZr$. All unique diffraction maxima ($h,k,\pm$) with 2θ ≤ 67.7° were measured on a four-circle computer-controlled diffractometer with a variable speed, 1° ω scan using graphite-monochromated Mo Kα radiation (0.71069 Å). The agreement factor between symmetry equivalent reflections was 0.025. After correction for Lorentz, polarization, and background effects, 5866 (80%) of the 7329 reflections were judged observed ($|F_o| \geq 3\sigma(F_o)$).[32] Structure solution using the heavy-atom method proved routine.[33] The Zr and Ni were positioned from the Patterson synthesis, and the non-hydrogen light atoms were revealed in successive difference Fourier syntheses. Block-diagonal least-squares refinements (minimization of $\sum w(|F_o| - |F_c|)^2$, where w is based on counting statistics modified by an ignorance factor of ρ = 0.03) with 64 anisotropic non-hydrogen light atoms, and all hydrogens included at calculated positions have converged to a current residual (R) of 0.061 and a weighted residual (R_w) of 0.077 for the observed reflections.[34] A final difference Fourier synthesis revealed a few peaks >1 e/Å^3, but these were generally less than 1.2 Å from the metal atoms.

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Registry No. 1, 97295-94-8; 2, 97315-56-5; 3, 97295-95-9; 4, 97295-96-0; 5, 97295-97-1; $5{\cdot}C_7H_8$, 97295-98-2; Cp^*ZrMe_3, 81476-64-4; $(COD)_2Ni$, 1295-35-8; $HOCH_2Ph_2P$, 5958-44-1.

Supplementary Material Available: Tables of bond distances, bond angles, observed and calculated structure factors, fractional coordinates, and anisotropic thermal parameters (56 pages). Ordering information is given on any current masthead page.

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(32) All crystallographic calculations were done on a PRIME 850 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were as follows: REDUCE and UNIQUE, data reduction programs by M. E. Leonowicz, Cornell University, 1978; MULTAN 78, a system of computer programs for the automatic solutions of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculation including Patterson syntheses) written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978; BLS78A, an anisotropic block-diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, a crystallographic illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Centre, 1978; and BOND, a program to calculate molecular parameters and prepare tables written by K. Hirotsu, Cornell University, 1978.

(33) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor., Gen. Crystallogr.* **1968**, *A24*, 321.

(34) $R = \sum ||F_o| - |F_c||/(\sum|F_o|)$; $R_w = [\sum w|F_o| - |F_c|)^2/(\sum w|F_o|2]^{1/2}$.