Synthesis of Complex 2. A solution of complex 1 (0.28 g, 0.5 mmol) in butyl nitrite (20 mL) was charged in a Fischer–Porter tube in air. The tube was evacuated and then pressurized with ethylene to 0.6 MPa and the mixture stirred at 60 °C. After 2 h the tube was cooled and vented to atmospheric pressure. An orange-brown solid was obtained by adding pentane to the orange solution (yield 0.244 g, 95%). Anal. Calcd for $C_{18}H_{15}N_2O_3Cl_2PPd$: C, 41.90; H, 2.91; N, 5.43; Cl, 13.77; Pd, 20.00. Found: C, 42.05; H, 3.30; N, 5.75; Cl, 13.77; Pd, 20.00. IR (cm^{-1}): ν(N=O) 1550; $\nu(NO_2)$ 1435 (asym), 1315 (sym); absence of ν(P—O) of phosphine oxide at 1145.

Characterization of 3,3'-Biisoxazoline. White crystals were recrystallized in methanol/pentane; mp 172.5 °C. IR (cm^{-1}): $\nu(C—H)_{aliphat}$ 2890, 2910, 2950, 2970, 3000; ν(C=N) 1425, 1465, 1550; ν(C—C) 825, 870, 925. Anal. Calcd for $C_6H_8N_2O_2$: C, 51.42; H, 5.70; N, 19.98; O, 22.90. Found: C, 51.43; H, 5.71; N, 20.00; O, 22.86. ^1H NMR (200 MHz, $CDCl_3$): δ 3.3 (t, J = 10.6 Hz, 4 H), 4.5 (t, J = 10.6 Hz, 4 H). ^{13}C NMR: δ 33 ($-CH_2-$), 70 ($-CH_2O-$), 151 (–C=N–). MS: m/e 140 (M), 53, 139, 41, 52, 112, 80, 82, 123, 66, 109, 70.

Characterization of 1-Nitroso-2-nitropropane (mp 128.5 °C). IR (cm^{-1}): $\nu(C—H)_{aliphat}$ 2930, 2950, 2980, 3010, 3040; ν(N=O) 1550; $\nu(NO_2)$ 1565 (asym), 1395 (sym). Anal. Calcd for $C_3H_6N_2O_3$: C, 30.42; H, 5.09; N, 23.67; O, 40.70. Found: C, 30.51; H, 5.08; N, 23.73; O, 40.68. ^1H NMR (400 MHz, CD_3CN): δ 1.32 (d, J = 6.8 Hz, 3 H), 4.72 (dd, J = 16 Hz, J' = 3 Hz, 1 H), 5.07 (dd, J = 16 Hz, J'' = 10 Hz, 1 H), 5.87 (m, 1 H). MS: m/e 41, 39, 72, 42, 44, 71, 43, 88, 54, 55, 119 (M + 1), 57.

Synthesis and Reactions of Nickel and Palladium Carbon-Bound Enolate Complexes

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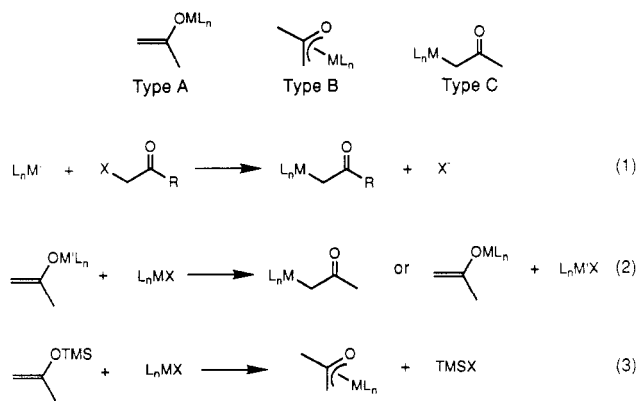
Nickel and palladium carbon-bound enolates of the general formula η^5-$C_5R_5(Ph_3P)MCHR'COR''$ (R = H, CH_3; R' = H, CH_3; R'' = *t*-Bu, Ph, O-*t*-Bu) were prepared. Cp*$(Ph_3P)NiCH_2CO_2$-*t*-Bu (**1e**) was characterized by X-ray diffraction. Compound **1e** crystallizes in the monoclinic space group $P2_1/n$ with unit-cell dimensions a = 13.6110 (20) Å, b = 12.7454 (13) Å, c = 17.8571 (23) Å, β = 105.544 (11)°, Z = 4, observed data 4091, R = 4.53%, and R_w = 4.19%. Reactions of these nickel and palladium enolates with aldehydes and other electrophilic reagents were examined. The nickel ketone enolates were shown to react with 2 equiv of benzaldehyde to deliver products resulting from a Tischtschenko-type oxidation/reduction process. $Cp(Ph_3P)NiCH_2CO$-*t*-Bu reacts with phosphines (L) to yield paramagnetic nickel(I) complexes of general formula $Cp(L)_2Ni$.

Introduction

Nickel and palladium enolates have been proposed as intermediates in numerous organic transformations.[1] Because of the usefulness of the aldol reaction for the construction of hydroxylated carbon chains, we have been interested in investigating nickel- and palladium-mediated aldol reactions. The term "enolate" is used as a generic name, applied to the tautomeric structures A, B, and C (Scheme I), implying that there is an association of the metal with the enol, 2-oxoalkyl, or η^3-oxaallyl unit. A limited number of palladium enolates have been prepared,[2,5] but nickel enolates have not yet been isolated.

Scheme I



In general, the three methods illustrated in Scheme I have previously been used for the preparation of transi-

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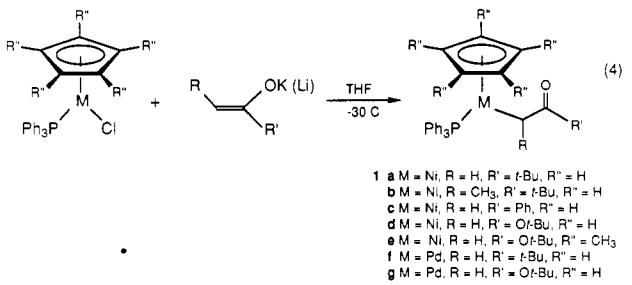
Table I. Spectroscopic Data for (η^5-C_5R_5'')(Ph_3P)MCH(R)COR'

compd no.	M	R	R'	R''	IR (KBr), cm^{-1}	proton resonance $\delta(\alpha$-$CHR)$ (J_{PH}, Hz)[a]	^{13}C resonance $\delta(J_{PC}$, Hz) α-C	carbonyl
1a	Ni	H	*t*-Bu	H	1632	1.36 (8.3)	−0.2 (13.7)[b]	227.5[d]
1b	Ni	CH_3	*t*-Bu	H	1630	1.37 (6.5)	13.6 (10.6)[b]	220.4
1c	Ni	H	Ph	H	1619	1.88 (7.9)	2.2 (14.3)[b]	206.4
1d	Ni	H	O-*t*-Bu	H	1675	0.99 (8.1)	−8.0 (18.7)[b]	182.8
1e	Ni	H	O-*t*-Bu	CH_3	1673	0.75 (8.3)	−0.9 (15.2)[a]	181.8
1f	Pd	H	*t*-Bu	H	1634	2.24 (5.3)	9.8 (6.7)[a]	220.8
1g	Pd	H	O-*t*-Bu	H	1682	2.02 (5.4)	0.8 (8.9)[a]	181.0
1h	Ni	H	CH=CH_2	H	1645	1.52 (8.0)	6.6 (13.2)[a]	196.4[c]

[a] C_6D_6. [b] THF-d_8. [c] Toluene-d_8. [d] CD_2Cl_2.

Scheme II



tion-metal enolates: (a) use of a metal anion to displace a halide or sulfonate ion from α-halo- or α-sulfonoxy carbonyl compound;[3,4] (b) use of a main-group enolate to displace halide from a metal complex;[5] and (c) reaction of an enol silane with a metal chloride or metal alkoxide.[2a,6,7] Using the second method, we have now developed a synthesis of nickel and palladium enolates in the $C_5R_5(L)MR'$ (R = H, CH_3; M = Ni, Pd) system. In this paper, we describe the synthesis, characterization, and chemistry of carbon-bound (type C) nickel and palladium enolates.

Results

Synthesis and Structural Characterization. Lithium and Grignard reagents have been shown to react with $C_5R_5(L)MX$ (R = H, CH_3; L = phosphine ligand; M = Pd, Ni; X = Cl, Br) to give $C_5R_5(L)MR'$ (R' = alkyl or aryl).[8] This procedure is useful for the high-yield preparation of the carbon-bound enolates of palladium and nickel. The following synthesis of $Cp(Ph_3P)NiCH_2CO$-*t*-Bu (**1a**) (Cp = C_5H_5, Cp* = $C_5(CH_3)_5$) is representative (see Scheme II). Addition of the potassium enolate of 3,3-dimethyl-2-butanone (pinacolone)[6] to a THF solution of Cp-(Ph_3P)NiCl at −30 °C yields, after recrystallization, dark brown crystals of **1a**; microcrystals of **1a** are forest green. Yields range from 60 to 85%. These complexes were all fully characterized by spectroscopic and analytical methods.

The carbon-bound structure is assigned on the basis of ^1H and ^{13}C NMR and infrared data; see Table I. The phosphorus–hydrogen coupling (J_{PH} = 5.3–8.3 Hz) observed in the methylene hydrogens (methine resonance for $Cp(Ph_3P)NiCH(CH_3)CO$-*t*-Bu) supports the metal–carbon bound tautomer. Organic carbonyl absorptions seen in the IR spectra at 1619–1682 cm^{-1} are also consistent with a carbon-bound enolate tautomer. Carbon-bound enolates of molybdenum, tungsten, manganese, rhenium, iron, rhodium, iridium, and palladium display organic carbonyl absorption bands[4,5,8c,9] between 1722 and 1624 cm^{-1}. Fast atom bombardment (FAB) mass spectrometry using sulfolane or *p*-nitrobenzyl alcohol matrices gave molecular

Table II. Crystal and Data Collection Parameters for 1e ($C_{34}H_{41}NiO_2P$)

(A) Crystal Parameters at −115 °C[a,b]

a = 13.6110 (20) Å	space group: $P2_1/n$
b = 12.7454 (13) Å	cryst system: monoclinic
c = 17.8571 (23) Å	fw = 419.14
α = 90.0°	Z = 4
β = 106.544 (11)°	d(calc) = 2.01 g/cm^{-1}
γ = 90.0°	μ(calc) = 7.4 cm^{-1}
V = 2969.6 (13) Å^3	

size of cryst = 0.18 × 0.19 × 0.36 mm

(B) Data Measurement Parameters

radiatn: Mo Kα (λ = 0.71073 Å)
monochromator: highly oriented graphite (2θ = 12.2°)
detector: cryst scinillation counter, with PHA
reflctns measd: $+h,+k,\pm l$
2θ range: 3°→45°
scan type: θ–2θ
scan width: $\Delta\theta$ = 0.65 + 0.35 tan θ
scan speed: 0.78–6.7 (θ, deg/min)
background: measd over 0.25($\Delta\theta$) added to each end of the scan
vertical aperture: 3.0 mm
horizontal aperture: (2.0 + 1.0 tan θ) mm
no. of reflctns collected: 4091
no of unique reflctns: 3874
no. of variables: 1721
intensity standards: (715), (474), (4411); measured every hour of X-ray exposure time; over the data collection period no decrease in intensity was observed
orientation: 3 reflctns were checked after every 100 measurements; crystal orientation was redetermined if any of the reflections were offset from their predicted positions by more than 0.1°; reorientation was not necessary during the data collection

[a] Unit-cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ near 30°. [b] In this and all tables of X-ray data, the esd's of all parameters are given in parentheses, right-justified to the least significant digit(s) given.

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Table III. Intramolecular Bond Distances (Å) for 1e

Ni-P	2.134 (1)	C28-C33	1.501 (3)
Ni-C1	2.027 (2)	C29-C34	1.500 (3)
Ni-C25	2.098 (2)	P-C7	1.835 (2)
Ni-C26	2.150 (2)	P-C13	1.834 (2)
Ni-C27	2.131 (2)	P-C19	1.842 (2)
Ni-C28	2.133 (2)	C7-C8	1.382 (2)
Ni-C29	2.171 (2)	C7-C12	1.389 (3)
Ni-Cp	1.761	C8-C9	1.387 (3)
C1-C2	1.414 (3)	C9-C10	1.380 (3)
C2-O1	1.221 (2)	C10-C11	1.375 (3)
C2-O2	1.369 (2)	C11-C12	1.379 (3)
O2-C3	1.470 (2)	C13-C14	1.378 (3)
C3-C4	1.507 (3)	C13-C18	1.388 (3)
C3-C5	1.510 (3)	C14-C15	1.391 (3)
C3-C6	1.521 (3)	C15-C16	1.366 (3)
C25-C26	1.439 (2)	C16-C17	1.374 (3)
C25-C29	1.436 (2)	C17-C18	1.386 (3)
C26-C27	1.394 (3)	C19-C20	1.384 (3)
C27-C28	1.459 (2)	C19-C24	1.391 (3)
C28-C29	1.388 (2)	C20-C21	1.384 (3)
C25-C30	1.498 (3)	C21-C22	1.391 (3)
C26-C31	1.498 (3)	C22-C23	1.369 (3)
C27-C32	1.497 (3)	C23-C24	1.396 (3)

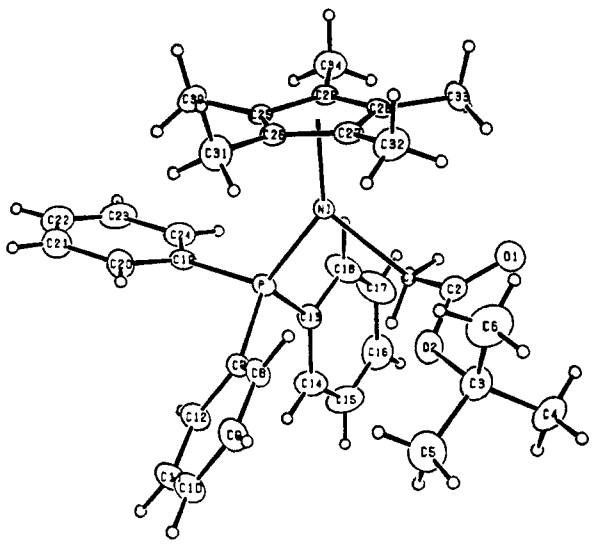

Figure 1. Perspective ORTEP diagram of **1e** illustrating the numbering scheme used in the tables. Thermal ellipsoids are scaled to represent the 50% probability surface, and the hydrogen atoms are shown as arbitrary small spheres for clarity.

ions with the appropriate isotope envelope. Satisfactory carbon and hydrogen combustion analyses were obtained for these complexes; however, phosphorus analysis sometimes gave low values.

Confirmation of the metal-carbon linkage was obtained by an X-ray crystallographic study on $Cp^*(Ph_3P)NiCH_2CO$-*t*-Bu (**1e**). Columnar crystals of complex **1e** were grown at −30 °C by diffusion of hexane into a toluene solution of the complex. X-ray data on a single crystal were collected at −115 °C under the conditions summarized in Table I. The structure was solved by Patterson methods and refined by standard least-squares and Fourier techniques. Structural refinement is described in the Experimental Section; details of the structure determination, including positional parameters and structure factors, are provided as supplementary material. Lattice parameters are listed in Table II, and relevant bond lengths and angles are listed in Tables III and IV. The ORTEP diagram shown in Figure 1 illustrates the nickel–carbon bound nature of the ester ligand; the carbonyl oxygen is not bonded to the nickel. As seen in other carbon-bound transition-metal enolate structures, the C1–C2 bond in **1e** is shorter than a normal single bond.[10] The dihedral angle between the

Table IV. Intramolecular Bond Angles (deg) for 1e

Cp-Ni-P	139.53	Ni-P-C7	113.67 (6)
Cp-Ni-C1	129.61	Ni-P-C13	112.05 (6)
C1-Ni-P	90.64 (5)	Ni-P-C19	120.54 (6)
Ni-C1-C2	119.66 (11)	C7-P-C13	106.87 (8)
O1-C2-O2	121.04 (17)	C7-P-C19	100.04 (8)
O1-C2-C1	127.32 (17)	C13-P-C19	102.07 (8)
O2-C2-C1	111.61 (15)	P-C7-C8	118.68 (13)
C2-O2-C3	121.57 (14)	P-C7-C12	122.52 (13)
O2-C3-C4	110.33 (15)	C8-C7-C12	118.54 (16)
O2-C3-C5	102.37 (15)	C7-C8-C9	120.30 (16)
O2-C3-C6	110.90 (16)	C8-C9-C10	120.44 (17)
C4-C3-C5	110.15 (17)	C9-C10-C11	119.58 (17)
C4-C3-C6	112.85 (18)	C10-C11-C12	120.03 (16)
C5-C3-C6	109.75 (18)	C7-C12-C11	121.09 (16)
C26-C25-C29	108.64 (15)	P-C13-C14	124.91 (14)
C25-C26-C27	107.05 (15)	P-C13-C18	116.61 (13)
C26-C27-C28	108.30 (15)	C14-C13-C18	118.48 (17)
C27-C28-C29	108.41 (15)	C13-C14-C15	120.65 (19)
C25-C29-C28	107.34 (15)	C14-C15-C16	120.47 (19)
C26-C25-C30	126.40 (16)	C15-C16-C17	119.48 (19)
C29-C25-C30	123.42 (16)	C16-C17-C18	120.43 (20)
C25-C26-C31	125.99 (16)	C13-C18-C17	120.45 (18)
C27-C26-C31	126.93 (17)	P-C19-C20	119.29 (13)
C26-C27-C32	126.26 (16)	P-C19-C24	121.83 (14)
C28-C27-C32	124.89 (16)	C20-C19-C24	118.84 (17)
C27-C28-C33	124.84 (16)	C19-C20-C21	121.17 (18)
C29-C28-C33	126.61 (17)	C20-C21-C22	119.50 (19)
C25-C29-C34	124.27 (16)	C21-C22-C23	120.03 (18)
C28-C29-C34	128.35 (17)	C22-C23-C24	120.43 (19)
		C19-C24-C23	120.02 (19)

planes containing C1–C2–O1 and P–Ni–C1 is 119.70 (0.07)°. Interaction of a nickel d orbital with the carbonyl π^*-orbital in effect lowers the carbonyl stretching frequency. This type of β-effect is seen in several other transition-metal enolate complexes.[3,11]

The pentamethylcyclopentadienyl ligand is clearly distorted toward an η^1–η^4-cyclobutadienide configuration. C25 is somewhat closer to nickel than the other ring carbon atoms and oriented trans to the ester ligand. In addition, the C26–C27 (1.394 (3) Å) and C28–C29 (1.388 (2) Å) bond lengths are shorter than the C26–C27 bond length (1.459 (2) Å). Bercaw observed this type of bonding mode in the Cp* ligand of a tungsten oxo complex.[12]

The ketone enolates of nickel are sensitive to air and moisture and do not withstand chromatography. The nickel ester enolates **1d** and **1e**, however, are more robust and can be chromatographed on alumina to remove impurities. Unlike the nickel enolate complexes, the palladium analogues are air-stable burgundy solids.

Reaction of Nickel Enolates with Alkylating and Silylating Agents. Alkylation of nickel enolate **1a** with iodomethane results in formation of $Cp(Ph_3P)NiI$ (74%) and 2,2-dimethyl-3-pentanone (33%, ethyl *tert*-butyl ketone) in C_6D_6 after 2 days at 45 °C. The reaction of **1a** with methyl tosylate at 45 °C for 6 days resulted in decomposition of **1a** to pinacolone (47%), and 95% of the methyl tosylate remained unchanged. Pearson has shown that methyl tosylate reacts slowly (or not at all) with transition-metal reagents that undergo alkylation by an electron-transfer mechanism.[13]

Addition of trimethylchlorosilane to **1a** leads to cleavage of the Ni–C bond and production of $Cp(Ph_3P)NiCl$ (73%

(10) See inter alia: Matieson, A. M.; Welsch, H. *Acta Crystallogr.* **1965**, *18*, 953. Vloon, W. J.; Hottentot, D.; Overbeek, A. R.; Stam, C. H. *Acta Crystallogr.* **1979**, *35*, 119. Huisgen, T.; Ott, H. *Tetrahedron* **1959**, *6*, 253.

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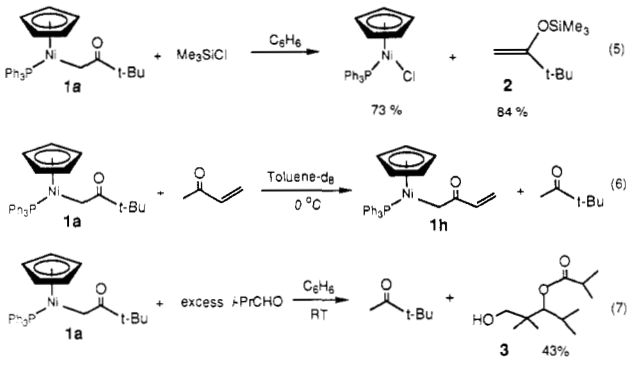
(13) Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541–1547.

Scheme III



isolated) and the enol silane **2** (84% by integration versus an internal standard, Scheme III).[14] The enol silane does not undergo Lewis acid promoted aldol condensation with benzaldehyde under the reaction conditions. Trimethylchlorosilane and **1d** do not react at ambient temperature or at 55 °C but could be induced to react slowly at 110 °C. After 2 days at 110 °C, 16% $Cp(Ph_3P)NiCl$ had formed; 67% of **1d** remained unreacted, but black metal had deposited on the reaction vessel walls. Enol silanes or other organic products were not observed. The palladium enolate **1g** and trimethylchlorosilane do not react at 55 °C.

Reaction of $Cp(Ph_3P)NiCH_2CO$-*t*-Bu (1a) with Weakly Acidic Proton Sources. The nickel ketone enolates are protonated by weak acids such as phenol and *tert*-butyl alcohol. When a solution of **1a** and alcohol in C_6D_6 was monitored by ^1H NMR spectrometry, we observed formation of 2,2-dimethyl-3-butanone (pinacolone) but no recognizable resonances for nickel-containing products. EPR spectra of reaction solutions showed the presence of paramagnetic decomposition products. Although we were unable to isolated any nickel alkoxides, we were able to isolate a nickel thiolate from a similar reaction. Treatment of **1a** with 1 equiv of thiophenol gave $Cp(Ph_3P)NiSPh$ in 42% yield after recrystallization.

Enolizable aldehydes and ketones donate a proton to $Cp(Ph_3P)NiCH_2CO$-*t*-Bu, liberating pinacolone and forming an enolate of the proton donor. This acid–base exchange process provides a synthetic route to nickel enolates that are otherwise inaccessible. For example, nickel enolate **1h** was prepared by allowing $Cp(Ph_3P)NiCH_2CO$-*t*-Bu and methyl vinyl ketone to react at 0 °C in toluene-d_8 (Scheme III). After 5 days 1 equiv of pinacolone and 64% of **1h** had formed (based on ^1H NMR integration versus an internal standard). Because of the sensitivity of **1h**, it was isolated in only 24% yield, as a dark green crystalline solid. Relevant spectral characteristics of **1h**, listed in Table I, demonstrate its carbon-bound structure. The IR absorption for the carbonyl group appears at 1645 cm^{-1} and coupling to phosphorus is observed in the ^1H and ^{13}C NMR spectra. The exchange process also occurs with acetophenone to give **1c**.

With enolizable aldehydes, a nickel aldehyde enolate is presumably formed. For example, reaction of isobutyryaldehyde and **1a** resulted in a complex mixture of products, of which the aldehyde self-condensation product **3** (shown in Scheme III), was isolated in 43% yield based on **1a**.

Reaction of Nickel Enolates with Phosphines: Formation of Paramagnetic M–C Bond Cleavage Products. Addition of tri-*n*-butylphosphine to $Cp(Bu_3P)NiCl$ results in the formation of the cationic nickel complex $Cp(Bu_3P)_2Ni^+Cl^-$.[15] If this ionization could be induced in nickel enolates by phosphines, one would expect that the resulting bis(phosphine)nickel/enolate ion pair would rapidly react with electrophilic substrates. To test this hypothesis, we added triphenylphosphine to a C_6D_6 solution of $Cp(Ph_3P)NiCH_2CO$-*t*-Bu (**1a**). Monitoring the reaction by ^1H NMR spectrometry showed initial formation of a small amount of pinacolone that increased over several hours as the amount of **1a** decreased. New nickel-containing products were not observed in the ^1H NMR spectra, and no solid precipitated from the solution.[16] Analysis of the ^1H and ^{13}P NMR spectra suggested rapid exchange of triphenylphosphine with an unobservable complex, since resolution of the ortho protons of free triphenylphosphine was lost while coupling to the ortho protons of the phosphine coordinated to **1a** were resolved. Furthermore, $^{31}P\{^1H\}$ NMR spectra (Figure 2) showed a sharp peak for coordinated phosphine at δ 43.3 and a broad resonance between δ −6 and δ −8 (width at half height, 100 Hz) due to uncoordinated phosphine. In addition, all resonances were slightly broadened, possibly indicating the presence of a paramagnetic species.

Observation of a solution of perdeuterated triphenylphosphine and **1a** in toluene-d_8 showed sharp phosphorus resonances for **1a** at δ 43.9 (PPh_3-d_{15}) and 43.3 (PPh_3). Again the uncoordinated phosphine (PPh_3-d_{15} and -d_0) was seen as a broad peak. Variable-temperature NMR spectra

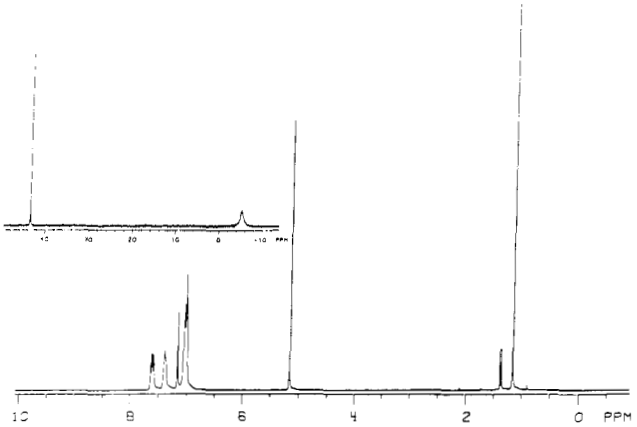
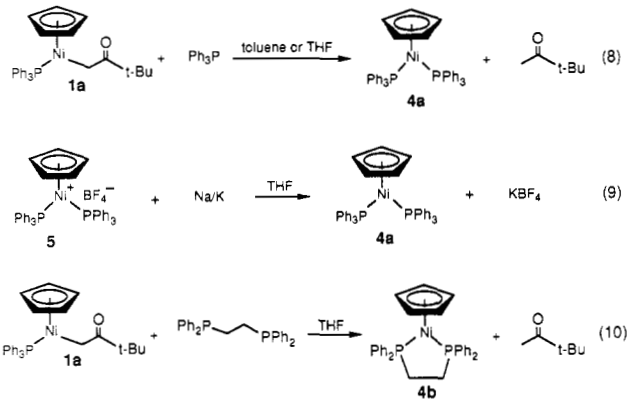


Figure 2. ^1H and $^{31}P\{^1H\}$ (inset) NMR spectra of $Cp(Ph_3P)NiCH_2CO$-*t*-Bu and Ph_3P in C_6D_6.

Scheme IV



(14) Cleavage of the nickel enolate by silyl chloride is competitive with reaction of nickel enolate and benzaldehyde; therefore, a mixture of silyl enol ether and benzoate aldol products is produced.

(15) (a) Sato, M.; Sato, F.; Yoshida, T. *J. Organomet. Chem.* **1971**, *26*, C49–C50. (b) Treichel, P. M.; Shubkin, R. L. *Inorg. Chim. Acta* **1968**, *2*, 485.

(16) $Cp(Ph_3P)_2Ni^+BF_4^-$ is nearly insoluble in C_6D_6.

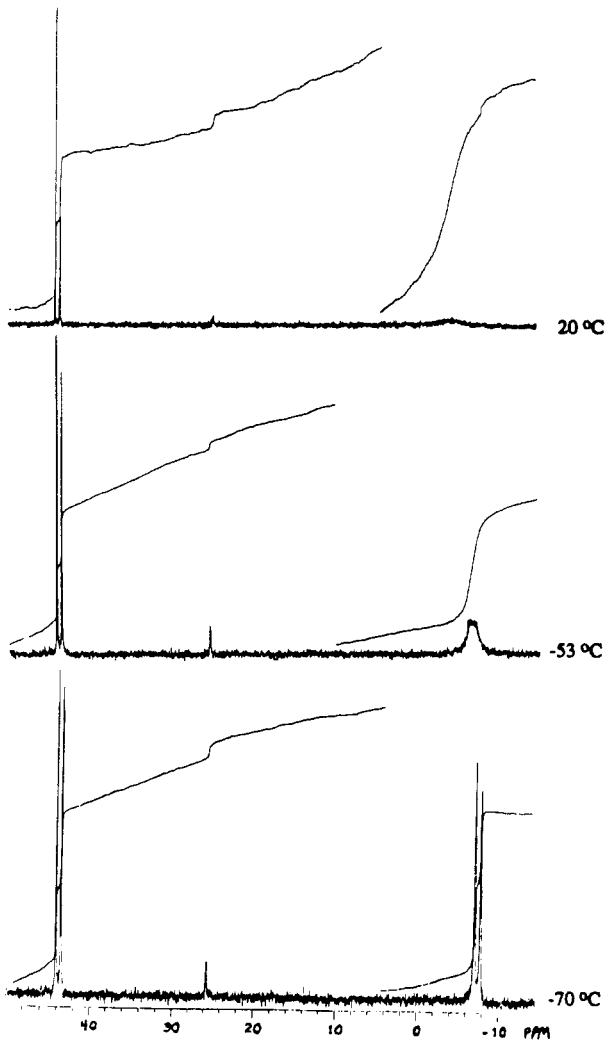


Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR spectrum of Cp-$(Ph_3P)NiCH_2CO$-*t*-Bu (d_0 and d_{15}) and Ph_3P (d_0 and d_{15}).

showed decoalescence at −70 °C of this broad peak to two distinct peaks at δ −7.17 (PPh_3-d_{15}) and −7.86 (PPh_3) (see Figure 3).

To gain information on the apparently paramagnetic product of this reaction, we conducted a series of EPR studies. At 22 °C, an EPR spectrum of a toluene solution of triphenylphosphine and **1a** revealed a signal with hyperfine splitting into three resonances in approximately a 1:2:1 intensity: g = 2.074; a = 0.0108 cm^{-1} (Figure 4). We assign this signal to $Cp(Ph_3P)_2Ni(1)$ (**4a** in Scheme IV); coupling of the unpaired electron on nickel to the equivalent phosphorus nuclei gives the observed 1:2:1 triplet. Addition of triphenylphosphine to the acetophenone enolate **1c** also forms **4a**. In contrast, ester enolate **1d** and triphenylphosphine did not give any detectable EPR signals or show signs of decomposition in ^1H NMR spectra of the reaction solution.

$Cp(Ph_3P)_2Ni$ has been mentioned in the literature, but spectra were not presented.[17] Therefore, an independent synthesis of $Cp(Ph_3P)_2Ni$ was developed. Reduction of $Cp(Ph_3P)_2Ni^+BPh_4^-$ (**5**) with Na/K in THF (reaction 2 in Scheme IV) gave a brown solution which displayed an EPR spectrum that matched the spectrum obtained from **1a** and triphenylphosphine. We were unable to isolate **4a** from

(17) (a) Bermudez, G.; Pletcher, D. *J. Organomet. Chem.* **1982**, *231*, 173–177. (b) Barefield, E. K.; Krost, D. A.; Edwards, D. S.; VanDerveer, D. G.; Trytko, R. L.; O'Rear, S. P.; Williamson, A. N. *J. Am. Chem. Soc.* **1981**, *103*, 6219–6222.

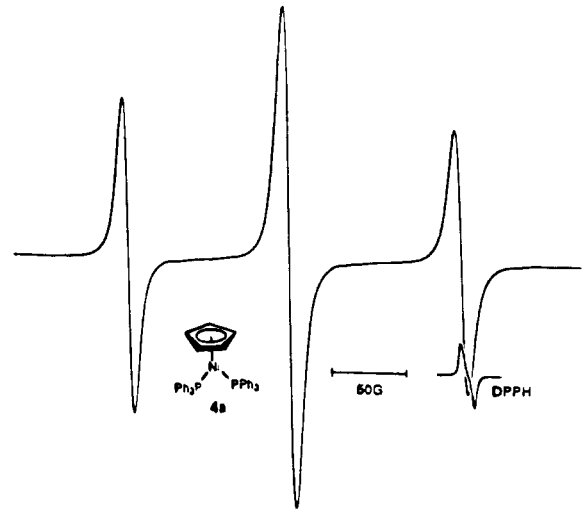


Figure 4. X-Band EPR spectrum of $Cp(Ph_3P)_2Ni(1)$ in toluene at 22 °C (g = 2.074, a = 0.0108 cm^{-1}) with the following parameters of modulation amplitude (G), microwave power (dB), and receiver gain: 10, 12, 2.0 × 10^4. The DPPH resonance (external standard, g = 2.0037) is included on the spectrum.

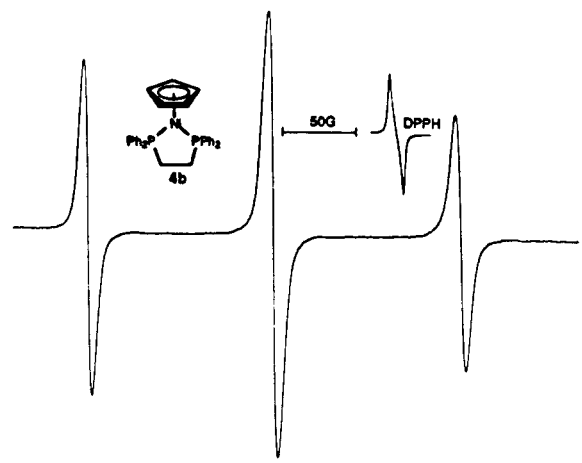


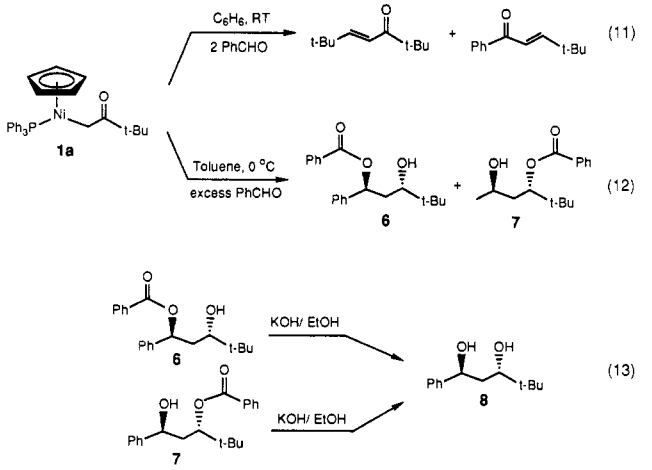
Figure 5. X-Band EPR spectrum of $Cp(Ph_2PCH_2CH_2PPh_2)Ni(1)$ in THF at 22 °C (g = 2.050, a = 0.0120 cm^{-1}) with the following parameters of modulation amplitude (G), microwave power (dB), and receiver gain: 10, 12, 4.0 × 10^4. The DPPH resonance (external standard, g = 2.0037) is included on the spectrum.

reaction mixtures because of its facile disproportionation to Cp_2Ni and $(PPh_3)_4Ni$.[17]

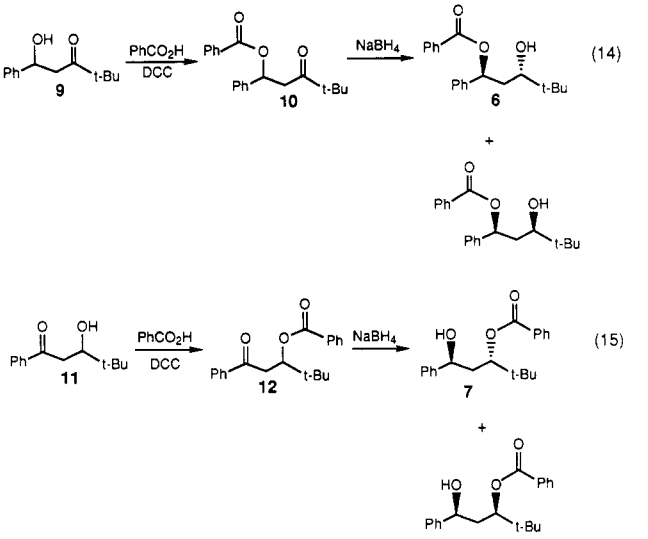
To investigate the possibility that pinacolone α-carbonyl radicals might be involved as intermediates in the reaction, 1,4-cyclohexadiene and triphenylphosphine were added to a solution of **1a** in C_6D_6, and the reaction was monitored by ^1H NMR spectrometry. After 2 days at ambient temperature, pinacolone (16%) and benzene (16%) had formed and nickel enoalte **1a** (84%) remained unchanged. To confirm 1,4-cyclohexadiene's ability to trap pinacolone radicals, a solution of hexaphenyldistannane, 1,4-cyclohexadiene, and α-bromopinacolone were irradiated in C_6D_6 at 6 °C. As expected, we observed 82% pinacolone, 17% α-bromopinacolone, 16% 1,4-cyclohexadiene, and 84% benzene in the ^1H NMR spectrum after 50 min of irradiation.

As further evidence for the formation of a nickel(1) complex in the nickel enolate/phosphine reaction, 1,2-bis(diphenylphosphino)ethane was added to **1a** in THF. As determined by ^1H NMR spectrometry, **1a** was completely consumed within 24 h and the resulting EPR spectrum showed three resonances in a 1:2:1 pattern with g = 2.050 and a = 0.0120 cm^{-1} (Figure 5); this agrees quite

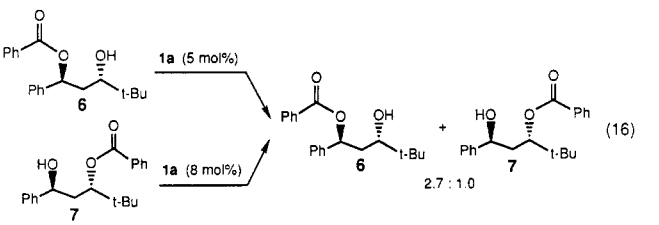
Scheme V



Scheme VI



Scheme VII



well with published spectra of **4b**.[17b]

Reaction of $Cp(Ph_3P)NiCH_2CO$-*t*-Bu (1a) and Benzaldehyde. Treatment of $Cp(Ph_3P)NiCH_2CO$-*t*-Bu (**1a**) with 2 equiv of benzaldehyde in benzene-d_6 at ambient temperature resulted in a complex mixture of organic products in about 8 h. Monitoring the reaction by ^1H NMR spectrometry showed disappearance of the reactants and appearance of two broad peaks at δ 3.2 and 3.4. Over the course of the reaction these broad peaks became smaller and resonances from the organic products increased. We suspect these broad peaks are due to a paramagnetic[18] or a fluxional nickel intermediate. By ^1H NMR analysis, the final major products are the isomeric enones *trans*-PhCOCH=CH-*t*-Bu and *trans*-PhCH=CHCO-*t*-Bu (see Scheme V). The formation of enone products can be reduced by use of a 5–10-fold excess of benzaldehyde and by keeping the reaction solution at 0 °C in toluene-d_8 or THF-d_8 instead of benzene-d_6. Under these reaction conditions, broad peaks are observed at intermediate stages in the ^1H NMR spectrum, but in this case, two different organic products identified as **6** and **7** (Scheme V; see below) are formed along with minor amounts of other products. Similar product mixtures are formed when the reaction is conducted in THF-d_8.

After acidic workup, isolation by chromatography on silica gel gave minor amounts of α,β-unsaturated ketones, benzyl alcohol, and the two major organic products **6** and **7**. The expected aldol product $PhCH(OH)CH_2CO$-*t*-Bu was detected at the level of 2–5% yield in several crude reaction mixtures. The combined isolated yield ranged from 59 to 67%; however, the ratios of **6** and **7** depended on the length of the reaction time, implying an equilibration.

Compounds **6** and **7** show hydroxyl and ester carbonyl absorptions at 3531 and 1705 cm^{-1} for isomer **6** and 3518 and 1699 cm^{-1} for isomer **7**. The presence of an ester functionality is supported by the carbonyl resonance in the ^{13}C NMR spectrum at δ 166.56 (compound **6**) and 167.83 (compound **7**). Confirmation of the structures of these materials and assignment of the relative stereochemistry of the alcohol and ester groups was determined by hydrolysis of **6** and **7**; each pure ester gave anti diol **8** (reaction 13 in Scheme V). Spectroscopic data for this compound matched with those of authentic **8** prepared by reduction of $PhCH(OH)CH_2CO$-*t*-Bu (**9**) with $NaBH_4$.[19]

In order to establish the location of the benzoate group in each of these compounds, we independently prepared both the "benzyl" benzoate **6** and the "neopentyl" benzoate **7**. The synthesis of these esters was not straightforward. Attempts to prepare the benzoate esters from the corresponding aldol and benzoyl chloride (or benzoic acid) with base (triethylamine) resulted in the production of α,β-unsaturated ketones. Trapping the anion of aldol **9** with benzoyl chloride provided only a small amount of **10**. A higher yield method was devised by using the mild esterification procedure of Hassner and Alexanian.[20] Reaction of aldol **9** with benzoic acid, dicyclohexylcarbodiimide (DCC), and a catalytic amount of (dimethylamino)pyridine (DMAP) in diethyl ether gave "benzyl" benzoate **10** in 89% yield (Scheme VI). The transformation of **11** to **12** was performed in the same way (43% yield, 22% recovery of **11**). Reduction of the ketone functionality in **10** and **12** with $NaBH_4$ in ethanol/ether gave a mixture of syn and anti monoesters of the corresponding diols. Following separation by chromatography, the spectroscopic data of the syn and anti compounds were compared to the products from the nickel-mediated reaction, establishing that the anti benzoates were the products formed from **1a** and benzaldehyde. No evidence for the syn benzoates was found in the reaction mixtures of the nickel enolate reaction before or after workup.

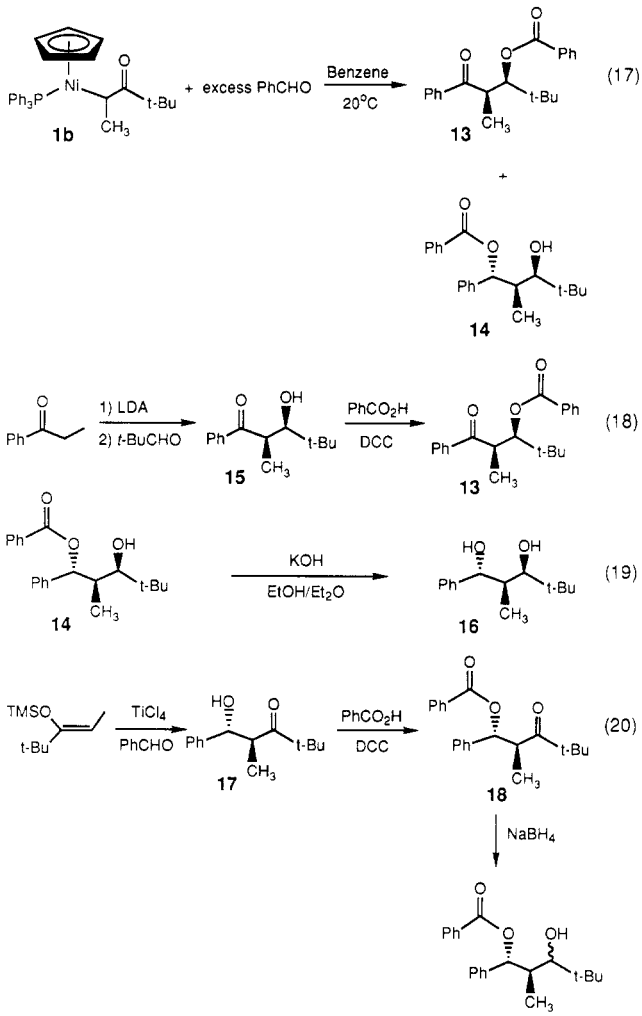
Quenching the nickel enolate/benzaldehyde reaction immediately after the disappearance of **1a** gives benzyl benzoate **6** as the major regioisomer. However, when the reaction mixture is allowed to stand at 0 °C for 4–8 h after the disappearance of **1a**, the more hindered "neopentyl" benzoate **7** is the major regioisomer. This apparent isomerization was investigated further by adding a catalytic amount of **1a** to pure **6**. When the reaction is monitored by ^1H NMR spectrometry, pinacolone and a mixture of **6**

(18) ^1H NMR resonances were not observed for the paramagnetic complex $Cp(Ph_3P)_2Ni(1)$, but EPR spectra of reaction solutions showed resonances for $Cp(Ph_3P)_2Ni(1)$.

(19) Kiyooka, S. I.; Kuroda, H.; Shimasaki, Y. *Tetrahedron Lett.* **1986**, *27*, 3009–3012.

(20) Hassner, A.; Alexanian, V. *Tetrahedron Lett.* **1978**, *46*, 4475–4478.

Scheme VIII



and **7** was observed. After 35 h, the ratio of **6** to **7** was 1.0:2.7 (Scheme VII). Resonances for nickel intermediates were not seen in ^1H or $^{13}P\{^1H\}$ NMR spectra. As expected, the "neopentyl" benzoate **7** was also isomerized to a 1.0:2.7 ratio of **6** to **7** by a catalytic amount of **1a**. In order to observe and possibly isolate the nickel intermediate, 1 equiv of **1a** and benzoate **6** were combined. Broad peaks between δ 3.2 and δ 3.5 were seen in the ^1H NMR spectrum along with a mixture of regioisomers of **6** and **7** and pinacolone. Before the reaction reached completion, β-elimination of the incipient nickel alkoxide gave some keto ester **12**. Several attempts to isolate a nickel alkoxide from this mixture were unsuccessful. In an effort to generate a nickel aldolate complex independently, a mixture of 0.15 equiv of **1a** and $PhCH(OH)CH_2CO$-*t*-Bu (**9**) was monitored by ^1H NMR spectrometry. This showed disappearance of **1a** and formation of pinacolone but no resonances that could be attributed to $Cp(Ph_3P)NiOCH(Ph)CH_2CO$-*t*-Bu. Within 1 h at 20 °C, the aldol **9** was converted to α,β-unsaturated ketone.

Reaction of $Cp(Ph_3P)NiCH(CH_3)CO$-*t*-Bu (1b) with Benzaldehyde. The secondary alkyl nickel enolate $Cp(Ph_3P)NiCH(CH_3)CO$-*t*-Bu (**1b**) and benzaldehyde react to give somewhat different products than those obtained from **1a** and at a much slower rate (typically 2 days at ambient temperature). The two products shown in Scheme VIII were obtained in a ratio varying from 9:1 to 1.7:1.0 in an overall yield ranging from 61 to 90%. The minor and major isomers were separated by liquid chromatography on silica gel.

The structure of the major product **13** was assigned on the basis of the following evidence. The presence of ester and ketone moieties were indicated by IR absorptions at 1718 and 1683 cm^{-1}; an OH stretching absorption was not observed. Resonances due to carbonyl groups were observed at δ 165.74 and 201.21 in the ^{13}C NMR spectrum. Analysis of the aryl region of the ^1H NMR spectrum, which showed two sets of doublets at δ 7.99 and 8.11, suggested that the ketone and ester were both attached to aryl groups.[21] Unfortunately, hydrolysis of the benzoate **13** gave a mixture of dehydrated products and β-hydroxy ketone that had apparently epimerized at the α-position. Therefore, the relative stereochemistry of the methyl and benzoate groups was determined by the synthetic sequence illustrated in reaction 18 of Scheme VIII. The spectral and analytical properties of syn benzoate **13** prepared by DCC coupling of benzoic acid and *syn*-β-hydroxy ketone **15** matched exactly with those of the major product obtained in the nickel reaction.

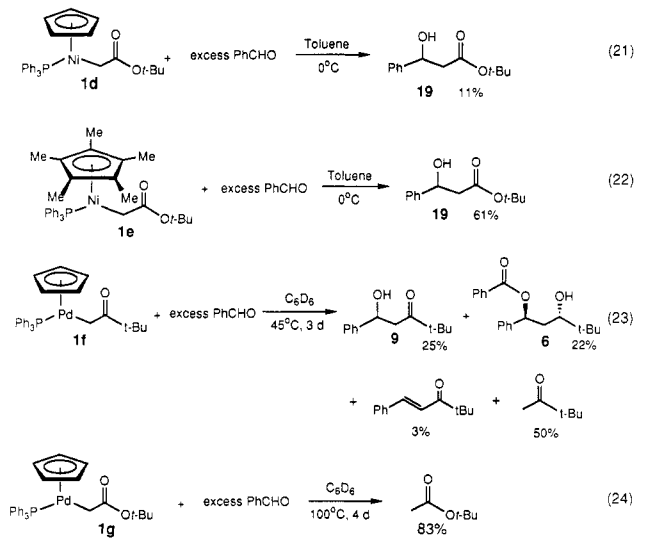
The minor isomer of the reaction of **1b** with benzaldehyde is the diol monoester **14**. The IR spectrum of this compound shows an OH stretching absorption at 3515 cm^{-1} and an ester carbonyl stretch at 1723 cm^{-1}. Presence of an ester functionality was also indicated by the resonance at δ 165.8 ppm in the ^{13}C NMR spectrum and the ortho protons at δ 8.06 in the ^1H NMR spectrum. By comparison of the chemical shifts of carbinol protons with several esters and alcohols of similar structure we concluded that the doublet at δ 3.56 was due to a carbinol proton adjacent to a *tert*-butyl group and the doublet at δ 5.89 was due to a benzylic proton of the esterified benzyl alcohol. The relative stereochemistry of the three stereocenters was tentatively assigned by analogy to those observed in the products of the reaction of **1a** with benzaldehyde and the stereochemistry of the major isomer **13**. Hydrolysis of **14** gave the diol **16**, which was identical with the minor diastereomer produced in the reduction of aldol **15** with $NaBH_4$. For absolute confirmation of the regiochemistry, **14** was prepared independently as illustrated in reaction 20 of Scheme VIII. The $NaBH_4$ reduction of **18** gave **14** as the minor diastereomer.

Reactions of Nickel Ester Enolates and Palladium Ketone and Ester Enolates with Benzaldehyde. The reactivity of ester enolates of nickel is quite different from that of the nickel ketone enolates. The former are nearly as unreactive as the analogous nickel alkyl compounds. For example, heating $Cp(Ph_3P)NiCH_3$ and benzaldehyde in C_6D_6 at 85 °C for 14 days gave no detectable organic products and 34% of the $Cp(Ph_3P)NiCH_3$ remained unreacted. Similarly, as shown in reaction 21 of Scheme IX, benzaldehyde and **1d** were heated to 110 °C for 9 h to yield the aldol product **19** in only 11% isolated yield; no benzoate esters were formed. The (pentamethylcyclopentadienyl)nickel derivative **1e** was slightly more reactive requiring only 6 days at 45 °C and yielding 61% of aldol **19** (Scheme IX, reaction 22). An organometallic product was also formed but was not characterized.

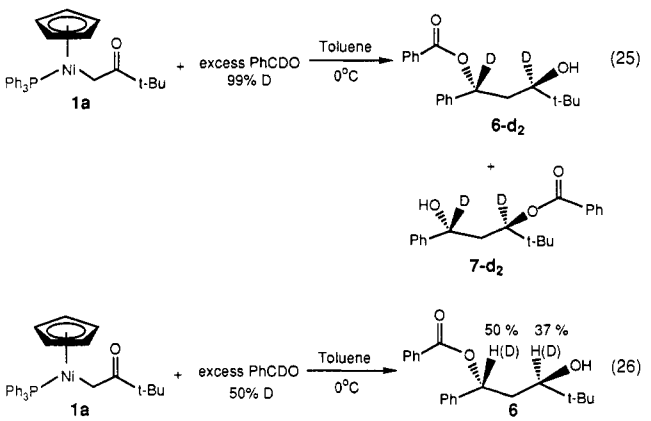
The palladium ketone and ester enolates are also very unreactive. To achieve aldol condensation, heating to 45 °C for 3 days was required to bring about reaction of **1f** and benzaldehyde. The products shown in Scheme IX (reaction 23) were formed in the following amounts: **6** (22%), **9** (25%), *trans*-PhCH=CHCO-*t*-Bu (3%), and

(21) Due to its electron-withdrawing character, a carbonyl group attached to an aryl ring shifts the ortho protons downfield approximately 0.5–0.7 ppm. Pretsch, E.; Seibl, J.; Simon, W.; Clerc, T. *Tables of Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag: Berlin, 1983; p H260.

Scheme IX



Scheme X



pinacolone (50%). Prolonged heating of palladium ester enolate complex **1g** with benzaldehyde at 85 °C for 12 days resulted in decomposition of the complex; aldol products were not detected in the reaction mixture by ^{1}H NMR spectrometry or after workup. *tert*-Butyl acetate could be accounted for in only 83% (Scheme IX, reaction 24).

Isotope Studies of the Nickel-Mediated Aldol Condensation/Reduction. To obtain more information about the hydride transfer leading to **6** and **7**, nickel enolate **1a** and benzaldehyde-d_1 (>99% deuterated at the aldehyde position) were allowed to react in toluene-d_8 at 0 °C. Analysis of the reaction products by ^{1}H and ^{2}H NMR spectrometry after isolation showed >98% deuteration at the methine positions in **6**-d_2 and **7**-d_2, as illustrated in Scheme X. Deuterium was not incorporated at the methylene position.

In a competition experiment, nickel enolate **1a**, 11 equiv of benzaldehyde-d_0, and 11 equiv of benzaldehyde-d_1 were allowed to react in toluene at 0 °C. Analysis of the product **6**-d_2 (the major product in this reaction) showed 50% deuterium incorporation at the benzylic position (carbon 1), which demonstrates that there is no isotope effect in the insertion of the first equivalent of benzaldehyde. At the neopentyl position (carbon 3), 37% deuterium incorporation was observed, giving a kinetic isotope effect of 1.70.

Discussion

Nickel and palladium 2-oxoalkyl complexes (M–C bound enolates) have been prepared in high yield by treatment of metal halides with alkali-metal enolates. These compounds have been characterized by spectroscopic and analytical techniques and by X-ray crystallography in the case of nickel ester enolate **1e**. We have found that the nickel ester enolates and the palladium complexes are quite robust in comparison to the nickel ketone enolates. The nickel ketone enolates react thermally with electrophilic reagents such as methyl iodide and trimethylchlorosilane and are protonated by weak acids. The latter property was utilized to prepare a nickel enolate of methyl vinyl ketone (MVK) by reaction of **1a** with MVK.

The formation of the paramagnetic complex **4a** from **1a** and phosphine was a surprising result. Nickel alkyl complexes and ester **1d** do not undergo thermal cleavage of the nickel–carbon bond, although (η^5-Cp)(PR_3)Ni(η^1-Cp) complexes have been postulated to lose of cyclopentadienyl radical upon addition of a second phosphine.[17] Barefield was unable to prepare a nickel(1) complex from the addition of excess phosphine to $Cp(Ph_2PCH_3)NiCH_2Ph$.[17b] However, he has shown that the reaction of nickelocene and phosphine gives $Cp(PR_3)Ni(1)$. Our radical trapping experiments showed that ketyl radical can be trapped by 1,4-cyclohexadiene in reactions of **1a** with phosphine. Thus, we believe addition of phosphine to complex **1a** induces a homolytic cleavage of the Ni–C bond.

The reaction of nickel complex **1a** with benzaldehyde was extensively studied. The isolated products **6** and **7** resemble the diol monoester compounds formed in the Tischtschenko reaction of aldehydes and a metal alkoxide.[22] We propose that the reactions of this nickel enolate with benzaldehyde take place by the mechanism illustrated in Scheme XI. In step 1, benzaldehyde coordinates to **1a** and then inserts into the Ni–C bond giving **21**. In step 3, a second insertion of aldehyde leads to **22**. Subsequent hydride transfer gives the nickel alkoxide **23**. Possible structures for intermediate **20** are illustrated at the bottom of Scheme XI. Complex **20a** is formally a 20-electron complex and may exist in a η^3-Cp form **20b** or as the square planar η^1-Cp isomer[23] **20c**. Alternatively, triphenylphosphine may dissociate prior to aldehyde coordination. Addition of phosphine to the nickel enolate in the presence of benzaldehyde appeared to have no effect on the rate of the aldol condensation/reduction; however, this result is difficult to interpret because of the decomposition of **1a** to $Cp(Ph_3P)Ni(1)$ in the presence of phosphine.

Studies on the secondary alkyl enolate **1b** gives us some insight into the carbon–carbon bond forming step. The anti stereochemistry of the ester and methyl groups in **14** is a consequence of the initial carbon–carbon bond forming step. Aldol reactions involving an open[24b,c] transition state lead to an anti stereochemistry and those involving a closed[24a] transition state lead to syn stereochemistry of the aldol products with enolates and enol silanes derived from ethyl *tert*-butyl ketone. If this step proceeds by attack of an oxygen-bound enolate on benzaldehyde, then an open

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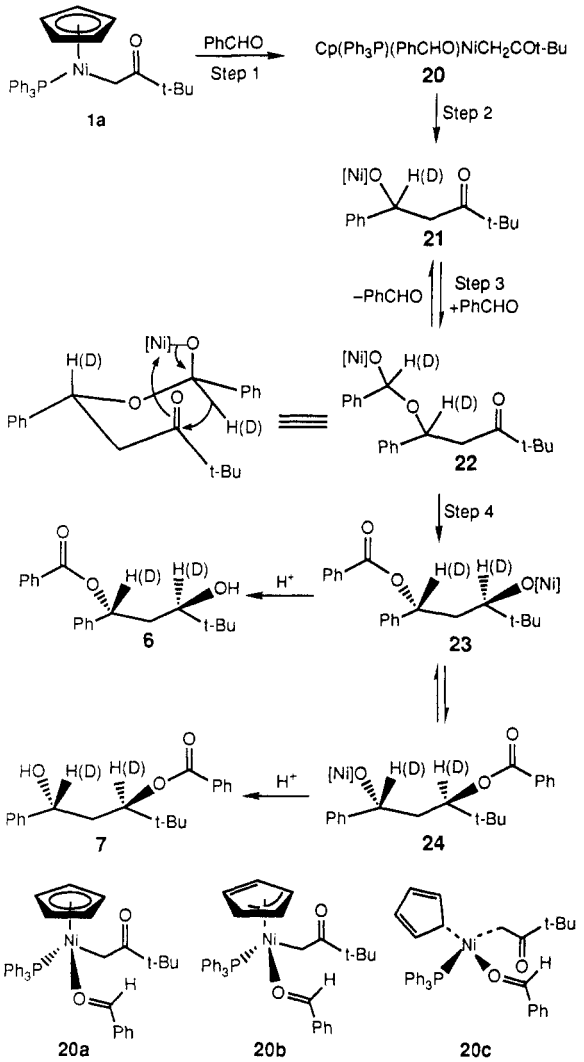
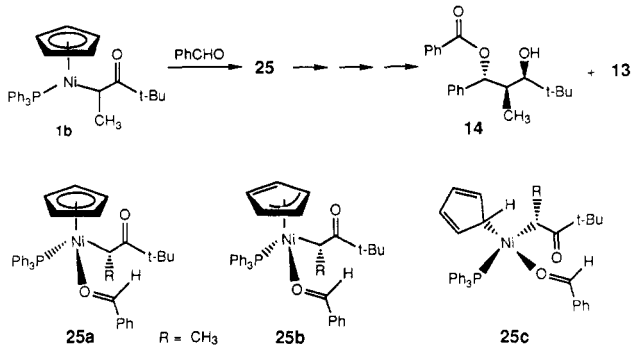
Scheme XI



transition state may be involved. However, we have no direct evidence for the intermediacy of a nickel–oxygen bound enolate; this bond forming step may proceed via migratory insertion of the C-bound enolate to coordinated aldehyde. The geometry of the intermediate involved may determine the orientation of the coordinated aldehyde prior to insertion and thus influence the product stereochemistry. Three proposed geometries for this intermediate, analogous to those illustrated for the unsubstituted system in Scheme XI (**20a–c**), are shown in Scheme XII. In complexes **25a** and **25b**, the coordinated aldehyde would probably orient itself with the phenyl group as far as possible from the bulky triphenylphosphine and cyclopentadienyl ligands. In addition, the methyl group of the enolate would prefer an orientation avoiding interactions with the Cp ring and the coordinated aldehyde. Insertion of aldehyde from either of these structural geometries (**25a** or **25b**) would give the observed anti stereochemistry in the resulting aldolate. Due to the relatively unhindered environment in the square-planar complex **25c**, the aldehyde could coordinate with either face of the aldehyde proximal to the enolate. A number of geometric isomers can be drawn for this square-planar complex if one considers the relative stereochemistry of the η^1-Cp ligand and the placement (cis instead of trans to the enolate) of the phosphine ligand. If the energy differences of these orientations are small, insertion would lead to a mixture of syn and anti diastereomers. Whether the nickel enolate reacts through a C-bound or O-bound form is a moot point

Scheme XII



if the aldehyde insertion is a reversible step because in this case the anti product observed may simply result from thermodynamic control.[24a] Without further evidence we cannot conclude which pathway is operative.

Our isotope competition study revealed no isotope effect for the first aldehyde insertion into the nickel–carbon bond. The absence of an isotope effect is expected, since only a hybridization change occurs and C–H or C–D bonds are not broken. After the initial benzaldehyde insertion, two steps are involved: (a) reaction of a second equivalent of benzaldehyde with **21** to give **22** and then (b) transfer of hydride (deuteride) to the carbonyl carbon to produce **23**. Since the insertion of the second benzaldehyde is a reaction very similar to the first benzaldehyde insertion, the isotope effect in this step should also be small, leading to a prediction of 50% deuterium incorporation in intermediate **21**. If intermediate **21** then were to immediately transfer hydride (deuteride) to the carbonyl carbon, **6** should also show 50% deuterium incorporation. However, we observe 37% deuterium incorporation in compound **6**. To account for this result, we propose that **21** and **22** are in equilibrium. The observed isotope effect than reflects the preferred intramolecular transfer of hydride over deuteride in the step leading to **23**. If **21** and **22** are in equilibrium, we also suspect an equilibration of aldolates **20** and **21**.

Another possible mechanism for step 4 (Scheme XI) should be considered. This is the possibility that a nickel hydride is generated (e.g. $Cp(Ph_3P)NiH$), and this is responsible for reduction of the carbonyl group in **6**. Nickel hydrides have been proposed as intermediates in many reactions, but isolated nickel hydrides are rare; in the cyclopentadienyl system, only $Cp(Cy_3P)NiH$ has been isolated.[25] Spectral evidence for a diamagnetic nickel hydride species in our reaction solutions has not been observed. However, nickel hydrides may arise from β-elimination of a nickel alkoxide to produce compound **13**. A small amount of benzyl alcohol is observed in the ^1H NMR spectrum of our crude reaction mixtures; they may result from reaction of benzaldehyde with a nickel hydride. However, the stereochemistry of the reduced aldol products provides evidence against a nickel hydride route for formation of these compounds. The reduction of β-hydroxy carbonyl compounds by various hydride sources has shown that a mixture of syn and anti products is produced with the syn isomer predominating.[19,26] Therefore, even though a small amount of nickel hydride may be present in our reaction mixtures, it is unlikely that the major pathway leading to the anti stereochemistry observed in **6** involves intermolecular reduction by nickel hydride.

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Thus, the most likely pathway in our system involves the intramolecular hydride transfer represented schematically in Scheme XI. This process is similar to that involved in the Meerwein–Ponndorf–Verley reduction of organic carbonyl compounds by aluminum alkoxides[27] and in the Tischtschenko reaction.[22] A six-membered-ring transition state for the hydride-transfer step places the *tert*-butyl and phenyl group in equatorial positions and gives the observed product **6** after hydrolysis of the nickel complex. In addition, this conformation places the nickel in a position to coordinate to the ketone, enhancing its electrophilicity. The anti stereochemistry of the carbinol atoms in **14**, formed from the secondary enolate **1b**, provides added evidence for intramolecular hydride transfer.

Product **7** is a regioisomer of **6** that we propose results from transesterification. We have shown that **6** isomerizes to **7** (and vice versa) with the addition of a catalytic amount of **1a**. In the reaction of **1a** and **6**, pinacolone is formed, presumably along with nickel alkoxide **23**. This equilibrates with **24** and then is protonated to give **7**. Unfortunately we were unable to obtain direct evidence for these nickel alkoxide intermediates.

The reactions of nickel ketone enolates appear to be limited to reactions of nonenolizable aldehydes. Reaction of **1a** with isobutyraldehyde gave an "esterol" product (**2**) similar to products **6** and **7**. Formation of isobutyraldehyde condensation product **2** can be rationalized by formation of a nickel aldehyde enolate followed by insertion of 2 equiv of aldehyde and then hydride transfer.

Conclusion

We have prepared a number of palladium and nickel C-bound enolates and studied their reactivity toward electrophilic substrates. The palladium enolates were found to be much less reactive than their nickel counterparts. Although the applicability of nickel enolates in organic synthesis is limited by the complicated nature of their reactions with aldehydes, we have uncovered some intriguing reactions of these compounds.

Experimental Section

General Data. All manipulations involving air-sensitive materials were performed under nitrogen or argon using Schlenk or vacuum line techniques[28] or in a Vacuum Atmospheres 553-2 inert-atmosphere glovebox equipped with a MO-40-1 inert gas purifier and −30 °C freezer.

Air-sensitive materials were exposed only to thoroughly dried and degassed solvents. Tetrahydrofuran (THF), diethyl ether, toluene, and benzene were distilled from Na/benzophenone under a nitrogen atmosphere. Hexane and pentane were distilled from CaH_2 under a nitrogen atmosphere. THF-d_8, toluene-d_8, and benzene-d_6 were stirred over Na/benzophenone and then transferred under vacuum prior to use. Acetone-d_6 and $CDCl_3$ were dried over molecular sieves. Methylene-d_2 chloride was dried over CaH_2 and vacuum transfered prior to use. Methyl iodide (Aldrich) was dried over Na/Pb alloy (Fluka) and distilled onto molecular sieves and copper wire. Benzaldehyde (Alfa), pinacolone (Aldrich), acetophenone (Aldrich), isobutyrlaldehyde (Aldrich), and pivaldehyde (Aldrich) were distilled before use. Nickelocene (Alfa) was sublimed. Triphenylphosphine (Mallinckrodt) was recrystallized from hexane; bis(diphenylphosphino)ethane (Aldrich) and methyl tosylate (Aldrich) were recrystallized from THF/hexane. Benzaldehyde-d_1,[29] ethyl *tert*-butyl ketone,[30] pentamethylcyclopentadienyllithium,[31] (pentamethylcyclopentadienyl)trimethyltin,[32] $(Ph_3P)_2NiCl_2$,[33] $[(Ph_3P)PdX_2]_2$ (X = Br, Cl),[34] potassium enolate of acetophenone and ethyl *tert*-butyl ketone,[6] lithium enolate of *tert*-butyl acetate,[35] and compounds **9**, **11**, **15**,[36] **16**,[37] **19**[35] were prepared accoring to published procedures. Other reagents were used as received.

^1H NMR spectra were recorded with use of a Bruker AM 400 (400 MHz), AM 500 (500 MHz), or a 300 MHz instrument assembled by Rudi Nunlist at the University of California, Berkeley (UCB), NMR facility. Chemical shifts are reported in units of parts per million (δ) with residual protons in the solvent as an internal standard (benzene-d_6, 7.15 ppm; methylene-d_2 chloride, 5.32 ppm; THF-d_8, 3.58 ppm; toluene-d_8, 2.09 ppm), except $CDCl_3$ for which tetramethylsilane was used as an internal standard. Significant ^1H NMR data are tabulated in order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), number of protons, and coupling constants in hertz. Hexamethyldisiloxane (Aldrich) was used as an internal standard in NMR tube reactions. All $^{13}C\{^1H\}$ NMR spectra were recorded at 75.5 MHz and are referenced by using the ^{13}C resonance of the solvent as an internal standard (methylene-d_2 chloride, 53.8 ppm; THF-d_8, 67.4 ppm; chloroform-d, 77.0 ppm; benzene-d_6, 128.0 ppm; toluene-d_8, 20.4 ppm). All $^{31}P\{^1H\}$ NMR spectra were recorded at 121.5 MHz and are reported in units of parts per million (δ) downfield from external 85% phosphoric acid (H_3PO_4) at 0 ppm. The ^2H NMR spectra (76.8 MHz) were recorded unlocked with a Bruker AM-500 spectrometer. Chemical shifts are relative to deuterium (natural abundance) in chloroform. X-band EPR spectra were recorded in toluene or THF with a Bruker ER200D-SRC instrument at 22 °C. Spectra were calibrated to external diphenylpicrylhydrazide (DPPH) at $g = 2.0037$. Solution infrared spectra were recorded in 0.025-mm NaCl cells with a Perkin-Elmer 1550 Fourier transform infrared spectrophotometer. IR data are reported as (solvent) cm^{-1}, intensity (s, strong; m, medium; w, weak), and are calibrated with polystyrene (1601 cm^{-1}). UV/vis spectra were recorded with a Hewlett-Packard Model 8450A spectrophotometer. Samples were prepared in a drybox, and spectra were recorded by using a quartz cell fused to a Kontes vacuum stopcock. Fast atom bombardment (FAB) mass spectra were recorded at the UCB mass spectral facility with a Kratos MS-50 (low-resolution) mass spectrometer using sulfolane or *p*-nitrobenzyl alcohol matrix. Elemental analyses were performed by the Microanalytical Laboratory operated by the College of Chemistry at UCB. Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are corrected only for thermometer distortion. Air-sensitive samples were sealed in capillary tubes under nitrogen. Flash column chromatographic separations by the method of Still, Kahn, and Mitra, were carried out by using either silica gel (Merck, 400 mesh) or Alumina (activity II) under nitrogen pressure.[38] Gas chromatographic analyses were preformed on a Hewlett-Packard 5890A gas chromatograph with a 30-m fused silica capillary (0.25 mm) column with DB-5 liquid phase (J and W Scientific) and interfaced to a Hewlett-Packard 3393A electronic integrator.

"Glass bombs" refer to cylindrical, medium, or heavy walled Pyrex vessels joined to Kontes K826510 high-vacuum Teflon

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stopcocks. Gas phase measurements were performed by measuring the pressure in known-volume bulbs with a MKS Baratron attached to a high vacuum line.

The X-ray crystal structure was solved by Patterson methods and refined by standard least-squares and Fourier techniques.[39] Peaks corresponding to the expected positions of most of the hydrogen atoms were found by difference Fourier techniques; hydrogens were included in the structure factor calculations in their expected positions but were not refined in least squares.

Potassium Enolate of Pinacolone. Pinacolone (3.0 mL, 0.024 mol) was added over 5 min to a toluene solution of potassium bis(trimethylsilyl)amide (30 mL of 15 wt %, 0.023 mol) at −78 °C in a 100-mL "Airless" flask. The solution was stirred at −78 °C for 30 min and then allowed to warm to room temperature while the solvent was removed under vacuum. The light yellow solid was slurried in hexane and filtered. The resulting off-white powder was rinsed with 5 mL of cold (−30 °C) 1:1 toluene/hexane and then dried under vacuum. The white solid (2.7 g, 87%) was stored in a drybox freezer at −30 °C with no noticeable decomposition after several months: IR (Nujol) 3091 (w), 1560 (s), 1456 (m), 1421 (m), 1385 (m), 1216 (m), 1196 (m), 1006 (m), 704 (s) cm^{-1}; IR (THF-d_8) 3093 (w), 2964 (m), 1567 (s), 1479 (m), 1456 (m), 1409 (m), 1302 (m), 1349 (m), 1297 (m), 1217 (m), 1199 (m) cm^{-1}; ^1H NMR (THF-d_8) δ 1.02 (s, 9), 2.71 (s, 1), 3.13 (s, 1); ^{13}C NMR (THF-d_8) δ 30.26, 38.62, 65.32, 182.53.

Cp(Ph$_3$P)NiCl. The method of Cross and Wardle[40] was used to prepare Cp(Ph$_3$P)NiCl in 85% yield from the metathesis reaction of Cp_2Ni and $(Ph_3P)_2NiCl_2$ in refluxing THF: mp 165–167 °C; IR (KBr) 3048 (m), 1480 (m), 1434 (s), 1397 (m), 1094 (s), 788 (s), 749 (s), 703 (s), 694 (s), 532 (s), 510 (s), 499 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 4.94 (s, 5), 7.00 (s, 9), 7.91 (m, 6); ^1H NMR (CS_2) δ 4.89 (s, 5), 7.32 (m, 9), 7.67 (m, 6); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 30.01. Literature values reported: mp 141 °C dec; ^1H NMR (CS_2) δ 4.91.

Cp(Ph$_3$P)NiBr. Preparation of Cp(Ph$_3$P)NiBr using the method of Cross and Wardle[40] yielded purple-red crystals in 61% yield: mp 157.5–158 °C; IR (KBr) 1480 (m), 1437 (s), 1097 (s), 1067 (m), 787 (s), 747 (s), 695 (vs), 535 (vs), 513 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 4.99 (s, 5), 6.99 (m, 9), 7.86 (m, 6); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 35.64. Literature data:[41] ^1H NMR (C_6D_6) δ 5.1.

Cp*(Ph$_3$P)NiBr. Cp*(Ph$_3$P)NiBr was prepared in 32% yield by the method of Yamazaki and Mise:[8b] mp 217–218 °C dec; IR (KBr) 1571 (m), 1479 (s), 1377 (m), 1156 (m), 1094 (s), 1068 (m), 1020 (m), 755 (s), 745 (s), 697 (s), 533 (s), 510 (s), 488 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 1.42 (d, 15, J_{PH} = 1.5), 7.13 (m, 9), 8.02 (m, 6); ^{13}C NMR (C_6D_6) δ 10.18, 104.27, 128.10 (d, J = 8.6), 129.59, 134.25, 135.27 (d, J = 11.4); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 40.68. Literature[8b] data: mp 209–211 °C dec; ^1H NMR (C_6D_6) δ 1.33 (J_{PH} = 1.6), and analysis.

Cp(Ph$_3$P)PdBr. The best method for the preparation of Cp(Ph$_3$P)PdBr uses a modification of the method of Yamazaki and Mise.[8b] $CpSn(CH_3)_3$ (35.5 mg, 0.155 mmol) was added to a stirred slurry of $[(Ph_3P)PdBr_2]$ (72.0 mg, 0.0689 mmol) in THF at room temperature. Within 2 h the orange solution became green and no solid $[(Ph_3P)PdBr_2]_2$ remained. (*Note*: Cp(Ph$_3$P)PdBr and Me_3SnBr react if allowed to stir longer than 2 h.) The solution was filtered through a short column of silica gel and eluted with ether. The solvent was removed under vacuum, and the resulting green solid was recrystallized from toluene/pentane at −40 °C. Dark green crystals of product were filtered and rinsed with pentane leaving 56.5 mg (80.4%). A second crop (12.5 mg, 27.8%) was obtained at −40 °C after concentration of the filtrate and addition of more pentane. Upon attempted melting, the crystals turned black at 138 °C but did not melt up to 255 °C: IR (KBr) 3053 (w), 1480 (m), 1436 (s), 1096 (s), 827 (m), 748 (s), 694 (s), 533 (s), 512 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 5.39 (d, 5, J_{PH} = 2.55), 6.98 (m, 9), 7.76 (m, 6); ^1H NMR (CS_2) δ 5.40 (J_{PH} = 2.5), 7.00 (m, 9), 7.78 (m, 6); ^{13}C NMR (C_6D_6) δ 101.61 (d, J_{PC} = 2.9), 128.48 (d, J_{PC} = 10.9), 130.64 (d, J_{PC} = 2.7), 133.89 (d, J_{PC} = 49.0), 134.62 (d, J_{PC} = 12.1); ^{13}P NMR (C_6D_6) δ 31.81. Anal. Calcd for $C_{23}H_{20}BrPPd$: C, 53.78; H, 3.92; Br, 15.55; P, 6.03. Found: C, 53.81; H, 4.03; Br, 15.38; P, 5.82. Literature[8b] data: mp 129–130 °C dec; ^1H NMR (CS_2) δ 5.42 (J_{PH} = 2.5).

Cp(Ph$_3$P)PdCl. A procedure analogous to that used in the preparation of Cp(Ph$_3$P)PdBr was employed to prepare Cp(Ph$_3$P)PdCl in 46% yield. The green crystals became black at 140 °C and did not melt up to 255 °C: IR (KBr) 3052 (w), 1480 (m), 1436 (s), 1096 (s), 827 (m), 768 (m), 749 (s), 695 (s), 532 (vs), 513 (s), 498 (m), 301 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 5.35 (s, 5), 6.99 (m, 9), 7.78 (m, 6); ^{13}C NMR (C_6D_6) δ 101.45 (d, J_{PC} = 2.65), 128.54 (d, J_{PC} = 11.16), 130.68 (d, J_{PC} = 2.35), 133.50 (d, J_{PC} = 49.2), 134.46 (d, J_{PC} = 6.98), ^{31}P NMR (C_6D_6) δ 47.47. Neither satisfactory elemental analyses nor EI mass spectra could be obtained on this complex. However, exact masses were determined for three ions in the molecular ion envelope using fast atom bombardment (FAB) mass spectrometry with *p*-nitrophenyl *n*-octyl ether employed as the matrix: calcd for $C_{23}H_{20}ClPPd$, 466.0031, 467.0042, 468.0019; found, 466.0030, 467.0052, 468.0039.

Cp(Ph$_3$P)NiCH$_2$CO-*t*-Bu (1a). The potassium enolate of pinacolone (152.8 mg, 1.144 mmol) was added as a solid to a solution of Cp(Ph$_3$P)NiCl (467.2 mg, 1.108 mmol) in 20 mL of THF at −30 °C. The dark purple-red solution immediately became dark brown. The solution was kept at −30 °C for 3 h and then was warmed to room temperature while the solvent was removed under vacuum. The gummy solid remaining was dissolved in toluene and filtered through Celite (diatomateous earth) to remove KCl. Pentane (10 mL) was layered over the brown solution followed by chilling to −30 °C. After several days, the dark brown crystals (297 mg, 55.2%) were filtered from the solution and rinsed with pentane and the residual solvent was removed under vacuum. A second crop of crystals (176 mg, 32.7%) was obtained upon chilling the concentrated filtrate: mp 119–127 °C (with decomposition); IR (KBr) 1632 (s), 1434 (s), 788 (s), 745 (s), 696 (s), 533 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 1.14 (s, 9), 1.36 (d, 2, J_{PH} = 8.33), 5.15 (s, 5), 6.98 (m, 9), 7.62 (m, 6); ^1H NMR (THF-d_8) δ 0.87 (s, 9), 0.94 (d, 2, J_{PH} = 7.88), 4.95 (s, 5), 7.37 (m, 9), 7.67 (m, 6); ^1H NMR (CD_2Cl_2) δ 0.90 (s, 9), 0.97 (d, 2, J_{PH} = 7.24), 4.98 (s, 5), 7.43 (m, 9), 7.66 (m, 6); ^{13}C NMR (THF-d_8) δ −0.17 (d, J_{PC} = 13.7), 28.76, 93.92 (d, J_{PC} = 1.4), 129.54 (d, J_{PC} = 9.9), 130.76 (d, J_{PC} = 1.5), 134.10, 134.59 (d, J_{PC} = 11.5), 227.49; $^{31}P\{^1H\}$ NMR (THF-d_8) δ 38.97; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 43.3; MS (FAB, sulfolane) 484 (M^+, 40%), 385 (100%); UV/vis (C_6H_6) λ 452 (ϵ = 1168), 672 (81). Anal. Calcd for $C_{29}H_{31}NiOP$: C, 71.78; H, 6.44; P, 6.38. Found: C, 72.01; H, 6.28; P, 6.71.

Cp(Ph$_3$P)NiCH(CH$_3$)CO-*t*-Bu (1b). Compound **1b** was prepared in 81% yield by a procedure analogous to that used for **1a**: mp 108–109 °C; IR (KBr) 3060 (w), 2962 (m), 1630 (s), 1620 (s), 1480 (m), 1440 (m), 1366 (m), 1346 (m), 1120 (s), 1100 (s), 968 (m), 800 (s), 760 (s), 705 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 1.23 (s, 9), 1.37 (d, 3, J = 6.50), 1.69 (dq, 1, J = 6.50, 14.40), 5.08 (s, 5), 7.02 (m, 9), 7.60 (m, 6); ^1H NMR (THF-d_8) δ 0.89 (d, 3, J = 6.40), 0.94 (s, 9), 1.45 (dq, 1, J = 6.40, 14.1), 4.88 (s, 5), 7.43 (m, 9), 7.65 (m, 6); ^{13}C NMR (THF-d_8) δ 13.61 (d, J_{PC} = 10.8), 28.95, 42.70, 94.68 (d, J_{PC} = 1.77), 128.66 (d, J_{PC} = 9.69), 130.80 (d, J_{PC} = 1.85), 133.76 (d, J_{PC} = 42.23), 134.52 (d, J_{PC} = 11.08), 220.39; $^{31}P\{^1H\}$ NMR (THF-d_8) δ 43.47; MS (FAB, *p*-nitrobenzyl alcohol) 498 (M^+, 75%), 385 (100%); UV/vis (C_6H_6) λ 460 (ϵ = 964), 670 (64). Anal. Calcd for $C_{30}H_{33}NiOP$: C, 72.17; H, 6.66; P, 6.20. Found: C, 72.47; H, 6.87; P, 5.85.

Cp(Ph$_3$P)NiCH$_2$COPh (1c). The potassium enolate of acetophenone[6] (47.6 mg, 0.301 mmol) was added to Cp(Ph$_3$P)NiBr (134.5 mg, 0.2886 mmol) in THF (10 mL) at −40 °C. The dark purple-red solution was allowed to warm to room temperature while being stirred. After 1 h at ambient temperature, the brown solution was filtered to remove KCl and concentrated under vacuum to 8 mL. Pentane was layered over the solution, and it was chilled to −40 °C. Brown crystals of Cp(Ph$_3$P)NiCH$_2$COPh (113 mg, 77.5%; mp 109–110.5 °C) were collected by filtration and rinsed with pentane. A second crop (9.7 mg, 6.6%) was obtained by concentration of the filtrate and crystallization at −40 °C: IR (KBr) 1619, 1435, 1265, 696, 534 cm^{-1}; ^1H NMR (C_6D_6) δ 1.88 (d, 2, J_{PH} = 7.94), 4.98 (s, 5), 7.00 (m, 9), 7.11 (m, 3), 7.67 (m, 6), 7.90 (m, 2); ^1H NMR (THF-d_8) δ 1.47 (d, 2, J_{PH} = 7.85), 4.82 (s, 5), 7.23 (m, 3), 7.42 (m, 9), 7.60 (m, 2), 7.71 (m, 6); ^{13}C NMR (THF-d_8) δ 2.23 (d, J_{PC} = 14.3), 93.80 (d, J_{PC} = 1.9), 128.31 (d, J_{PC} = 15.2), 129.15 (d, J_{PC} = 9.9), 130.88 (d, J_{PC} = 2.1), 130.96,

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134.68 (d, J_{PC} = 11.3), 134.69, 206.43; $^{31}P\{^1H\}$ NMr (C_6D_6) δ 43.62; MS (FAB, sulfolane) 504 (M^+, 46%); 385 (100%), 320 (35%); UV/vis (C_6H_6): λ 460 (ε = 1260), 674 (92). Anal. Calcd for $C_{31}H_{27}NiOP$: C, 73.70; H, 5.39; P, 6.13. Found: C, 73.70; H, 5.46; P, 5.77.

Cp(Ph_3P)NiCH$_2$CO$_2$-*t*-Bu (1d). The lithium enolate of *tert*-butyl acetate (36.0 mg, 0.295 mmol) in 1 mL of THF was added to a solution of Cp(Ph_3P)NiCl (116 mg, 0.275 mmol) in 8 mL of THF at −30 °C. Removal of the THF in vacuo, followed by crystallization of the crude product from toluene/pentane at −30 °C, yielded 90.9 mg (66.1%) of dark green crystals, mp 122–134 °C. This complex crystallized with 0.5 equiv of pentane/molecule of **1d** in the lattice (confirmed by integration of ^1H NMR spectra and analysis): IR (KBr) 1675 (s), 1480 (m), 1436 (s), 1244 (s), 1168 (s), 1096 (s), 1050 (m), 963 (m), 786 (m), 755 (m), 746 (s), 697 (s), 535 (s), 513 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 0.99 (d, 2, J_{PH} = 8.08), 1.56 (s, 9), 5.23 (s, 5), 7.02 (m, 9), 7.69 (m, 6); ^1H NMR (THF-d_8) δ 0.47 (d, 2, J_{PH} = 7.99), 1.46 (s, 9), 5.03 (s, 5), 7.38 (m, 9), 7.67 (m, 6); ^{13}C NMR (THF-d_8) δ −8.02 (d, J_{PC} = 18.7), 28.97, 77.03, 93.10 (d, J_{PC} = 4.4), 130.74 (d, J_{PC} = 2.1), 134.73 (d, J_{PC} = 11.8), 135.23, 182.83; $^{31}P\{^1H\}$ NMR (THF-d_8) δ 37.08; MS (FAB, *p*-nitrobenzyl alcohol) 500 (M^+, 30%), 444 ($M^+ - C_4H_8$, 25%), 385 (100%). Anal. Calcd for $C_{29}H_{31}NiO_2P \cdot C_5H_{12}$ (average of two runs): C, 70.39; H, 6.94; P, 5.76. Found: C, 70.78; H, 6.81; P, 5.83.

Cp*(Ph_3P)NiCH$_2$CO$_2$-*t*-Bu (1e). The lithium enolate of *tert*-butyl acetate (20.6 mg, 0.169 mmol) was added to a solution of Cp*(Ph_3P)NiBr (73.2 mg, 0.136 mmol) in THF (5 mL) at −30 °C. After 12 h at −30 °C, the dark red solution was allowed to warm to room temperature and the THF was removed under vacuum. The product was dissolved in 1:1 toluene/hexane and filtered to remove LiBr. When the dark red solution was chilled to −30 °C, brown crystals formed. These crystals were filtered and rinsed with hexane, and the residual solvent was removed under vacuum leaving 25.4 mg (36%) of **1e**, mp 154–159 °C dec. The filtrate was stripped of solvent and redissolved in toluene/hexane. A second crop of 11.5 mg of dark powder was obtained for a combined yield of 52%: IR (KBr) 3048 (w), 2916 (w), 1673 (s), 1482 (w), 1452 (w), 1434 (m), 1362 (w), 1293 (m), 1166 (m), 1107 (m), 1094 (w), 1036 (w), 774 (w), 697 (s), 534 (s), 514 (w) cm^{-1}; ^1H NMR (C_6D_6) δ 0.75 (d, 2, J_{PH} = 8.25), 1.40 (s, 9), 1.57 (d, 15, J_{PH} = 1.02), 7.06 (m, 9), 7.77 (m, 6); ^1H NMR (toluene-d_8) δ 0.64 (d, 2, J_{PH} = 8.28), 1.38 (s, 9), 1.55 (d, 15, J_{PH} = 1.12), 7.06 (m, 9), 7.73 (m, 6); ^{13}C NMR (C_6D_6) δ −0.88 (d, J_{PC} = 15.2), 9.99, 28.93, 76.46, 100.89 (d, J_{PC} = 2.3), 127.91 (d, J_{PC} = 5.6), 129.52 (d, J_{PC} = 1.6), 133.45 (d, J_{PC} = 40.2), 134.94 (d, J_{PC} = 11.6), 181.75; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 50.44; MS (FAB, *p*-nitrobenzyl alcohol) 570 (M^+, 20%); 455 (75%); 308 (base). Anal. Calcd for $C_{34}H_{41}NiO_2P$: C, 71.47; H, 7.23; P, 5.42. Found: C, 71.60; H, 7.30; P, 4.90.

Cp(Ph_3P)PdCH$_2$CO-*t*-Bu (1f). The potassium enolate of pinacolone (15.8 mg, 0.114 mmol) was added to a solution of Cp(Ph_3P)PdBr (57.9 mg, 0.113 mmol) in THF (5 mL) at −30 °C. The dark green solution of Cp(Ph_3P)PdBr became dark brown upon addition of the enolate anion. After 6 h at −30 °C, the THF was removed under vacuum while the solution was warmed to ambient temperature. The crude product was dissolved in toluene (5 mL) and was filtered through Celite. Hexane (10 mL) was layered onto the brown solution, and the solution was chilled to −30 °C. A brown solid (10.0 mg) was collected and found to be impure palladium enolate based on the ^1H NMR spectrum. A second crop of pure **1f** (21.6 mg, 36.5%) was obtained by addition of more hexane (10 mL) to the filtrate: mp 124–127 °C dec; IR (KBr) 1634 (s), 1435 (m), 1153 (m), 1095 (m), 746 (m), 696 (s), 534 (s), 512 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 1.20 (s, 9), 2.24 (d, 2, J_{PH} = 5.3), 5.66 (d, 5, J_{PH} = 1.6), 7.00 (m, 9), 7.53 (m, 6); ^{13}C NMR (C_6D_6) δ 9.85 (d, J_{PC} = 6.66), 28.96, 43.47, 100.41 (d, J_{PC} = 2.55), 128.41 (d, J_{PC} = 10.54), 130.30 (d, J_{PC} = 1.85), 133.85, 134.23 (d, J_{PC} = 12.71), 220.80; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 38.87; MS (FAB, sulfolane) 532 (M^+, 30%), 467 (90%), 433 (base). Anal. Calcd for $C_{29}H_{33}PdOP$: C, 65.36; H, 5.86; P, 5.81. Found: C, 64.81; H, 5.89; P, 3.15. Despite repeated attempts, improvement in these values could not be obtained.

Cp(Ph_3P)PdCH$_2$CO$_2$-*t*-Bu (1g). The lithium enolate of *tert*-butyl acetate (29 mg, 0.024 mmol) was added to a THF (5 mL) solution of $CpPh_3PPdCl$ (94 mg, 0.20 mmol) at −30 °C. The dark green solution became dark red-brown as the reaction proceeded. After 2 h at −30 °C, the THF was removed under vacuum while warming the reaction solution was warmed to room temperature. The brown oil was dissolved in toluene and filtered through Celite. Diffusion of hexane into the toluene solution at −30 °C gave dark red-brown crystals (95 mg, 87%). Recrystallization from diethyl ether/hexane yielded 93 mg (85%) of pure Cp(Ph_3P)PdCH$_2$CO$_2$-*t*-Bu from two crops: mp 143–144 °C; IR (KBr) 3055 (w), 2973 (w), 1682 (s), 1480 (w), 1436 (m), 1363 (w), 1237 (s), 1168 (s), 1096 (m), 1079 (m), 763 (m), 753 (m), 695 (s), 532 (s), 511 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 1.54 (s, 9), 2.02 (d, 2, J_{PH} = 5.38), 5.74 (d, 5, J_{PH} = 1.8), 6.99 (m, 9), 7.60 (m, 6); ^{13}C NMR (C_6D_6) δ 0.83 (d, J_{PC} = 8.9), 28.74, 77.17, 99.23 (d, J_{PC} = 2.5), 128.46 (d, J_{PC} = 10.6), 130.31 (d, J_{PC} = 2.0), 134.35 (d, J_{PC} = 12.9), 134.43 (d, J_{PC} = 45.9), 181.00; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 42.40; MS (FAB, sulfolane) 548 (M^+, 35%), 483 (75%), 427 (80%), 263 (base). Anal. Calcd for $C_{29}H_{31}O_2PPd$: C, 63.45; H, 6.38. Found: C, 63.80; H, 6.82.

Cp(Ph_3P)NiSPh. Thiophenol (20 μL, 0.19 mmol) was added to Cp(Ph_3P)NiCH$_2$CO-*t*-Bu (59 mg, 0.12 mmol) in toluene (5 mL) under nitrogen. After the brown solution was stirred 23 h at ambient temperature, hexane (20 mL) was layered over the solution and it was cooled to −78 °C. Dark green crystals formed after several hours; these were filtered off and then rinsed with hexane, leaving 43 mg. Recrystallization of these crystals from toluene/hexane at −30 °C yielded 25 mg (42%) of dark green crystals: mp 172–173 °C; IR (KBr) 3048 (w), 1575 (m), 1480 (m), 1471 (m), 1434 (s), 1098 (s), 788 (s), 754 (s), 736 (s), 736 (m), 702 (s), 689 (s), 536 (s), 512 (m), 494 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 5.11 (s, 5), 6.98 (m, 13), 7.74 (m, 7); ^1H NMR (CD_2Cl_2) δ 5.11 (s, 5), 6.88 (m, 3), 7.36 (m, 11), 7.68 (m, 6); ^{13}C NMR (CD_2Cl_2) δ 94.17 (d, J_{PC} = 2.0), 122.17, 127.42, 128.47 (d, J_{PC} = 10.1), 130.43 (d, J_{PC} = 2.0), 132.97, 133.58 (d, J_{PC} = 1.8), 133.99 (d, J_{PC} = 10.88); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 40.05; MS (FAB, sulfolane) 494 (M^+). Anal. Calcd for $C_{29}H_{25}NiPS$: C, 70.33; H, 5.09; P, 6.25; S, 6.47. Found: C, 70.16; H, 5.29; P, 5.94; S, 6.20.

Reaction of 1a and Methyl Iodide. Cp(Ph_3P)NiCH$_2$CO-*t*-Bu (37 mg, 0.077 mmol) was dissolved in C_6D_6 in an NMR tube fitted with a Cajon adapter.[42] The solution was degassed by three freeze–pump–thaw cycles, and a known volume of methyl iodide (0.086 mmol) was condensed into the tube. The tube was flame-sealed and warmed to 45 °C. After 58 h at 45 °C, ^1H NMR analysis of the solution showed Cp(Ph_3P)NiI (51%, some had precipitated from the solution), 11% pinacolone, and 33% ethyl *tert*-butyl ketone. The identities of pinacolone and ethyl *tert*-butyl ketone were confirmed by GC analysis. The Cp(Ph_3P)NiI remaining in solution was precipitated from the reaction mixture by addition of pentane and isolated in 73% yield (29 mg): mp 139–141 °C; IR (KBr) 1480 (m), 1437 (s), 1098 (s), 786 (m), 700 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 5.06 (s, 5), 6.99 (s, 9), 7.80 (m, 6); ^1H NMR ($CDCl_3$) δ 5.22 (s, 5), 7.41 (m, 9), 7.76 (m, 6); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 40.61. Spectra correlated with literature values:[43] ^1H NMR ($CDCl_3$) δ 5.22 (s, 5), 7.38 (m, 9), 7.78 (m, 6).

Reaction of 1a and Methyl Tosylate. An NMR tube was loaded with **1a** (17 mg, 0.036 mmol), methyl tosylate (6.9 mg, 0.037 mmol), and C_6D_6 (0.62 mL). The tube was degassed and sealed under vacuum[42] and then heated to 45 °C. ^1H NMR analysis of the solution after 3 days showed 53% **1a**, 98% methyl tosylate, and 47% pinacolone. After 6 days at 45 °C, 2% **1a**, 95% methyl tosylate, and 79% pinacolone were observed. No ethyl *tert*-butyl ketone was observed. Apparently, **1a** decomposed to pinacolone under these conditions without significant reaction with methyl tosylate.

Reaction of 1a and Trimethylchlorosilane. An NMR tube was loaded with **1a** (10 mg, 0.021 mmol), trimethylchlorosilane (3.0 mL, 0.024 mmol), and C_6D_6 (0.5 μL). The capped tube was left at ambient temperature for 24 h, whereupon ^1H NMR analysis showed pinacolone enol silane **2** (84%) and Cp(Ph_3P)NiCl (68%; some product had precipitated). The remaining Cp(Ph_3P)NiCl was precipitated from the solution by addition of pentane and isolated in 73% yield (6.4 mg). IR and NMR data of these

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compounds matched with authentic samples.

Cp(Ph$_3$P)NiCH$_2$COCH=CH$_2$ (1h). Methyl vinyl ketone (50.0 μL, 0.601 mmol) and Cp(Ph$_3$P)NiCH$_2$CO-*t*-Bu (78.3 mg, 0.161 mmol) were dissolved in 1.4 mL of toluene-d_8 in an NMR tube. The tube was degassed by freeze–pump–thawing three times and sealed under vacuum.[42] After 5 days at 0 °C, 1 equiv of pinacolone and the nickel enolate of methyl vinyl ketone **1h** (64% by ^{1}H NMR) were formed. In a drybox, the NMR tube was opened and the solution transferred to a 25-mL vial. Hexane (5 mL) was layered over the dark brown solution, and the solution was chilled to −30 °C. The first crop of brown powder was impure; however, a second crop was obtained by addition of more hexane (10 mL) to the solution and chilling this solution to −30 °C. Over several days, dark green crystals grew; these were filtered, rinsed with hexane, and residual solvent was removed under vacuum leaving 17.4 mg (23.7%) of **1h**: mp 81–83 °C dec; IR (KBr) 1645 (s), 1601 (m), 1436 (m), 698 (s), 536 (s) cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 1.46 (d, 2, J_{PH} = 7.91), 5.05 (s, 5), 5.14 (dd, 1, J = 2.0, 10.1), 6.05 (dd, 1, J = 10.1, 17.1), 6.27 (dd, 1, J = 2.0, 17.1), 7.02 (m, 9), 7.61 (m, 6); ^{13}C NMR (toluene-d_8, 100.60 MHz) δ 6.48 (d, 2, J_{PC} = 15), 93.42, 121.16, 127.33, 128.47 (d, J_{PC} = 11), 130.0, 134.99 (d, J_{PC} = 11), 134.02 (d, J_{PC} = 44), 138.83, 196.36; ^{31}P{^{1}H} (C$_6$D$_6$) δ 41.98; ^{1}H NMR (toluene-d_8) δ 44.95; MS (FAB, sulfolane) 454 (M$^+$, 25%), 385 (base). Anal. Calcd for C$_{27}$H$_{25}$NiOP: C, 71.25; H, 5.54; P, 6.80. Found: C, 71.50; H, 5.75; P, 5.68.

Reaction of 1a and Isobutyraldehyde. Isobutyraldehyde (200 μL, 2.20 mmol) was added to a benzene solution (2 mL) of **1a** (86 mg, 0.18 mmol) at ambient temperature. After 4 h, the red-brown solution was quenched with 3 mL of 1 M CF$_3$CO$_2$H and the layers separated. The aqueous phase was extracted with three successive 10-mL portions of ether, and the combined extracts were washed successively with saturated NaHCO$_3$, water, and brine. The yellow solution was dried over MgSO$_4$, then filtered, and concentrated by rotary evaporation. The crude product was chromatographed on silica gel eluting with 6:1 hexane/ethyl acetate. Compound **3** was obtained in 43% yield (13 mg) based on **1a**: IR (CCl$_4$) 3525 (w), 2969 (s), 1713 (s); ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.86 (s, 3), 0.94 (d, 3, J = 6.88), 0.97 (d, 3, J = 6.77), 3.02 (d, 1, J = 11.73), 3.23 (d, 1, J = 11.79), 4.76 (d, 1, J = 2.56); ^{13}C NMR (125.7 MHz, CDCl$_3$) δ 17.68, 19.23, 19.26, 19.57, 22.28, 22.93, 28.26, 34.55, 39.98, 69.96, 79.22, 178.33. Anal. Calcd for C$_{12}$H$_{24}$O$_3$: C, 66.63; H, 11.18. Found: C, 66.50; H, 11.23.

Generation of Paramagnetic Nickel Complexes from Cp(Ph$_3$P)NiCH$_2$CO-*t*-Bu (1a). Triphenylphosphine (9 mg, 0.03 mmol) and **1a** (3 mg, 0.006 mmol) were dissolved in toluene (0.3 mL) in an EPR tube at room temperature in a drybox. The X-band EPR spectrum showed a three-line pattern with g = 2.074 and a = 0.0108 cm^{-1} at a microwave frequency of 9.77 GHz. A sample prepared in THF showed an EPR spectrum with a similar three-line pattern with g = 2.074 and a = 0.0109 cm^{-1} at a microwave frequency of 9.76 GHz. We assign this signal to Cp(Ph$_3$P)$_2$Ni(1). Attempts to isolate this paramagnetic compound from the reaction solution were unsuccessful, presumably due to facile disproportionation to nickelocene and tetrakis(triphenylphosphine)nickel.[17]

To confirm the identity of Cp(Ph$_3$P)$_2$Ni(1), it was prepared independently. Cp(Ph$_3$P)Ni$^+$BF$_4^-$ (3.0 mg) was dissolved in 0.5 mL of THF and added to excess 2:1 Na/K (about 4 mg). The bright yellow solution became amber and then brown. After 20 min, the solution was filtered through Celite into an EPR tube. The brown solution showed a three-line pattern centered at g = 2.073 and a = 0.0108 cm^{-1}. The microwave frequency was 9.76 GHz.

As further evidence for the formation of a paramagnetic nickel(1) complex, a solution of the bis(diphenylphosphino)ethane derivative was prepared. Bis(diphenylphosphino)ethane (5 mg, 0.01 mmol) and **1a** (3 mg, 0.006 mmol) were dissolved in THF (0.3 mL) in an EPR tube in a drybox. The EPR spectrum of the brown solution showed a three-line pattern with g = 2.050 and a = 0.0120 cm^{-1} (126 G) at a microwave frequency of 9.76 GHz. The published g value for Cp(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Ni(1) is 2.068 (a = 122 G) at 25 °C.[17b] Attempts to isolate this paramagnetic nickel complex were also unsuccessful.

Reaction of Cp(Ph$_3$P)NiCH$_2$CO-*t*-Bu (1a) and PhCHO. Benzaldehyde (200 μL, 1.97 mmol) and **1a** (147 mg, 0.303 mmol) were dissolved in toluene in a Pyrex bomb equipped with stir bar and chilled to 0 °C. After being stirred 7 h at 0 °C, the dark brown solution was quenched with 5 mL of 1 M CF$_3$CO$_2$H. The layers were separated, and the aqueous layer was extracted with 4 × 10 mL of diethyl ether. The combined organic portions were washed successively with 2 × 25 mL of water, 2 × 25 mL of saturated aqueous NaHCO$_3$, and 25 mL of water and brine. The yellow solution was dried over MgSO$_4$ and filtered, and the solvent was removed by rotary evaporation. The yellow oil was submitted to chromatography on silica gel eluting with 10% ethyl acetate in hexane. Products isolated were **6** (26 mg, 27%), **7** (32 mg, 33%), and **12** (7 mg, 7%). Data for *t*-BuCH(OH)CH$_2$CH(O$_2$CPh)Ph (**6**): ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.92 (s, 9), 1.81 (ddd, 1, J = 10.9, 2.5, 13.5), 2.19 (ddd, 1, J = 10.9, 1.5, 13.5), 2.50 (d, 1, J = 4.7), 3.37 (ddd, 1, J = 4.7, 1.5, 10.9), 6.31 (dd, 1, J = 2.5, 10.9), 7.30 (m, 1), 7.31 (m, 2), 7.37 (m, 2), 7.46 (m, 2), 7.58 (m, 1), 8.10 (dd, 2, J = 1.01, 7.09); ^{1}H NMR (C$_6$D$_6$) δ 0.93 (s, 9), 1.83 (ddd, 1, J = 2.4, 10.8, 13.0), 2.18 (ddd, 1, J = 1.5, 10.9, 13.0), 2.34 (d, 1, J = 4.8), 3.40 (ddd, 1, J = 1.5, 4.8, 10.8), 6.60 (dd, 1, J = 2.4, 10.9), 7.06 (m, 6), 7.35 (d, 2, J = 7.5), 8.17 (dd, 2, J = 8.3, 1.5); ^{13}C NMR (CDCl$_3$, 125.76 MHz) δ 25.75, 34.57, 39.85, 74.25, 75.11, 126.15, 127.91, 128.45, 128.60, 129.75, 130.08, 133.17, 141.16, 166.56; IR (CCl$_4$) 3639 (w), 3531 (br w), 2960 (m), 1705 (s), 1602 (m), 1276 (s) cm^{-1}. Anal. Calcd for C$_{20}$H$_{24}$O$_3$: C, 76.89; H, 7.74. Found: C, 76.78; H, 7.87.

Data for PhCH(OH)CH$_2$CH(O$_2$CPh)-*t*-Bu (**7**): ^{1}H NMR (CDCl$_3$) δ 1.03 (s, 9), 1.91 (m, 2), 3.53 (d, 1, J = 3.75), 4.55 (dt, 1, J = 3.35, 10.18), 5.23 (dd, 1, J = 2.52, 10.75), 7.23 (m, 1), 7.34 (m, 3), 7.49 (m, 2), 7.61 (m, 2), 8.10 (d, 2, J = 7.06); ^{1}H NMR (C$_6$D$_6$): δ 0.85 (s, 9), 1.95 (m, 2), 3.46 (d, 1, J = 3.82), 4.68 (dt, 1, J = 10.05, 3.21), 5.48 (dd, 1, J = 10.65, 2.39), 7.11 (m, 6), 7.32 (d, 2, J = 7.09), 8.17 (dd, 2, J = 1.5, 8.0); ^{13}C NMR (CDCl$_3$) δ 26.14, 34.66, 40.11, 69.68, 79.11, 125.53, 128.29, 128.48, 129.72, 129.81, 133.29, 167.83; IR (CDCl$_3$) 3500 (m), 1695 (s) cm^{-1}; IR (CCl$_4$): 3518 (m), 1699 (s) cm^{-1}. Anal. Calcd for C$_{20}$H$_{24}$O$_3$: C, 76.89; H, 7.74. Found: C, 77.09; H, 7.89. Compound **12** was identified by comparison of spectra to authentic material; data are listed below.

Preparation of 6 and 7 via 10 and 12. Compound **10** was prepared in 89% yield from aldol **9** by the method of Hassner and Alexanian.[20] Data for *t*-BuCOCH$_2$CH(O$_2$CPh)Ph (**10**): ^{1}H NMR (CDCl$_3$) δ 1.10 (s, 9), 2.93 (dd, 1, J = 17.1, 5.2), 3.39 (dd, 1, J = 17.1, 8.2), 6.50 (dd, 1, J = 8.2, 5.2), 7.4 (m, 8), 8.01 (d, 2, J = 5.0), ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 25.81, 43.31, 44.16, 72.60, 126.28, 127.98, 128.44, 129.43, 130.43, 130.06, 132.81, 140.03, 165.11, 211.20; IR (KBr) 1728 (vs), 1700 (s), 1274 (vs), 1117 (s), 710 (s) cm^{-1}. Anal. Calcd for C$_{20}$H$_{22}$O$_3$: C, 77.34; H, 7.14. Found: C, 77.64; H, 7.03.

Reduction of **10** with excess NaBH$_4$ in ethanol/ether at 0 °C gave a mixture of syn and anti diastereomers (2.3:1.0) of the corresponding hydroxy compound. The isomers were separated by chromatography on silica gel eluting with 6:1 hexane/ethyl acetate. The data for anti isomer **6** were identical with those listed for anti isomer **6** above. Data for the syn isomer, *t*-BuCH(OH)CH$_2$CH(O$_2$CPh)Ph: mp 86–88 °C; ^{1}H NMR (CDCl$_3$) δ 0.86 (s, 9), 1.74 (d, 1, J = 5.11), 2.14 (m, 2), 3.13 (d, 1, J = 8.94), 6.19 (dd, 1, J = 8.04, 6.47), 7.40 (m, 8), 8.06 (d, 2, J = 6.98); ^{13}C NMR (CDCl$_3$): d 25.46, 34.90, 38.27, 76.32, 76.83, 126.90, 128.12, 128.31, 128.55, 129.55, 130.35, 132.91, 140.01, 165.64; IR (CDCl$_3$) 3610, 1716 cm^{-1}. Anal. Calcd for C$_{20}$H$_{24}$O$_3$: C, 76.89; H, 7.74. Found: C, 76.73; H, 8.01.

Compounds **12** and syn and anti isomers (4:1) of **7** were prepared by the methods described above for **10** and **6**. Compound **12** was isolated in 43% yield, and 22% of aldol **11** was recovered. Also, *trans*-PhCOCH=CH-*t*-Bu was isolated in 28% yield. Data for PhCOCH$_2$CH(O$_2$CPh)-*t*-Bu (**12**): ^{1}H NMR (CDCl$_3$) δ 1.07 (s, 9), 3.24 (dd, 1, J = 16.04, 3.53), 3.36 (dd, 1, J = 16.04, 8.52), 5.60 (dd, 1, J = 3.53, 8.52), 7.40 (m, 4), 7.50 (m, 2), 7.95 (m, 4); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 25.92, 35.11, 39.35, 77.06, 128.13, 128.17, 128.50, 129.53, 130.28, 132.67, 133.01, 136.91, 165.62, 197.48; IR (CDCl$_3$) 3155 (w), 2967 (s), 1721 (s), 1691 (s), 1275 (s) cm^{-1}. Anal. Calcd for C$_{20}$H$_{22}$O$_3$: C, 77.39; H, 7.14. Found: C, 77.54; H, 7.27. The reduction of **12** was carried out in the same way as for compound **10**, and the ratio of syn to anti isomers was 4.0:1.0. The spectral properties of anti isomer **7** were identical with those listed previously for anti isomer **7**. Data for syn isomer **7**: ^{1}H NMR (CDCl$_3$) δ 0.95 (s, 9), 2.16 (m, 2), 2.71 (br, 1), 4.77 (t, 1, J = 6.7), 4.88 (dd, 1, J = 3.34, 7.66), 7.30–7.60 (m, 8), 8.06 (m, 2);

^{13}C NMR ($CDCl_3$) δ 25.76, 35.12, 40.36, 73.19, 79.61, 126.12, 127.68, 128.39, 128.48, 129.68, 130.44, 132.98, 144.11, 166.89; IR (CCl_4) 3614 (w), 3065 (br), 2969 (m), 1718 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.35; H, 7.33.

Equilibration of Compounds 6 and 7. $Cp(Ph_3P)NiCH_2CO$-*t*-Bu (0.5 mg, 0.001 mmol) was added to a solution of compound **6** (8.0 mg, 0.026 mmol) in C_6D_6 (0.55 mL). The equilibration was monitored by ^1H NMR spectrometry. After 11 h, the nickel enolate had been consumed to give pinacolone and presumably the NMR silent nickel alkoxide; the ratio of "benzyl" benzoate **6** to "neopentyl" benzoate **7** was 1.5:1.0, based on integration of the benzylic proton resonances. Equilibration was reached after 35 h, with a final ratio of 1.0:2.7 for **6** and **7**, respectively. Starting with **7** and $Cp(Ph_3P)NiCH_2CO$-*t*-Bu (8 mol %), equilibration to a final ratio of 1.0:2.7 was achieved after 44 h. In both reactions, a small amount of the benzoates was converted to the ester ketones **10** and **12**, presumably via β-elimination of the nickel alkoxide intermediate.

Reaction of $Cp(Ph_3P)NiCH_2CO$-*t*-Bu (1a) and PhCDO. Benzaldehyde-d_1 (100 μL, 0.975 mmol; 99%D) was added to a solution of **1a** (67.2 mg, 0.138 mmol) in 0.85 mL of toluene-d_8. The capped NMR tube was wrapped with Teflon tape and kept at 0 °C in an ice bath. The reaction was monitored by ^1H NMR spectrometry. After 4 h, **1a** had been consumed and the reaction was quenched with 1 mL of 1 M CF_3CO_2H. The aqueous solution was extracted with 3 × 10 mL of diethyl ether. The combined organic extracts were washed successively with water, saturated $NaHCO_3$, water, and then brine. The solution was dried over $MgSO_4$ with activated charcoal. The yellow solution was filtered, and the solvent was removed by rotary evaporation. The crude oil was chromatographed on silica gel (Merck, 200-400 mesh) eluting with 10% ethyl acetate in hexane. Compounds **6**-d_2 and **7**-d_2 (25 mg) were obtained in 60% combined yield. The percent deuterium in these compounds was determined from the ^1H NMR spectra because the molecular ion in the mass spectrum was not large enough to accurately calculate this value. The amount of deuterium incorporated into the benzylic and neopentyl positions of **6** and **7** was determined to be >98%. Data for **6**-d_2: ^2H NMR ($CHCl_3$) δ 4.55 (s), 5.24 (s); ^1H NMR ($CDCl_3$) δ 0.92 (s, 9), 1.80 (d, 1, J = 14.5), 2.18 (d, 1, J = 14.5), 2.48 (s, 1), 7.31 (m, 5), 7.45 (m, 2), 7.58 (m, 1), 8.10 (d, 2, J = 7.1); MS (EI) 314 (M^+, 0.2%), 135 (37%), 105 (base). Data for **7**-d_2: ^2H NMR ($CHCl_3$) δ 3.36 (s), 6.31 (s); ^1H NMR ($CDCl_3$) δ 1.03 (s, 9), 1.90 (d, 1, J = 14.4), 2.01 (d, 1, J = 14.4), 3.54 (s, 1), 7.23 (m, 1), 7.34 (m, 4), 7.49 (m, 2), 7.61 (m, 1), 8.10 (d, 2, J = 7.1); MS (EI) 314 (M^+, 0.3%), 135 (24%), 105 (base). The isotope competition reaction was conducted in the same way as this reaction except that 11 equiv (50.0 μL) of benzaldehyde-d_0 and 11 equiv (50.0 μL) of benzaldehyde-d_1 were added to **1a** (21.7 mg) in toluene (0.75 mL). The percent deuterium in products **6** and **7** are as follows: 50% at the benzylic position of **6**, 37% at the neopentyl position of **6**, 50% at the benzylic position of **7**, and 37% at the neopentyl position of **7**.

Reaction of $Cp(Ph_3P)NiCH(CH_3)CO$-*t*-Bu (1d) and Benzaldehyde. Benzaldehyde (100 μL, 0.984 mmol) and **1b** (111 mg, 0.221 mmol) were dissolved in toluene and allowed to stand at room temperature for 72 h. The dark brown solution was quenched and workup up in the same way as previously described for **1a**. Benzyl alcohol was observed in a ^1H NMR spectrum of the crude reaction mixture but was not isolated. After chromatography, compounds **13** and **14** were isolated in 54% and 45% yields, respectively. Data for $PhCOCH(CH_3)CH(O_2CPh)$-*t*-Bu (**13**): mp 93–94 °C; ^1H NMR ($CDCl_3$) δ 0.97 (s, 9), 1.21 (d, 3, J = 7.1), 3.96 (dq, 1, J = 7.1, 8.0), 5.73 (d, 1, J = 8.0), 7.50 (m, 4), 7.60 (m, 2), 7.99 (d, 2, J = 7.4), 8.11 (d, 2, 7.2); ^{13}C NMR ($CDCl_3$) δ 15.38, 26.66, 35.99, 41.00, 79.86, 128.27, 128.39, 128.79, 128.84, 129.68, 130.0, 132.86, 133.06, 165.74, 201.21; IR (thin film) 2969 (m), 1718 (vs), 1683 (vs), 1272 (s), 1220 (s), 1112 (s), 1070 (s), 709 (vs) cm^{-1}. Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.83; H, 7.44. Data for $PhCH(O_2CPh)CH(CH_3)CH(OH)$-*t*-Bu (**14**): ^1H NMR (400 MHz, $CDCl_3$) δ 0.85 (d, 3, J = 6.97), 0.93 (s, 9), 1.76 (d, 1, J = 5.51), 2.43 (m, 1), 3.56 (d, 1, J = 5.55), 5.89 (d, 1, J = 8.41), 7.28–7.39 (m, 7), 7.44 (m, 1), 8.06 (m, 2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 11.23, 26.77, 35.67, 39.17, 76.54, 80.05, 127.12, 127.96, 128.41, 128.46, 129.62, 133.06, 139.63, 165.8; IR (thin film) 3515 (m), 1723 (s) cm^{-1}. Anal. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.33; H, 8.21.

Independent Synthesis of 13. The method of Hassner and Alexanian[20] was used to prepare **13** as described below. Benzoic acid (75 mg, 0.62 mmol), dicyclohexylcarbodiimide (DCC, 105 mg, 0.509 mmol), and (dimethylamino)pyridine (DMAP, 2.7 mg, 0.022 mmol) were added to a stirring solution of aldol **15**[36] (60 mg, 0.27 mmol) in ether (20 mL). The solution was stirred for 8.5 h and then filtered through Celite to remove the urea. The Celite was rinsed with ether, and the combined filtrates were concentrated and chromatographed on silica gel eluting with 6:1 hexane/ethyl acetate. Compound **13** was obtained in 28% yield (41 mg), and 44% (26 mg) of aldol **15** was recovered. The spectral properties of **13** were identical with those reported above.

Hydrolysis of 14. Compound **14** (8.6 mg, 0.026 mmol) was dissolved in ethanol (1 mL)/ether (2 mL), and 1 drop of 2 M KOH was added. The reaction mixture was allowed to stand for 19 h at room temperature and then was neutralized with aqueous 0.1 M HCl. The volatile solvent was removed by rotary evaporation and the acidic solution extracted with 3 × 10 mL of ether. The combined organic portions were washed with 2 × 10 mL of 2M KOH, water, saturated NH_4Cl, water, and brine. After the solution was dried over $MgSO_4$, the ether was removed leaving a quantitative yield (5.8 mg) of the expected diol **16**: ^1H NMR ($CDCl_3$) δ 0.81 (s, 9), 1.10 (d, 3, J = 7.03), 1.5 (br, 1), 2.08 (m, 1), 3.50 (d, 1, J = 1.05), 4.72 (d, 1, J = 4.46), 7.33 (m, 5); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 12.62, 26.66, 35.22, 39.91, 76.51, 79.34, 125.86, 127.08, 128.25, 144.02; IR ($CDCl_3$) 33445 (br), 3155 (m), 2957 (s), 1492 (s), 1476 (s), 1383 (s), 1248 (s); high-resolution MS (FAB in NaCl), m/e calcd for $(M + Na)^+$, $^{12}C_{14}{}^1H_{22}{}^{16}O_2{}^{23}Na$, 245.1512, m/e found 245.1506.

Reduction of 15. Aldol **15** (29.5 mg, 0.134 mmol) was dissolved in ethanol (9 mL)/ether (10 mL) and chilled to 0 °C. $NaBH_4$ (86.1 mg, 2.28 mmol) was added to the stirred solution under nitrogen. The reaction was kept at 0 °C for 3 h and then allowed to warm to ambient temperature. After being stirred 20 h, the reaction was quenched with 10 mL of 1 M HCl and the volatile solvent removed by rotary evaporation. The acidic solution was extracted with 4 × 10 mL of ether, and the combined organic layers were washed successively with $NaHCO_3$, water, and brine. After the solution was dried over $MgSO_4$, the ether was removed and the crude colorless oil (33.2 mg) was chromatographed on silica gel eluting with 6:1 hexane/ethyl acetate. The all-syn diol **16** was obtained pure in 58% yield (17.2 mg). Later fractions contained a mixture of the two diastereomers in 27% yield (8.1 mg). Data for the all syn isomer, $PhCH(OH)CH(CH_3)CH(OH)$-*t*-Bu: ^1H NMR ($CDCl_3$) δ 0.83 (d, 3, J = 7.00), 0.96 (s, 9), 2.08 (m, 1), 2.5 (br, 1), 3.67 (d, 1, J = 1.13), 4.94 (d, 1, J = 2.90), 7.33 (m, 5); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 6.19, 26.85, 35.76, 40.36, 80.23, 83.50, 125.76, 127.01, 128.12, 143.20; IR ($CDCl_3$): 3610 (m), 3500 (br), 2966 (s), 2872 (m), 1480 (m), 1452 (s), 1101 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.64; H, 9.97. Found: C, 75.98; H, 9.99. The ^1H and ^{13}C NMR spectra of the other diastereomer, with the benzyl OH anti relative to the methyl and the other OH, matched with those obtained for the product resulting from hydrolysis of **14**.

Preparation of 14 via 17 and 18. Compound **18** was prepared in 20% yield from aldol **17** by the method of Hassner and Alexanian.[20] Aldol **17** was recovered in 32% yield. Data for $PhCH(O_2CPh)CH(CH_3)CO$-*t*-Bu (**18**): mp 127–128 °C; ^1H NMR ($CDCl_3$) δ 0.89 (d, 3, J = 6.93), 1.22 (s, 9), 3.66 (m, 1), 6.10 (d, 1, J = 10.31), 7.35 (m, 5), 7.45 (m, 3), 7.95 (m, 2); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 15.80, 26.29, 44.76, 44.94, 78.77, 127.48, 128.19, 128.34, 128.45, 129.47, 130.14, 132.78, 138.69, 164.81, 216.33; IR (CCl_4) 2971 (m), 1730 (s), 1710 (s), 1268 (s) cm^{-1}. Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.79; H, 7.42.

Compound **18** (32 mg, 0.098 mmol) was reduced with $NaBH_4$ (30 mg, 0.80 mmol) in a ethanol/ether solution (5 mL each) at ambient temperature. After being stirred 5 h, the reaction was quenched with 5 mL of 1 M HCl and the volatile solvent was removed by rotary evaporation. The remaining aqueous solution was extracted with 4 × 8 mL of ether, and the combined organic layers were washed successively with water, saturated $NaHCO_3$, water, and brine. Chromatography on silica gel eluting with 6% ethyl acetate in hexane gave 14 mg (44%) of **14** (as a mixture of diastereomers) and a fraction containing starting material **18** and transesterified reduced product $PhCH(OH)CH(CH_3)CH(O_2CPh)$-*t*-Bu (16 mg, 48%). The ^1H and ^{13}C NMR spectra of

the minor diastereomer matched with those of the product **14** from the reaction of nickel enolate **1b** with benzaldehyde. Data for the major isomer of $PhCH(O_2CPh)CH(CH_3)CH(OH)$-*t*-Bu with the benzoate and OH groups in an anti relationship relative to the methyl group: ^1H NMR ($CDCl_3$) δ 0.87 (d, 3, J = 6.98), 0.99 (s, 9), 2.44 (m, 1), 3.4 (br s, 1), 3.18 (d, 1, J = 6.5), 6.28 (d, 1, J = 7.2), 7.26–7.48 (m, 8), 8.07 (d, 2, J = 9.5); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 17.18, 26.44, 36.14, 39.87, 78.22, 82.36, 127.61, 127.72, 128.15, 128.36, 129.63, 132.89, 139.35, 163.71; high-resolution MS (FAB in NaCl), m/e calcd for $(M + H)^+$, $^{12}C_{21}{}^1H_{27}{}^{16}O_3$, 327.1980, m/e found 327.1962.

Reaction of $Cp(Ph_3P)NiCH_2CO_2$-*t*-Bu (1d) with PhCHO. An NMR tube was loaded with benzaldehyde (25 μL, 0.25 mmol), **1d** (9.8 mg, 0.020 mmol), and C_6D_6 (0.70 mL). The solution was degassed and the tube was flame-sealed under vacuum.[42] After the olive-green solution was heated at 110 °C for 9 h, the reaction was quenched and worked up in the usual manner. After chromatography of the crude product on silica gel, 0.5 mg (11%) of $PhCH(OH)CH_2CO_2$-*t*-Bu (**19**) was isolated. Data for this compound were identical with those of an authentic sample of **19**:[35] ^1H NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 9), 2.62 (dd, 1, J = 16.27, 4.40), 2.68 (dd, 1, J = 16.27, 8.40), 5.07 (m, 1), 7.27 (m, 1), 7.34 (m, 4); ^1H NMR (C_6D_6) δ 1.28 (s, 9), 2.43 (dd, 1, J = 16.0, 3.8), 2.54 (dd, 1, J = 16.0, 8.9), 3.24 (br s, 1), 5.00 (dd, 1, J = 3.9, 8.9), 7.10 (m, 3), 7.26 (m, 2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.01, 44.23, 70.34, 81.44, 125.66, 127.59, 128.39, 142.58, 171.81; IR (thin film) 3443 (br), 2979 (m), 1729 (s), 1394 (m), 1369 (s), 1151 (s), 758 (m), 701 (s) cm^{-1}. Literature data:[44] IR (film) 3450, 2970, 1730, 1390, 1360, 1140, 770 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.40 (s, 9), 2.56 (dd, 2, J = 6, 8), 3.92 (s, 1), 5.02 (dd, 1, J = 6, 8), 7.18–7.40 (m, 5); ^{13}C NMR ($CDCl_3$) δ 27.98, 44.66, 70.41, 125.83, 127.44, 128.28, 143.19, 171.36.

Reaction of $Cp^*(Ph_3P)NiCH_2CO_2$-*t*-Bu (1e) with PhCHO. Benzaldehyde (10 μL, 0.098 mmol) and **1e** (11.5 mg, 0.020 mmol) were dissolved in C_6D_6 in an NMR tube. After the sample was degassed the tube was flame-sealed under vacuum.[42] The solution was heated to 45 °C for 7 days, whereupon an ^1H NMR spectrum of the solution showed that 6% of **1e** remained and the organic products were present in the following amounts: 34% *tert*-butyl acetate, 60% **19**. Organometallic products were observed in the ^1H NMR spectrum but were not identified. The spectral data for **19** were identical with those listed above.

Reaction of $Cp(Ph_3P)PdCH_2CO$-*t*-Bu (1f) with PhCHO. Benzaldehyde (15 μL, 0.15 mmol) and **1f** (10.0 mg, 0.019 mmol) were dissolved in toluene-d_8 in an NMR tube. The solution was degassed, and the tube was flame-sealed under vacuum.[42] After the solution was heated for 3 days at 45 °C, ^1H NMR analysis showed that the palladium complex had been consumed. The solution was quenched with 1 M CF_3CO_2H and worked up in the usual manner. The products were determined by integration of the ^1H NMR spectrum of the crude product. The yields were pinacolone (50%), $PhCH(OH)CH_2CO$-*t*-Bu (**9**) (25%), PhCH=CHCO-*t*-Bu (3%), and **6** (22%). The data for **9** correlated with those of an authentic sample:[36] mp 25–27 °C; ^1H NMR ($CDCl_3$) δ 1.13 (s, 9), 2.88 (d, 2, J = 6.0), 3.57 (d, 1, J = 3.0), 5.13 (dt, 1, J = 3.0, 6.0), 7.35 (m, 5); ^1H NMR (C_6D_6) δ 0.80 (s, 9), 2.48 (dd, 1, J = 3.25, 17.44), 2.62 (dd, 1, J = 8.90, 17.44), 3.40 (br s, 1), 5.12 (dt, 1, J = 8.90, 3.20), 7.11 (m, 1), 7.18 (m, 2), 7.33 (d, 2, J = 7.0); IR (CCl_4) 3509 (m), 2971 (s), 1698 (s), 1367 (s), 1072 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.58; H, 8.82. Literature data[36] are as follows: mp 22–23 °C; IR (CCl_4) 3530, 1695 cm^{-1}; ^1H NMR (CCl_4) δ 1.03 (s, 9), 2.3–2.9 (m, 2), 4.9–5.2 (m, 1), 7.0–7.4 (m, 5); ^1H NMR ($CDCl_3$)[45] δ 1.2 (s, 9), 2.95 (d, 2), 3.65 (m, 1), 4.9–5.2 (m, 1), 7.3 (m, 5); MS (m/e, relative intensity) 131 (100), 106 (28), 105 (28), 103 (25), 77 (41), 57 (53), 51 (20), 43 (18).

Reaction of $Cp(Ph_3P)PdCH_2CO_2$-*t*-Bu with PhCHO. Benzaldehyde (10 μL, 0.098 mmol) and **1g** (8.4 mg, 0.015 mmol) were dissolved in C_6D_6 in an NMR tube. After three freeze–pump–thaw cycles the tube was flame-sealed under vacuum.[42] The purple-red solution was heated to 85 °C and monitored at intervals by ^1H NMR spectrometry. After 4 days at 85 °C, 84% of **1g** remained. Finally, after 12 days at 85 °C, the palladium complex had been consumed; black metal covered the NMR tube walls. *tert*-Butyl acetate (83%) was observed in the ^1H NMR spectrum of the dark red-brown solution. Another sample prepared analogously was heated to 110 °C for 4 days, whereupon the palladium complex had been consumed and 29% *tert*-butyl acetate was observed. The reaction solution was quenched with 1 M CF_3CO_2H and worked up in the usual manner. Some benzaldehyde was recovered, but no aldol products were isolated or observed in the crude reaction mixture.

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Registry No. **1a**, 123124-19-6; **1b**, 123124-20-9; **1c**, 123124-21-0; **1d**, 123124-22-1; **1e**, 123124-23-2; **1f**, 123124-24-3; **1g**, 123124-25-4; **1h**, 123124-26-5; **2**, 17510-46-2; **3a**, 18491-15-1; **4a**, 79361-90-3; **4b**, 79361-89-0; **5**, 42442-08-0; **6**, 123124-07-2; **6**-d_2, 123124-13-0; **7**, 123124-08-3; **7**-d_2, 123124-78-7; **9**, 42052-52-8; **10**, 123124-10-7; **12**, 123124-09-4; **13**, 123124-14-1; **14**, 123124-15-2; **15**, 84466-84-2; **16**, 123124-16-3; **16** (all syn), 123166-00-7; **18**, 123124-17-4; **19**, 5397-27-3; $Cp(Ph_3P)NiCl$, 31904-79-7; Cp_2Ni, 1271-28-9; $(Ph_3P)_2NiCl_2$, 14264-16-5; $Cp(Ph_3P)NiBr$, 1298-79-9; $Cp^*(Ph_3P)NiBr$, 69239-97-0; $Cp(PPh_3)PdBr$, 31741-89-6; $CpSn(CH_3)_3$, 2726-34-3; $[(Ph_3P)PdBr_2]$, 123124-27-6; $Cp(Ph_3P)PdCl$, 84893-34-5; CH_2=C(OK)-*t*-Bu, 123124-28-7; $Cp(Ph_3P)NiSPh$, 51869-82-0; $Cp(Ph_3P)NiI$, 1298-82-4; PhCHO, 100-52-7; *syn*-*t*-BuCH(OH)$CH_2CH(O_2CPh)Ph$, 123124-11-8; *syn*-$PhCH(OH)CH_2CH(O_2CPh)$Bu-*t*, 123124-12-9; *trans*-PhCOCH=CH-*t*-Bu, 29569-93-5; PhCDO, 3592-47-0; $PhCH(O_2CPh)CH(CH_3)CH(OH)$-*t*-Bu, 123165-99-1; $PhCH(OH)CH(CH_3)CH(O_2CPh)$-*t*-Bu, 123124-18-5; PhCH=CHCO-*t*-Bu, 538-44-3; pinacolone potassium enolate, 55440-76-1; pinacolone, 75-97-8; potassium bis(trimethylsilyl)-amide, 40949-94-8; acetophenone potassium enolate, 59175-43-8; *tert*-butyl acetate lithium enolate, 53503-61-0; thiophenol, 108-98-5; ethyl *tert*-butyl ketone, 564-04-5; methyl iodide, 74-88-4; methyl tosylate, 80-48-8; trimethylchlorosilane, 75-77-4; methyl vinyl ketone, 78-94-4; isobutyraldehyde, 78-84-2; *tert*-butyl acetate, 540-88-5.

Supplementary Material Available: Further details of the structure determination of complex **1e** including tables of positional parameters, anisotropic thermal parameters, root-mean-square amplitudes of anisotropic displacement, and selected torsional angles (5 pages); a table of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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