aallyllithium reagents *after* the intermediates were thermally equilibrated.[10]

Acknowledgment. We thank the National Institutes of Health and the Robert A. Welch Foundation for financial support of this work and the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant (to M.N.). The Varian XL-200 NMR spectrometer used in this work was purchased, in part, with funds provided by the National Science Foundation (CHE78-03230). We also thank C. Gluchowski for providing the NMR data for the lithium enolate of acetaldehyde.

[(Trimethylsilyl)acetyl]trimethylsilane, a Versatile Synthon for Stereoselective Syntheses of Functionalized Trisubstituted Olefins

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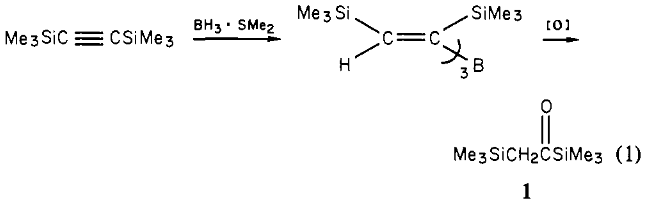
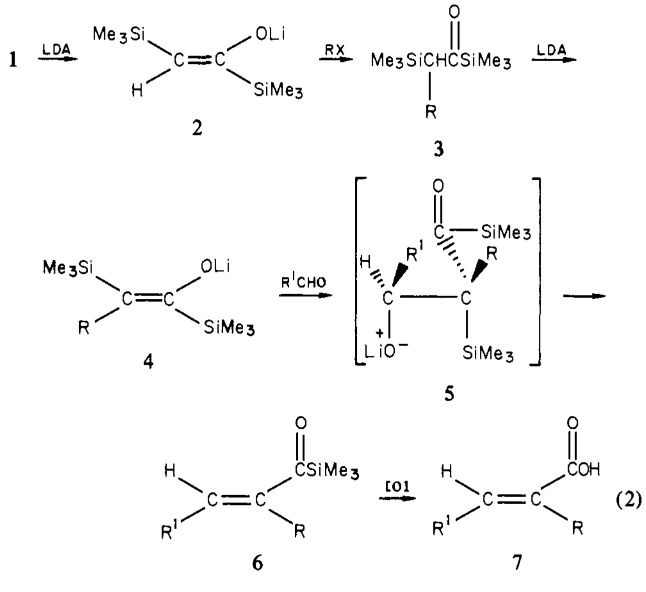
Recently we reported that monohydroboration of bis(trimethylsilyl)acetylene with borane-methyl sulfide complex followed by oxidation of the resultant trivinylborane with anhydrous trimethylamine oxide and a hydrolytic workup affords [(trimethylsilyl)acetyl]trimethylsilane (**1**, eq 1).[1] Compound **1** is unique in that it contains both the α- and β-ketosilane structural features which endow it with considerable potential value as a synthon for a wide variety of transformations. Thus, we describe here its efficient elaboration into trisubstituted olefins of defined stereochemistry via sequential deprotonation-alkylation-deprotonation-aldolization reactions (eq 2). Such transformations are of special importance in that many biogenetically interesting isoprenoid molecules and insect pheromones embody trisubstituted olefinic moieties.[2]





Treatment of **1** in THF with lithium diisopropylamide (LDA) resulted in the nearly exclusive formation of the (*E*)-enolate **2** as evidenced by its conversion into the (*E*)-alkenylsilyl ether on treatment with chlorotrimethylsilane.[3] The formation of the (*E*)-enolate **2** reflects the known tendency of the trimethylsilyl group in vinylsilanes to occupy the sterically more favorable trans positions.[4] Alkylation of **2** with reactive alkyl halides proceeded readily to furnish the α-substituted [(trimethylsilyl)acetyl]trimethylsilane **3**. Deprotonation of **3** with LDA produced the new enolate **4**. When **4** ($R = CH_3$) was treated with chlorotrimethylsilane, the 360-MHz ^1H NMR spectrum of the resultant alkenylsilyl ether exhibited only one CH_3 singlet (δ 1.60). Moreover, its examination on a 96-m SE-30 glass capillary column revealed the presence of a single product. Thus, by analogy with **2** it appears that the trans arrangement of the bulky trimethylsilyl moieties also prevails in the enolate **4**, at least when it contains an R group with moderate steric requirements.

The last step in the olefin synthesis (eq 2) involved treatment of **4** with an appropriate aldehyde. Elimination of the oxygen and trimethylsilyl moieties from the resultant crossed aldol condensation product **5** proceeded spontaneously at -78 °C and produced the *E*-disubstituted α,β-unsaturated acylsilane **6**.[5] For establishment of the stereochemistry and the isomeric purities of the olefins obtained, the acylsilane group in **6** was oxidized to the carboxylic acid with alkaline hydrogen peroxide.[6] It has been shown that (*E*)- and (*Z*)-2,3-dialkyl-substituted acrylic acids of the type **7** exhibit distinct chemical shifts for the vinyl protons.[7] On the basis of spectral and GLC data of the α,β-unsaturated acylsilanes **6** and the corresponding acids **7** it was concluded that they also possess the *E* configuration and that they were at least 98% isomerically pure.

Typical procedures for the preparation of **6** and **7** ($R = CH_3$, $R^1 = sec\text{-}C_4H_9$) are as follows. To a solution of diisopropylamine (22.0 mmol) in 40 mL of THF at -78 °C was added a solution of *n*-butyllithium (20.0 mmol, 2.4 M) in hexane. The mixture was stirred for 15 min at 0-5 °C, treated at -78 °C with a solution of **1**[8] (20.0 mmol) in 5 mL of THF, warmed to 0-5 °C, and stirred at this temperature for 30 min to obtain the enolate **2**. Alkylation of **2** was achieved by addition at -25 °C of a solution of methyl iodide (20.0 mmol, 2 M) in THF. The mixture was stirred for 4 h at -25 °C and then let warm to 25 °C. The resultant solution of α-methylated acylsilane **3** was added via an addition funnel to a solution of LDA (20.0 mmol, prepared as described above) maintained at 0-5 °C. The mixture was stirred for 1 h at 25 °C, and then the enolate **4** formed was treated at -78 °C with a solution of 2-methylbutyraldehyde (22.0 mmol) in THF (20 mL) over a 30-min period. The resultant yellow slurry was stirred for an additional 15 min at -78 °C, warmed to 25 °C, and poured into a separatory funnel containing 25 mL of 1 N HCl. After extraction with ether the combined organic phases were washed with saturated aqueous NaCl and dried over $MgSO_4$. Distillation

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[1] Miller, J. A.; Zweifel, G. *Synthesis* **1981**, 288.

[2] For a recent summary of trisubstituted olefin syntheses, see: Marfat, A.; McGuirk, P. R.; Kramer, R.; Helquist, P. *J. Am. Chem. Soc.* **1977**, *99*, 253.

[3] The ^1H NMR (360-MHz) spectrum of the silyl enol ether showed only one singlet at 5.0 ppm in the vinyl proton region. A similar vinyl proton chemical shift for the silyl enol ether derived from propionyltrimethylsilane has been observed by: Kleschick, W. A. Ph.D. Thesis, University of California, Berkeley, 1977.

[4] Zweifel, G.; On, H. P. *Synthesis* **1980**, 803. Zweifel, G.; Murray, R. E.; On, H. P. *J. Org. Chem.* **1981**, *46*, 1292.

[5] For the preparation of monosubstituted α,β-unsaturated acylsilanes, see: Minami, N.; Abe, T.; Kuwajima, I. *J. Organomet. Chem.* **1978**, *145*, Cl. Reich, H. J.; Olson, R. E.; Clark, M. C. *J. Am. Chem. Soc.* **1980**, *102*, 1423.

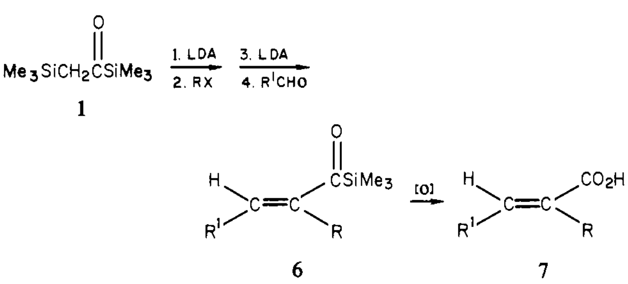
[6] Zweifel, G.; Backlund, S. *J. Am. Chem. Soc.* **1977**, *99*, 3184.

[7] For **7**, $R = CH_3$; $R^1 = C_2H_5$, $n\text{-}C_4H_9$, $sec\text{-}C_4H_9$, C_6H_5, the IR and NMR spectral data were in good agreement with those reported in the literature for these compounds.

[8] The original procedure reported for the preparation of **1**[1] was modified in that after oxidation of the trivinylborane (20 mmol) with anhydrous trimethylamine oxide[9] the reaction mixture was poured into a mixture of ether (60 mL) and water (30 mL) maintained at 0-5 °C. The reaction mixture was stirred vigorously at this temperature for 15 min and then worked up in the usual way. It should be noted that **1** has to be used shortly after its preparation since it isomerizes to the silyl enol ether even when stored at low temperatures.

[9] Köster, R.; Morita, Y. *Liebigs Ann. Chem.* **1967**, *704*, 70.

Table I. Yields of α,β-Unsaturated Acylsilanes 6 and Acids 7 Derived from [(Trimethylsilyl)acetyl]trimethylsilane (1)



RX	R^{1}CHO R^1 =	6 yield, %	7 yield, %
CH_3I	C_2H_5	82	89
	n-C_4H_9	78	87
	i-C_3H_7	90	89
	sec-C_4H_9	85	93
	t-C_4H_9	72[d]	93
	C_6H_5	84	96
	n-$C_4H_9C{\equiv}C$	78	93
	(E)-$CH_3CH{=}CH$	91	94
C_2H_5I		84[e]	97
$(CH_3)_2C{=}CHCH_2Br$		92[f]	92
$H_2C{=}CHCH_2Br$	n-C_4H_9	80[e]	95
$C_6H_5CH_2Br$	CH_3	84[g]	97

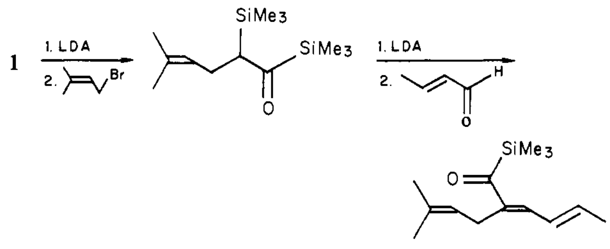
[a] Isolated yields. [b] The IR, ^{1}H NMR, UV, and mass spectral data of the olefins obtained were consistent with assigned structures. [c] Yields are based on pure 6. [d] The aldehyde was added to the enolate at 0 °C, and then the reaction mixture was stirred for 2 h at 25 °C. [e] The alkylating agent (2.0 equiv) was added to the enolate at 0 °C, the mixture was stirred for 15 h at 25 °C, excess reagent was removed (1 torr), and then the mixture was diluted with THF. [f] Alkylation was carried out at 0 °C and then for 4 h at 25 °C. [g] Alkylation was carried out at 0 °C and then for 20 h at 25 °C.

through a short path column yielded 85% of **6** (R = CH_3; R^1 = *sec*-C_4H_9) as a bright yellow liquid: bp 73–75 °C (4 torr); $n^{24}{}_D$ 1.4556.[10]

The α,β-unsaturated acylsilane obtained as above (5.0 mmol) was diluted with THF (10 mL) and 3 N NaOH (2 mL), heated to 35–40 °C, and then oxidized by adding dropwise 1 mL of 30% H_2O_2 at such a rate as to maintain the temperature during the addition below 50 °C. Workup and distillation [Kugelrohr, 75 °C (10^{-4} torr)] afforded 93% of (E)-2,4-dimethyl-2-hexenoic acid, a mandibular gland secretion of ants.[11,12]

Although our primary aims in the present work were synthetic, the nearly exclusive formation of the (E)-olefins **6** and **7** from this novel reaction sequence deserves some comments. It is well documented that β-alkoxysilanes undergo syn elimination producing the corresponding olefins.[13] Therefore, provided that the (E)-α,β-unsaturated acylsilanes **6** obtained in this study represent the kinetic elimination products, the crossed aldol condensation **4** → **5** must have proceeded in a stereoselective manner to give the β-alkoxysilane intermediates **5**. It has been shown that condensations of lithium enolates and aldehydes are subject to kinetic stereoselection.[14] On the basis of this premise the reaction of the enolate **4** with an aldehyde should produce the β-alkoxysilane **5**. In this connection it is interesting to note that the reactions of the enolates derived from deprotonation of (trimethylsilyl)acetic acid[15] and its esters[16] with aldehydes produced mixtures of the corresponding monosubstituted α,β-unsaturated acids and esters, respectively, indicating nonstereoselective formation of the corresponding enolates.

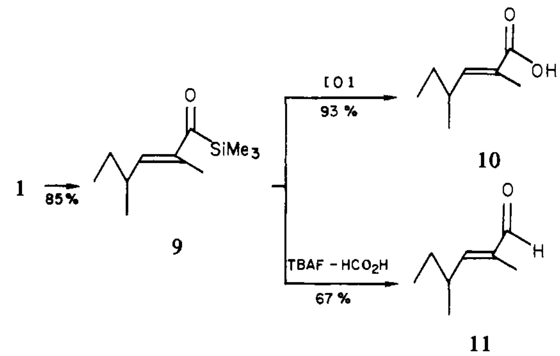
The present route to functionally substituted olefins has great potential in that it allows for considerable flexibility in the choice of the alkylating agent and aldehyde components. As shown in Table I, both methyl and ethyl iodide may be employed as alkylating agents. Unfortunately the reaction of higher alkyl halide homologues with the enolate **2** are too sluggish to by synthetically useful. However, alkylations of **2** with allylic and benzylic bromides proceeded readily, with γ,γ-dimethylallyl bromide reacting without rearrangement of the double bond. The crossed aldol reaction **4** → **5** accommodates a wide variety of aldehyde structures (Table I). It should be noted that Michael additions do not compete in reactions of the enolates **4** with α,β-unsaturated aldehydes. The versatility of the present olefin synthesis is illustrated by the stereoselective preparation of the triene **8** using γ,γ-dimethylallyl bromide and *trans*-crotonaldehyde (eq 3).



(3)

8

An additional important feature of the portrayed olefin synthesis is the fact that the acylsilane moiety in **6** provides for further structural transformations as exemplified in eq 4.[17] For example, oxidation of the α,β-unsaturated acylsilane **9** with alkaline hydrogen peroxide cleanly produces the α,β-unsaturated acid **10**. Also, we have recently found that treatment of the unsaturated acylsilane **9** with tetrabutylammonium fluoride (1.1 equiv) in the presence of formic acid (95–97%, 3 equiv) for 24 h at 75 °C converts them into the corresponding α,β-unsaturated aldehyde **11**.[18,19]



(4)

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(10) Spectral data for **6**: IR (neat) 1635 (C=C), 1590 (C=O), 1250 ($SiCH_3$), 845 cm^{-1} ($SiCH_3$); NMr (CCl_4) δ 6.2 (dq, J = 10, 1 Hz, 1 H, CH=C), 2.3–2.7 (m, 1 H, CHC=C), 1.6 (d, J = 1 Hz, 3 H, C=CCH_3), 1.2–1.6 (m, 2 H, CH_2), 1.0 (d, J = 7 Hz, 3 H, CH_3), 0.8 (t, J = 7 Hz, 3 H, CH_3), 0.1 (s, 9 H, $SiMe_3$); exact mass m/e 198.1421 (calcd for $C_{11}H_{22}OSi$: 198.1441).

(11) The physical constants and the spectral data were in good agreement with those reported in the literature for the (E)-acid. Katzenellenbogen, J. A.; Utawanit, T. *J. Am. Chem. Soc.* **1974**, *96*, 6153.

(12) Although isolation of the unsaturated acylsilane is not necessary, it should be worked up and concentrated prior to oxidation.

(13) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780. Hudrlik, P. F.; Peterson, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 1464. Chan, T. H. *Acc. Chem. Res.* **1977**, *10*, 442.

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(15) Grieco, P. A.; Wang, C. L. J.; Burke, S. D. *J. Chem. Soc. Chem. Commun.* **1975**, 537.

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(17) For other interesting transformations of the acylsilane group, see: Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 95. Sato, T.; Arai, M.; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, *99*, 5827. Reich, H. J.; Rusek, J. J.; Olson, R. E. *Ibid.* **1979**, *101*, 2225. Reich, H. J.; Olson, R. E.; Clark, M. C. *Ibid.* **1980**, *102*, 1423.

(18) We have not yet optimized the reaction conditions for this transformation.

(19) After submitting the manuscript, a paper describing the conversion of aryl-substituted acylsilanes to the corresponding aldehydes, using potassium fluoride or tetrabutylammonium fluoride, appeared: Schinzer, D.; Heathcock, C. H. *Tetrahedron Lett.* **1981**, 1881.

In summary, [(trimethylsilyl)acetyl]trimethylsilane (**1**) represents a valuable synthon in that it may be elaborated in a stereoselective, stepwise manner into di- and trisubstituted enolates and disubstituted α,β-unsaturated acylsilanes. The latter olefin synthesis provides an alternative to the Wittig olefination with the additional feature that the acylsilane group may be converted into a number of synthetically useful functionalities.[17]

Acknowledgment. We thank the National Science Foundation for support of this investigation.

Cyclopentadienylbis(ligand)nickel(I): Synthesis and Characterization, Including the X-ray Structure of η^5-Cyclopentadienyl-1,1′-bipyridylnickel(I). Observations on the Mechanism of Substitution of Nickelocene

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The chemistry of nickel in the formal 1+ oxidation state is very poorly defined at present. Although several complexes have been isolated,[1] many have resulted from fortuitous syntheses and most are poorly characterized with respect to structure and reactivity patterns. Nickel(I) species are potential intermediates in reactions that involve Ni(0) $\rightleftharpoons$ Ni(II) conversions, but few efforts have been made to detect them. Evidence is slowly accumulating that indicates Ni(I) species participate in chemistry that is unrelated to their role in a Ni(0) $\rightleftharpoons$ Ni(II) process. For example, various Ni(I) species are claimed to undergo oxidative-addition (to the 3+ state)[2] and to react with oxygen[3a] (to give an adduct) and olefins.[3b]

This communication is a preliminary report on the synthesis and characterization of Ni(I) complexes of formula $[(C_5H_5)NiL_2]$[4] ($L = R_3P$, R_2POR, $RP(OR)_2$, $P(OR)_3$; L_2 = diphos,[5] arphos,[5] bpy, *o*-phen) including the X-ray structure of CpNi(bpy). Our results indicate that these species are intimately involved in a number of reactions of cyclopentadienylnickel complexes. Two examples of this type of Ni(I) complex have been reported. Uhlig and Walther first isolated $CpNi[PhP(n\text{-}Bu)_2]_2$ according to reaction 3[6] and later from (2)[7] (Table I). More recently $\mathrm{Cp}\overline{\mathrm{NiN(Ph)NNN}}\mathrm{Ph}$ was prepared from Cp_2Ni and PhN_3.[8]

Each of the reactions listed in Table I produced an EPR active product, although when L was a phosphorus(III) ester the EPR signal decayed after a short time regardless of the method of preparation. The same EPR active products were obtained in several cases by electrochemical reduction of $[CpNiL_2]^+$ salts. Sample spectra are shown in Figure 1. Spectra of complexes that contain identical phosphorus ligands consist of 1:2:1 triplets except for the $PhP(OMe)_2$ and $P(OMe)_3$ complexes which give a doublet of doublets.[9,10] Superhyperfine splitting was not resolved in the

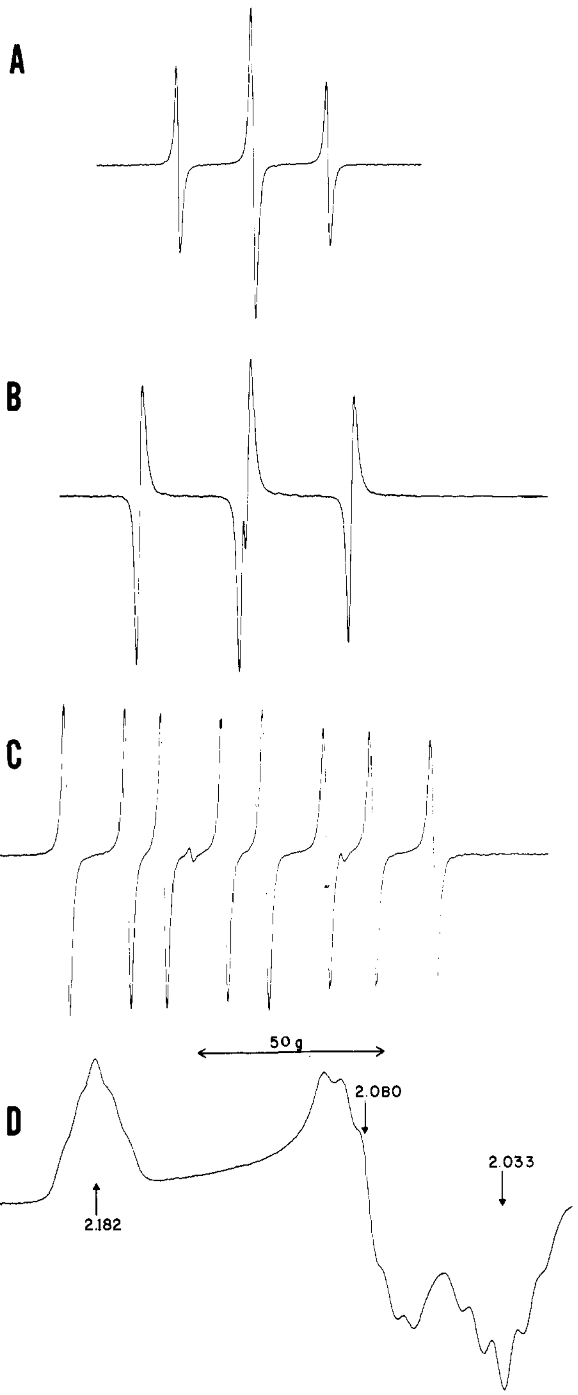

Figure 1. EPR spectra of $CpNiL_2$ Complexes. (A) CpNi(diphos): THF, 25 °C; $g = 2.068$, $A = 122$ G. (B) $CpNi[PPh(OMe)_2]_2$: toluene, 25 °C; $g = 2.052$, $A_1 = 170$ G, $A_2 = 180$ G. (C) CpNi(arphos): THF, 25 °C; $g = 2.075$, $A_P = 100$ G, $A_{As} = 170$ G. (D) CpNi(bpy): THF, −196 °C; $g_1 = 2.184$, $g_2 = 2.080$, $g_3 = 2.033$, $A_1 = 8.4$ G, $A_2 = 8.8$ G, $A_3 = 11.3$ G (from simulated spectrum).

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(1) Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1980**, *33*, 87.

(2) (a) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547. Smith, G.; Kochi, J. K. *J. Organomet. Chem.* **1980**, *198*, 199 and references cited. (b) Healy, K. P.; Pletcher, D. *J. Organomet. Chem.* **1978**, *161*, 109. Gosden, C.; Healy, K. P.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1978**, 972. (c) Tait, A. M.; Hoffman, M. Z.; Hayon, E. *Inorg. Chem.* **1976**, *15*, 934.

(3) (a) Vasilevskis, J.; Olson, D. C.; Loos, K. *Chem. Commun.* **1970**, *1718*. (b) D'Aniello, M. J., Jr.; Barefield, E. K. *J. Am. Chem. Soc.* **1978**, *100*, 1474. Another claim for Ni(I)-olefin chemistry has been discounted: Druliner, J. D.; English, A. D.; Jesson, J. P.; Meakin, P.; Tolman, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 2156.

(4) Hereafter C_5H_5 will be abbreviated as Cp when the group is known or suspected to be bonded in pentahapto fashion.

(5) Diphos is $Ph_2PCH_2CH_2PPh_2$; arphos is $Ph_2AsCH_2CH_2PPh_2$.

(6) Uhlig, E.; Walther, H. *Z. Chem.* **1971**, *11*, 23.

(7) Uhlig, E.; Walther, H. *Z. Anorg. Allg. Chem.* **1974**, *409*, 89.

(8) Overbosch, P.; van Koten, G.; Overbeek, O. *J. Am. Chem. Soc.* **1980**, *102*, 2091.

(9) The reason for the nonequivalence of the two donors in not known.

(10) Mixed ligand complexes result from reaction of $CpNiL_2$ with L′. The following complexes have been identified: $\{CpNi[PhP(n\text{-}Bu)_2][P(OMe)_3]\}$, $g = 2.057$, $A_{P_1} = 189$ G, and $A_{P_2} = 135$ G; $\{CpNi[P(n\text{-}Bu)_3][P(OMe)_3]\}$, $g = 2.055$, $A_{P_1} = 212$ G, and $A_{P_2} = 140$ G; $\{CpNi[PhP(n\text{-}Bu)_2](CO)\}$, $g = 2.036$ and $A_P = 150$ G. For comparison, the parameters of the precursor complexes are as follows: $PhP(n\text{-}Bu)_2$, $g = 2.076$, $A = 117$ G; $P(n\text{-}Bu)_3$, $g = 2.075$, $A = 125$ G; for the bis(trimethyl phosphite) complex, $g = 2.051$ and $A = 193$ and 208 G.

0002-7863/81/1503-6219$01.25/0