was supported in part by a grant from the Ministry of Education, Science, and Culture in Japan.

Supplementary Material Available: Table of HF/6-31G* vibrational frequencies of dihydrosilylene-oxygen adduct and its isotopomers in the triplet state (1 page). Ordering information is given on any current masthead page.

An Unusually Lower Barrier to Reductive Elimination of an 18-Electron η^3-Allyl(organo)nickel(II) Complex Than Those of a 16-Electron η^3-Allyl Counterpart and a 16-Electron η^1-Allyl Isomer

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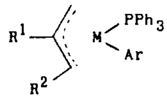
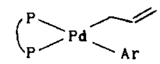
In spite of a versatile role played by reductive elimination of η^3-allylmetal complexes in organic transformations,[1-3] little has been known concerning the mechanistic details of this step. We wish to report a novel finding that the coupling of allyl and aryl groups on Ni is much more facile in an η^3-allyl form with 18-electron configuration than in both a 16-electron η^3-allyl counterpart and a 16-electron η^1-allyl isomer. This trend, not observed in the η^3-allylpalladium chemistry,[4] seems of particular relevance to the origin of some unique ligand and metal effects upon reactivity and selectivity in catalyses.[1,5] Acceleration of reductive elimination upon change of electron count on Ni from 16 to 18 has precedence in alkylnickel chemistry,[6] but none has revealed such a remarkable rate enhancement, in a quantitative manner, as is disclosed here.

Spontaneous reductive elimination of η^3-allyl(aryl)nickel(II) complexes **1**[7] in toluene proceeded smoothly to afford high yields (>85%) of allylbenzene derivatives (eq 1). The first-order rate constant (k_1)[8] of eq 1 for **1a** and **1b** was found independent of the amount of excess PPh_3 (up to 5 equiv) added,[9] as in eq 1 for the palladium analogue **2**.[4] The ratio of k_1 for **1a** versus that[4] for **2** at 0 °C ($k_1[Ni]/k_1[Pd] = 26$) provides the first direct comparison of the reactivity, between organonickel and palladium complexes with the identical composition, for the reductive elimination proceeding through a common mechanism.[10]



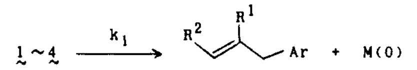
1 or **2**



3

	M	R^1	R^2	Ar
1a	Ni	H	H	$C_6H_3Cl_2$-2,5
1b	Ni	Me	H	C_6F_5
1c	Ni	H	Me	C_6F_6
2	Pd	H	H	$C_6H_3Cl_2$-2,6

	Ar	diphos
3a	$C_6H_3Cl_2$-2,6	dppe
3b	$C_6H_3Cl_2$-2,6	dppen
3c	C_6F_6	dppen



$$\mathbf{1} \sim \mathbf{4} \xrightarrow{k_1} R^2CH{=}C(R^1)CH_2Ar + M(0) \quad (1)$$

Particularly noteworthy are the contrasting behaviors of **1** and **2** with respect to both structure and reactivity when chelating diphosphine ($Ph_2PCH_2CH_2PPh_2$ dppe; Z-$Ph_2PCH{=}CHPPh_2$ dppen) was added to these complexes. Thus, **2** and its C_6F_5 analogue reacted with the diphosphines quite rapidly to give η^1-allylpalladium complexes **3**[4,7b,11] which are *less reactive*[12] as compared to the reductive elimination of the parent η^3-allyl complexes. On the other hand, addition of the diphosphines to **1** dramatically *enhanced* the reductive elimination rate, which is attributed to formation of quite reactive, 18-electron η^3-allyl complexes **4**, as discussed below.

Attempts to isolate **4** from the solution containing any of **1** and the diphosphines even at temperatures below 0 °C were unsuccessful. Nor could we obtain any spectral clue to an intermediate in the rapid reductive elimination caused by adding dppe or dppen (1-2 equiv) to **1a** at -50 °C (half-life ≤ 0.5 h). However, NMR (^1H, ^{13}C, ^{31}P) spectra[13] and the color (reddish-orange)[14] of a solution obtained by mixing **1b** or **1c** with dppen (1 equiv) below -20 °C were sufficiently informative. Thus, the ^{31}P spectra showed complete dissociation of PPh_3 from Ni and coordination of both phosphorus atoms of dppen, and the ^{13}C chemical shifts of newly

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(1) (a) Keim, W.; Behr, A.; Roper, M. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 52. (b) Jolly, P. W. Chapter 56, ref 1a. (c) Tolman, C.; Faller, J. W. *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983; p 64.

(2) (a) Consiglio, G.; Piccolo, O.; Roncetti, L.; Morandini, F. *Tetrahedron* **1986**, *42*, 2043-2053. (b) Hegedus, L. S.; Thompson, D. H. P. *J. Am. Chem. Soc.* **1985**, *107*, 5663-5669. (c) Hayashi, T.; Konishi, M.; Yokota, K.; Kumada, M. *J. Organomet. Chem.* **1985**, *285*, 359-373. (d) Benn, R.; Bussemeier, B.; Holle, S.; Jolly, P. W.; Mynott, R.; Tkatchenko, I.; Wilke, G. *Ibid.* **1985**, *279*, 63-86. (e) Hiyama, T.; Wakasa, N. *Tetrahedron Lett.* **1985**, *26*, 3259-3262. (f) Consiglio, G.; Morandini, F.; Piccolo, O. *J. Chem. Soc., Chem. Commun.* **1983**, 112-114. (g) Cherest, M.; Felkin, H.; Umpleby, J. D.; Davies, S. G. *Ibid.* **1981**, 681-682.

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(4) Kurosawa, H.; Emoto, M.; Ohnishi, H.; Miki, K.; Kasai, N.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1987**, *109*, 6333-6340.

(5) For example, nickel catalysts are generally more effective than palladium catalysts in cyclooligomerization of dienes.[3b] Also, chelating diphosphine/nickel systems are unique catalysts for regio- and enantioselective allylic alkylations as compared to the analogous palladium systems.[2a,c,e-g,3c]

(6) (a) McKinney, R. J.; Roe, D. C. *J. Am. Chem. Soc.* **1986**, *108*, 5167-5173. (b) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *Ibid.* **1984**, *106*, 8181-8188. (c) Komiya, S.; Abe, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1983**, *2*, 1466-1468.

(7) (a) Prepared in a manner similar to that[4] for the palladium analogue. (b) All new complexes isolated gave satisfactory analytical and spectral results.

(8) (a) Rates were followed by observing the coupling products by GLC and ^1H NMR (see ref 4). The initial concentrations of the complexes were 0.1 M (^1H NMR) and 0.02 M (GLC). The decomposition of **1a** was run in the presence of excess PhC≡CPh in order for the clean kinetics to be attained, with the role of PhC≡CPh being attributed possibly to stabilization of the Ni(0) species formed (cf. ref 8b,c for the palladium case). k_1 (h^{-1}) in toluene is as follows: **1a** 0.077 (0 °C); **1b** 0.382 (101 °C), 1.34 (116 °C), 5.15 (127 °C). (b) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868-1880. (c) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933-4941.

(9) Excess of free PPh_3 caused no change at all in ^1H NMR spectra of **1a** and **1b**.

(10) Theoretical prediction: Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857-1867.

(11) Kurosawa, H.; Urabe, A.; Miki, K.; Kasai, N. *Organometallics* **1986**, *5*, 2002-2008.

(12) For example, k_1 (h^{-1}) in toluene at 40 °C are as follows: **2**, 0.693; **3a**, 0.0578; **3b**, 0.0866.

(13) (a) **4b**: ^1H NMR (toluene-d_8, -20 °C), δ 1.59 (t, $J_P = 3$ Hz, CH_3), 2.15 (br t, $J_P = 4.5$ Hz, $-CH_2$); ^{13}C NMR (CD_2Cl_2, -80 °C) δ 22.2 (CH_3), 58.4 and 61.1 (allyl terminal), 109.1 (allyl center); ^{31}P NMR (CD_2Cl_2, -80 °C) δ (external H_3PO_4) 21.3 and 39.5, $J_{P-P} = 150$ Hz. **4c**: ^1H NMR (toluene-d_8, -20 °C) δ 0.68 (dt, $J_H = 6$, $J_P = 4.5$ Hz, CH_3), 1.23 (q, $J_H = J_P = 9$ Hz, $-CH_2$), 3.32 (br, -C*H*Me), 5.21 (dt, $J_H = 9$, 10 Hz, -CH-); ^{13}C NMR (CD_2Cl_2, -50 °C) δ 19.7 (CH_3), 48.2 (-*C*H_2), 78.0 (-*C*HMe), 96.1 (allyl center); ^{31}P NMR (CD_2Cl_2, -80 °C) δ 23.0 and 38.5 (very br, J_{P-P} not resolved). (b) Lowering the temperature down to -90 °C resulted in only broadening of the ^1H NMR spectra. (c) Nonequivalent signals of two allyl terminal carbons in **4b** as well as those of two phosphorus nuclei of dppen in **4b** and **4c** coalesced to one signal (δ 59.6, 29.9, 30.0, respectively) at above -50 °C.

(14) The 16-electron complexes of the type Ni(η^3-allyl)(Ar)(PR_3) and Ni(CH_3)(Ar)(PR_3)$_2$ are all yellow colored.

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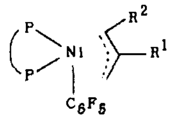
formed complexes unambiguously indicated the allyl groups to be bound to Ni solely in an η^3-fashion. The ^{1}H spectra of **4c** exhibited only one resonance for the syn and anti protons of the allylic terminal, suggesting syn–anti proton exchange via a short-lived η^1-allylnickel complex **5** rapid on the NMR time scale.[13b] The four allylic hydrogens of **4b** also appeared as only one resonance,[13b] presumably attributable to both rapid syn–anti proton exchange and rapid site exchange of the two allylic termini.[13c] The latter process is most probably associated with the well-known intramolecular rearrangement of d^8, 5-coordinated complexes.[15] The occurrence of this rearrangement in **4** manifested itself also in the coalescence of the two ^{31}P resonances of **4b** and **4c** at the higher temperatures.[13c] This coalescence cannot be attributable to intermolecular phosphine exchange nor to occurrence of a monodentate dppen ligand, since the spin couplings between some allyl ligand hydrogens and two equivalent ^{31}P nuclei were observed in the higher temperature ^{1}H NMR spectra.



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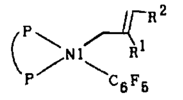

6

	R^1	R^2	diphos
4a	Me	H	dppe
4b	Me	H	dppen
4c	H	Me	dppen

On raising the temperature of the solution containing **4** to above −20 °C, rapid, nearly quantitative formation of the pentafluoroallylbenzenes occurred. The kinetics of this process for **4a** and **4b** were followed by ^{1}H NMR spectroscopy at −19 to 10 °C to show clean first-order dependence of the rate on the amount of the complex, with k_1[16] being unvaried on changing the amount of added diphosphine (1–2 equiv) and PPh$_3$ (0–4 equiv). Of particular note is the great difference between the activation energy ($\Delta H^{\ddagger}$) for the reductive elimination from 18-electron complex **4b** (59 ± 4 kJ/mol)[17] and that from 16-electron complex **1b** (122 ± 10 kJ/mol).[17] The ratio of the rate constants at −10 °C for **4b** versus **1b** (9×10^{-9} h^{-1}, extrapolated) amounts to 10^8.

A possibility that the short-lived species **5** is responsible for the enhanced reactivity of **4** appears less likely[18] for the following reasons. Provided that the relative reactivity of 16-electron η^3-allyl and 16-electron η^1-allyl forms described in the palladium complexes (**2** > **3**) also applies in the case of the nickel complexes **1** and **5**, the order of the reactivity is deduced to be **4** ≫ **1** > **5**. The considerably low reactivity of **5** is also consistent with the slow rate of the reductive elimination of a related complex, Ni(CH$_3$)(C$_6$F$_5$)(dppen)[14,19] ($\Delta H^{\ddagger}$ = 98 ± 2 kJ/mol), since the competitive experiments employing η^1-allyl(methyl)metal complexes of Pt^{IV} and Au^{III} suggested[20] the reactivity of the η^1-allyl group with respect to the reductive elimination to be comparable to that of the methyl. The coupling from 18-electron η^1-allylnickel, Ni(η^1-allyl)(Ar)(PR$_3$)$_3$ appears also unlikely in view of the rate from **4** being independent of the added phosphine. Efforts are under way to gain insight into structures of 18-electron η^3-allylnickel complexes and their relevance to the low barrier exit[6b] to the C–C coupling step.

Acknowledgment. Partial support of this work by grants from the Ministry of Education, Science and Culture is acknowledged.

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[15] (a) English, A. D.; Ittel, S. D.; Tolman, C. A.; Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 117–120, and references therein. (b) DuBois, D. L.; Meek, D. W. *Inorg. Chem.* **1976**, *15*, 3076–3083. (c) Shapley, J. R.; Osborn, J. A. *Acc. Chem. Res.* **1973**, *6*, 305–312.

[16] k_1 (h^{-1}) in toluene for **4a** is 0.767 (10 °C) and for **4b** 0.347 (−19 °C), 0.925 (−10 °C), and 4.10 (2 °C).

[17] $\Delta S^{\ddagger}$ (J/K mol) is as follows: **4b**, −88 ± 35 (−19 °C); **1b**, 3 ± 40 (101 °C). The large negative value in the former case might be attributed, in part, to freezing of fluxional movements in **4** at the transition state for the C–C coupling.

[18] Participation into the rapid C–C coupling of alternative four-coordinated η^1-allyl species having a structure considerably distorted from a regular square-planar geometry, though no precedence of this type of organonickel complexes has been known, remains to receive further experimental and theoretical scrutiny.

[19] Prepared from *trans*-Ni(CH$_3$)(C$_6$F$_5$)(PPh$_3$)$_2$ and dppen in tetrahydrofuran.[7b] Rate constant (h^{-1}) in benzene is 5.4 (90 °C), 2.4 (82 °C), and 0.78 (71 °C), independent of added PPh$_3$ (0–5 equiv) and dppen (3 equiv). $\Delta S^{\ddagger}$ = −32 ± 15 J/K mol.

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Optically Active 2-Ethenyl-1,3-dioxolanones as 3-Carbon Synthons. Allylnickel Derivatives as Homoenolate Equivalents

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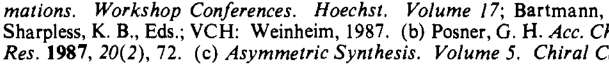
The development of reversed polarity synthons[1] and new methods for organic stereocontrol[2] are important concerns of current synthetic organic research. We report herein (1) a new, allylnickel approach to homoenolate equivalent chemistry[3] and (2) the coupling of this methodology with a new enantioselective aldol equivalent reaction[4] as part of a new approach to 3-carbon synthon stereocontrol.

As detailed elsewhere,[5] optically active 2-ethenyl-1,3-dioxolan-4-ones are available in a single step by condensation of acrolein with optically active (R)- or (S)-2-hydroxy acids (eq 1, R = Me, Ph, c-C$_6$H$_{11}$).



(1)

In other work, we have shown that these compounds undergo Lewis acid[6] and palladium[7]-catalyzed conjugate addition reactions with organic nucleophiles. We now report that the metal-centered nucleophile, bis(1,5-cyclooctadiene)nickel(0),[8] reacts with

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[1] Reviews: (a) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239. (b) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.

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[5] A procedure similar to that employed in the preparation of the 5,5-pentamethylene analogue by Soulier et al.[5a] was followed. In all cases, the 2-ethenyl-1,3-dioxolanone products are isolated as 2:1 cis/trans mixtures suitable for stereoselective applications. (a) Farines, M.; Soulier, J. *Bull. Soc. Chim. Fr.* **1970**, 332. (b) Friebe, T. L.; Krysan, D. J.; Mackenzie, P. B., manuscript in preparation.

[6] Grisso, B. A.; Friebe, T. L.; Mackenzie, P. B., submitted for publication.

[7] (a) Friebe, T. L.; Krysan, D. J.; Mackenzie, P. B. 194th National Meeting of the American Chemical Society, 1987; New Orleans, LA. (b) Friebe, T. L.; Mackenzie, P. B., manuscript in preparation.

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