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

Hideo Kurosawa,* Hiroaki Ohnishi, Mitsuhiro Emoto,
Yoshikane Kawasaki, and Shinji Murai

Department of Applied Chemistry
Osaka University, Suita, Osaka 565, Japan

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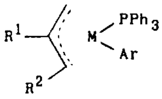
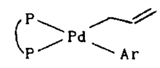
In spite of a versatile role played by reductive elimination of η^3-allylmetal complexes in organic transformations,[1-3] little has been known concerning the mechanistic details of this step. We wish to report a novel finding that the coupling of allyl and aryl groups on Ni is much more facile in an 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]



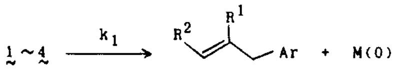
1 or **2**

	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_5
2	Pd	H	H	$C_6H_3Cl_2$-2,5



3

	Ar	diphos
3a	$C_6H_3Cl_2$-2,5	dppe
3b	$C_6H_3Cl_2$-2,5	dppen
3c	C_6F_5	dppen



(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.

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(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]

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(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 $PhC{\equiv}CPh$ in order for the clean kinetics to be attained, with the role of $PhC{\equiv}CPh$ 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.

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(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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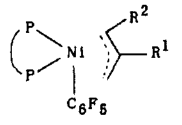
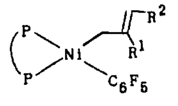
formed complexes unambiguously indicated the allyl groups to be bound to Ni solely in an η^3-fashion. The ^{1}H spectra of **4c** exhibited only one resonance for the syn and anti protons of the allylic terminal, suggesting syn–anti proton exchange via a short-lived η^1-allylnickel complex **5** rapid on the NMR time scale.[13b] The four allylic hydrogens of **4b** also appeared as only



4



5

	R¹	R²	diphos
4a	Me	H	dppe
4b	Me	H	dppen
4c	H	Me	dppen

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.

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, $Ni(CH_3)(C_6F_5)$(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, $Ni(\eta^1\text{-allyl})(Ar)(PR_3)_3$ 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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(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*-$Ni(CH_3)(C_6F_5)(PPh_3)_2$ 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). $\Delta S^{\ddagger} = -32 \pm 15$ J/K mol.

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

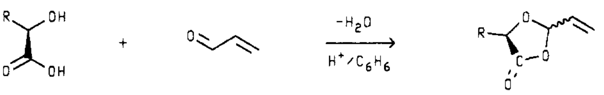
Damian J. Krysan and Peter B. Mackenzie*

Department of Chemistry, Northwestern University
Evanston, Illinois 60208

Received June 6, 1988

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_6H_{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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(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.

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