Preparation and reductive elimination of (.eta.3-allyl)(aryl)nickel(II) complexes: unusually facile .eta.3-allyl-aryl coupling on nickel having an 18-electron configuration

Hideo Kurosawa, Hiroaki Ohnishi, Mitsuhiro Emoto, Naoto Chatani, Yoshikane Kawasaki, Shinji Murai, and Isao Ikeda

Organometallics, **1990**, 9 (12), 3038-3042• DOI: 10.1021/om00162a014 • Publication Date (Web): 01 May 2002

Preparation and Reductive Elimination of (η^3-Allyl)(aryl)nickel(II) Complexes: Unusually Facile η^3-Allyl–Aryl Coupling on Nickel Having an 18-Electron Configuration†

Hideo Kurosawa,* Hiroaki Ohnishi, Mitsuhiro Emoto, Naoto Chatani, Yoshikane Kawasaki, Shinji Murai, and Isao Ikeda

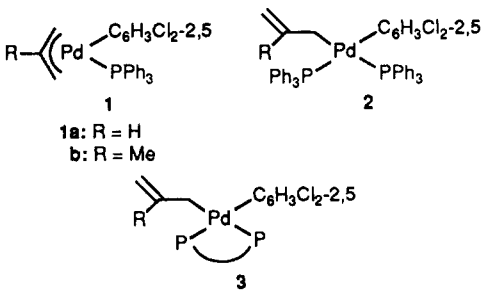
Department of Applied Chemistry, Osaka University, Suita, Osaka 565, Japan

Received April 11, 1990

The preparation and NMR spectral characterization of complexes of the type (η^3-allyl)(aryl)(triphenylphosphine)nickel(II) (aryl = $C_6H_3Cl_2$-2,5, C_6F_5), **4**, are described. Addition of PPh_3 to a solution of **4** did not result in the formation of (η^1-allyl)nickel intermediate as was deduced from ^1H NMR measurements, in contrast to the ready conversion of (η^3-allyl)palladium to (η^1-allyl)palladium species. The (dichlorophenyl)nickel derivative underwent reductive elimination ca. 26 times as fast as the corresponding palladium complex. Addition of chelating diphosphine ($Ph_2PCH_2CH_2PPh_2$, (*Z*)-$Ph_2PCH{=}CHPPh_2$) to the solution of the above nickel complexes afforded stereochemically nonrigid 18-electron η^3-allyl complexes, Ni(η^3-allyl)(aryl)(diphos), **5**, which have been characterized by low-temperature ^1H, ^{13}C, and ^{31}P NMR spectra for the C_6F_5 analogues. This behavior is again different from that of the palladium analogue, which has an identical composition in which the 16-electron η^1-allyl form is the ground-state structure. The kinetics of the reductive elimination of complexes **5** revealed that these undergo reductive elimination quite readily, with $\Delta H^{\ddagger}$ being ca. 60 kJ/mol lower than those values for the parent 16-electron counterparts **4**. Also presented is evidence against the significant contribution of a short-lived 16-electron η^1-allyl isomer of **5** to the enhanced reactivity with regard to the C–C coupling step in the diphosphine/allylnickel system.

Much attention has been paid to a class of homogeneous catalyses in which reductive elimination of allyl(organo)-metal complexes plays a key role.[1-3] *tert*-Phosphine complexes of Ni and Pd are among the most common catalysts in these reactions. At first glance, the two metal catalysts may behave in a similar way in each step of the overall catalytic cycle. However, it seems of particular interest to note that nickel complexes are more effective in certain catalyses such as cyclooligomerization of dienes[3b] and that chelating diphosphine/nickel systems are unique catalysts for regio- and enantioselective allylic alkylations as compared to analogous palladium systems.[2a,c,e-g,3c]

We have been interested in gaining deep insight into the mechanism of the reductive elimination of allyl(orgno)-metal complexes.[4] Kinetic studies on the reductive elimination of (η^3-allyl)palladium complexes **1** in the presence

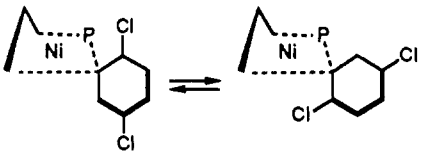


1a: R = H
b: R = Me

3a: R = H, diphos = dppe
b: R = H, diphos = dppen
c: R = Me, diphos = dppe
d: R = Me, diphos = dppen

of excess PPh_3 revealed that C–C bond formation takes place directly from this η^3-allyl form, but not from an (η^1-allyl)palladium(II) intermediate **2**.[4a] Complex **2** was found by ^1H NMR spectroscopy to exist only as a transient species during a rapid allylic syn–anti proton exchange, but substitution of chelating diphosphine

Scheme I



($Ph_2PCH_2CH_2PPh_2$, dppe; and (*Z*)-$Ph_2PCH{=}CHPPh_2$, dppen) for two molecules of PPh_3 resulted in the formation of a stable η^1-allyl species **3**,[4a,5] which underwent less facile reductive elimination than **1**.

In order to compare the reactivity patterns of the nickel complexes with the palladium complexes, we have studied the preparation and reductive elimination of (η^3-allyl)-

† Dedicated to the memory of the late Prof. J. K. Stille.

(1) (a) Keim, W.; Behr, A.; Roper, M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 52. (b) Jolly, P. W. ref 1a, Chapter 56. (c) Tolman, C.; Faller, J. W. In *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.

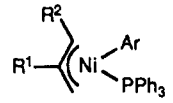
(3) (a) Trost, B. M.; Walchli, R. *J. Am. Chem. Soc.* **1987**, *109*, 3487-3488. (b) Goliaszewski, A.; Schwartz, J. *Tetrahedron* **1985**, *41*, 5779-5789. (c) Fiaud, J. C.; Aribi-Zouioueche, L. *J. Organomet. Chem.* **1985**, *295*, 383-387. (d) Trost, B. M.; Herndon, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 6835—6837. (e) Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *Ibid.* **1984**, *106*, 4833-4840. (f) Temple, J. S.; Riediker, M.; Schwartz, J. *Ibid.* **1982**, *104*, 1310-1315. (g) Matsushita, H.; Negishi, E. *Ibid.* **1981**, *103*, 2882-3884.

(4) (a) Kurosawa, H.; Emoto, M.; Ohnishi, H.; Miki, K.; Kasai, N.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1987**, *109*, 6333-6340. (b) Kurosawa, H.; Emoto, M.; Urabe, A.; Miki, K.; Kasai, N. *Ibid.* **1985**, *107*, 8253-8254.

(5) (a) Kurosawa, H.; Urabe, A.; Miki, K.; Kasai, N. *Organometallics* **1986**, *5*, 2002-2008. (b) Numata, S.; Okawara, R.; Kurosawa, H. *Inorg. Chem.* **1977**, *16*, 1737-1741.

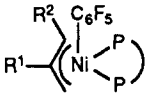
0276-7333/90/2309-3038$02.50/0

(organo)nickel(II) complexes of the type **4**. Here we de-



4

4a: $R^1 = R^2 = H$, $Ar = C_6H_3Cl_2$-2,5
b: $R^1 = R^2 = H$, $Ar = C_6H_5$
c: $R^1 = Me$, $R^2 = H$, $Ar = C_6F_5$
d: $R^1 = H$, $R^2 = Me$, $Ar = C_6F_5$



5

5a: $R^1 = Me$, $R^2 = H$, diphos = dppe
b: $R^1 = R^2 = H$, diphos = dppen
c: $R^1 = Me$, $R^2 = H$, diphos = dppen
d: $R^1 = H$, $R^2 = Me$, diphos = dppen

scribe a novel finding that the addition of the chelate diphosphine to 16-electron (η^3-allyl)nickel(II) complexes **4** results in the formation of 18-electron η^3-allyl species **5**, which shows by far greater reactivity than **4** with respect to reductive elimination.[6]

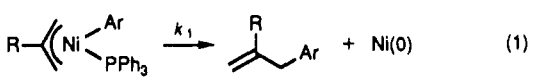
Results and Discussion

Preparation and Reaction of 16-Electron (η^3-Allyl)nickel. Yellow complexes **4a–d** were prepared from Ni(η^3-allyl)X(PPh_3) (X = Cl, Br) and ArZnCl in THF. Employing ArLi instead of ArZnCl resulted in a much less clean reaction, with Ni(C_6F_5)$_2$(PPh_3)$_2$ being isolated as one of the products from Ni(η^3-C_3H_5)Cl(PPh_3) and C_6F_5Li. ^1H NMR data are shown in Table I.

^1H NMR spectra of **4a** in toluene-d_8 and CD_2Cl_2 at −20 °C showed the presence of two isomers (ca. 1:1), possibly arising from the restricted rotation of the 2,5-dichlorophenyl group (Scheme I). We could observe no coalescence of the resonances due to the two isomers up to ca. 30 °C, and raising the temperature further resulted in very rapid decomposition of the complex. The corresponding palladium complex **1a** did not show such isomerism under similar conditions,[4a] presumably because of the less steric crowding about the organic ligands in the Pd complex than in the Ni complex, which in turn may originate from the larger covalent radii of Pd than of Ni.

The ^1H and ^{13}C NMR data of **4d** indicated the existence of only one isomer where the methyl is located syn to the central H and trans to PPh_3. The ^1H NMR spectra of **4a–d** did not change upon adding excess PPh_3 (up to 4 equiv), whereas the same experiments with the Pd analogues resulted in coalescence of the syn and the anti protons, which is a consequence of the formation of a short-lived η^1-allyl species such as **2** and its trans isomer.[4a,5b] Thus, the weaker tendency of the Ni complex to form η^1-allyl species than that of the Pd complex is indicated.

Complex **4a** slowly underwent reductive elimination in toluene at 0 °C to afford the coupling product (eq 1). The



(1)

yield of the coupling product was ca. 90% if the PhC≡CPh or CH_2=$CHCH_2Cl$ was added but dropped to ca. 50% in the absence of these additives. Presumably, metallic nickel precipitates in the latter case induced an undesirable decomposition of **4a**. The first-order rate constants for the reductive elimination of **4a** are summarized in Table II. Interestingly, addition of PhC≡CPh (0.1 M) to **4a** (0.02 M) had no effect on the rate of the formation of the coupling product. The rate constant of the spontaneous reductive elimination of **4a** was not affected by adding PPh_3 (up to 5 equiv). The ratio of k_1 for **4a** at 0 °C in toluene (0.077 h^{-1}) versus the corresponding rate constant for **1a** (0.0029 h^{-1}), which was extrapolated from the activation parameters obtained at higher temperatures,[4a] is k_1-[Ni]/k_1[Pd] = 26. This comparison, the first for the organonickel and the organopalladium reactivity for the reductive elimination, with the complex composition and reaction pathway being identical with each other, is in good agreement with the theoretical prediction[7] that dialkylnickels give a lower activation barrier to redutive elimination than do dialkylpalladiums.

The C_6F_5 derivatives **4b–d** are much less reactive than the dichlorophenyl derivative **4a**. Heating a toluene solution of **4c** at above 100 °C resulted in a clean formation of the coupling product in more than 90% yield (eq 1), with the rate being first-order with respect to the complex. The first-order rate constants for **4c** under various conditions are also shown in Table II.

Addition of PPh_3 (5 equiv) again had no effect on the reaction rate (Table II). On the other hand, addition of fumaronitrile to **4c** even at 25 °C induced a dramatic increase in the reductive elimination rate (Table II), with the rate being dependent on the amount of fumaronitrile added (eq 2; k_2 = 0.43 h^{-1} M^{-1}). These behaviors are sim-

$$\text{rate} = k_{obsd}[\mathbf{4c}] = k_2[\text{CNCH=CHCN}][\mathbf{4c}] \quad (2)$$

ilar to those observed in the olefin-enhanced reductive elimination of (η^3-allyl)palladium complexes.[4a] No intermediate species could be detected in the ^1H NMR spectra during the olefin-enhanced reductive elimination of **4c**.

Formation of 18-Electron (η^3-Allyl)nickel(II) Complexes. Addition of 1 equiv of dppe or dppen to toluene solutions of **4a–d** at room temperature caused immediate formation of the coupling product in almost quantitative yields. No intermediate species could be detected in the NMR spectra during the rapid reductive elimination caused by adding the diphosphine to **4a** at −50 °C (half-life less than 0.5 h). Presumably, an equilibrium between **4a** and any intermediate species that is quite labile with respect to reductive elimination lies far to the side of **4a**. On the other hand, addition of dppen (1 equiv) to solutions of **4b–d** at −60 °C resulted in an immediate color change from yellow to reddish orange where the NMR measurements showed that **4b–d** had disappeared completely, but no coupling product was yet formed. The NMR spectral data relevant to structural characterization of the species formed from **4b–d** and dppen are shown in Table III.

All the ^1H, ^{13}C, and ^{31}P NMR spectra were temperature dependent. The variable-temperature spectral aspect observed includes little chemical shift change and only coalescing phenomena of some resonances at the higher temperatures, as described below.

The ^1H NMR spectra of **4b–d** were not variant down to −80 °C except that each resonance became broader as the temperature was lowered. We could not observe any clear, frozen ^1H NMR spectra down to ca. −90 °C because of the extreme broadness of the resonances. The spectral feature (Table III) is essentially as expected from rapid exchange of all four allylic hydrogens in **4b**/dppen and **4c**/dppen and of the two methylene hydrogens in **4d**/dppen. The appearance of the spin couplings between some allylic ligand hydrogens and two ^{31}P nuclei is consistent with the chelate structure of dppen.

The ^{13}C NMR data were sufficiently informative to allow assignment concerning the way of binding of the allyl ligand. Thus, the ^{13}C shifts of the allyl skeleton in complexes formed from **4b–d** and dppen at −85 °C (Table III) are well in accord with the presence of a η^3-bound allylic

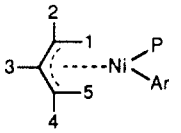
(6) Preliminary communication: Kurosawa, H.; Ohnishi, H.; Emoto, M.; Kawasaki, Y.; Murai, S. *J. Am. Chem. Soc.* **1988**, *110*, 6272–6273.

(7) Tatsumi, K.; Hoffman, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857–1867.

Table I. ^{1}H NMR Data of (η^3-Allyl)nickel(II) Complexes 4[a]

	δ				
complex	1	2	3	4	5
4a[b]					
isomer 1	1.75 d, J = 13	2.94 vbr	4.89 m	3.50 br	2.37 br d, J = 13
isomer 2	1.91 d, J = 13	c	c	3.82 br d, J = 8	c
4b	1.75 d, J = 14	3.00 br	4.83 m	3.70 ddd, J = 2, 3, 7	2.57 dd, J = 14, 5
4c	1.85 s	2.78 br	1.77 s	3.43 br	2.60 d, J = 5
4d	1.55 d, J = 14	2.79 br	4.78 dt, J = 8, 14	1.24 t, J = 6	3.48 br m

[a] In toluene-d_8 at 25 °C except as noted. δ in ppm, J in Hz, Proton numbering scheme is



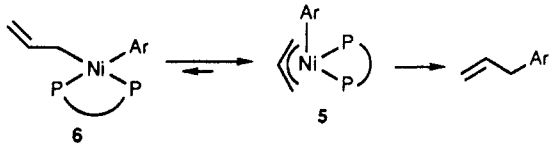
[b] At −20 °C. In CD_2Cl_2: δ (1) 1.87 d, J = 13; δ (2) 3.03 br; δ (3) 5.20 m; δ (4) 3.57 br d, J = 8, 3.72 br d, J = 8; δ (5) 2.51 br d, J = 13, 2.85 br d, J = 13. [c] Overlapped with other resonances.

Table II. First-Order Rate Constants for the Reductive Elimination of (η^3-Allyl)nickel Complexes 4 in Toluene[a]

complex	temp/°C	additive	concn/M	k_{obsd}/h^{-1}
4a	0	none		0.069[b]
		PhC≡CPh	0.2	0.077
		PhC≡CPh PPh_3	0.2 0.02	0.071
		PhC≡CPh PPh_3	0.2 0.1	0.084
4c	101	PPh_3	0.5	0.382
	116	none		1.21
		PPh_3	0.5	1.46
	127	PPh_3	0.5	5.15
	25	FN[c]	0.444	0.208
		FN[c]	0.956	0.463
		FN[c]	1.35	0.599

[a] Initial concentration is 0.02 M (**4a**) and 0.1 M (**4c**). [b] Initial rate. [c] FN: (*E*)-CNCH=CHCN.

Scheme II

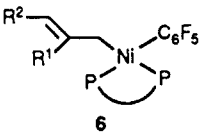


moiety but not of a η^1-bound allylic one. We could not observe any resonances in the region where the (η^1-allyl)nickel species is expected[2d,8] to resonate. The two nonequivalent terminal carbon resonances in **4b**/dppen and **4c**/dppen coalesced to a single resonance at higher temperatures (Table III).

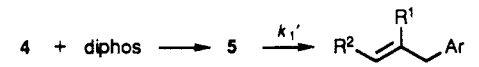
The ^{31}P spectra showed complete dissociation of PPh_3 from Ni. Coordination of both phosphorus atoms of dppen to Ni is also indicated by the appearance of two nonequivalent, equal-intensity ^{31}P signals at much lower fields than the free dppen resonance for **4c**/dppen and **4d**/dppen at −85 °C. The ^{31}P spectrum of **4b**/dppen at −90 °C showed only one, very broad resonance. At −30 °C, all of these signals became sharp singlets.

All of the above spectral features suggest that the complex formed from **4** and dppen takes an 18-electron η^3-allyl structure **5** in the ground state in which two allylic terminal carbons and two phosphorus atoms are chemically nonequivalent and undergo rapid exchange with each other at higher temperatures. One simplified model for **5** would be a trigonal bipyramid with each of the bidentate dppen and allyl ligands occupying equatorial and apical coordination sites. However, there may be several modifications of such a model, and any conclusive identification of the precise structure remains unsolvable.

The allylic syn–anti proton exchange in **5** may proceed through a short-lived η^1-allyl intermediate **6**.[9] Also, complex **5** would be very prone to undergo rapid, intramolecular rearrangements that accompany the site exchanges of phosphorus and allyl carbons, as was often observed in various d^8, 5-coordinated complexes.[10]



Reductive Elimination of 18-Electron (η^3-Allyl)nickel Complexes. Raising the temperature of the solution containing **5a–d** to above −20 °C resulted in rapid, almost quantitative formation of the coupling products (eq 3). The kinetics of this process for the 2-methallyl com-



(3)

plexes **5a** and **5c** were followed by ^{1}H NMR spectroscopy at −19–10 °C to show a clean first-order dependency of the rate on the amount of complex. The relevant rate data are summarized in Table IV.

The first-order rate constant (k_1') was not affected by the addition of excess dppen and PPh_3 (Table IV). Of particular note is the great difference between the activation energy ($\Delta H^\ddagger$) for the reductive elimination from the 18-electron complex **5c** (59 ± 4 kJ/mol; $\Delta S^\ddagger$ = −88 ± 35 J/(K mol)) and from the 16-electron complex **4c** (122 ± 10 kJ/mol; $\Delta S^\ddagger$ = 3 ± 40 J/(K mol)). The origin of the large negative $\Delta S^\ddagger$ value in the former reaction is not clear at the moment but perhaps has some bearing on the very fluxional nature of **5c**, which should be frozen out, more or less, at the transition state of C–C coupling. The ratio of the rate constant at −10 °C for **5c** versus **4c** (9×10^{-9} h^{-1}, extrapolated) is 10^8.

It seems appropriate here to consider a possibility that the short-lived η^1-allyl species **6** is responsible for the enhanced reactivity of **5**. If this possibility is real, then the intrinsic reactivity of **6** should be much higher than the

(8) Henc, B.; Jolly, P. W.; Salz, R.; Stobbe, S.; Wilke, G.; Benn, R.; Mynott, R.; Seevogel, K.; Goddard, R.; Kruger, C. *J. Organomet. Chem.* **1980**, *191*, 449–475.

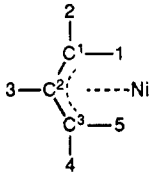
(9) Vrieze, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 441.

(10) (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.

Table III. NMR Data of (η^3-Allyl)nickel Complexes Formed from 4 and Dppen[a]

starting complex	δ (^{1}H) 1	2	3	4	5	δ (^{13}C) 1	2	3	Me	δ (^{31}P)
4b	2.49 dt, J = 8, 5	*b*	5.58 quint, J = 8	*b*	*b*	56.2 (55.4)	93.1 (91.1)	56.2 (57.0)		46.2 s (46.0 vbr)
4c	2.15 br t, J = 4.5	*b*	1.59 t, J = 3	*b*	*b*	59.6 (58.4)	109.5 (109.1)	59.6 (61.1)	22.2 (22.2)	29.9 s, (21.3 d) (39.5 d), J = 150
4d	1.23 quar, J = 9	*b*	5.21 dt, J = 10, 9	0.68 dt, J = 6, 4.5	3.32 br	48.2 (48.2)	96.6 (96.1)	78.1 (78.0)	19.5 (19.7)	30.0 s (23.0 vbr) (38.5 vbr)

[a] ^{1}H NMR in toluene-d_8 at −20 °C and ^{13}C and ^{31}P NMR in CD_2Cl_2 at −30 °C (data at −85 °C are shown in parentheses). δ in ppm, J in Hz. δ (^{31}P) relative to external H_3PO_4. Proton and carbon numbering scheme is



[b] The same as δ (H_1).

Table IV. First-Order Rate Constants for the Reductive Elimination of (η^3-Allyl)nickel Complexes 5[a] in Toluene

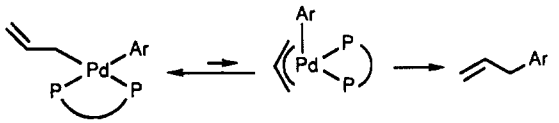
complex	temp/°C	additive	concn/M	k_{obsd}/h^{-1}
5a	10	dppe	0.2	0.767
5c	2	dppen	0.1	3.22
		dppen	0.2	4.08
		dppen	0.1	4.13
		PPh_3	0.3	
	−10	dppen	0.2	0.925
	−19	dppen	0.2	0.347

[a] Generated in situ from 0.1 M **4c** and an indicated amount of dppe or dppen at −60 °C.

observed rate of the reductive elimination for the system **4** plus diphosphine, since the concentration of **6** is so tiny compared to **5**. In order to test the high reactivity of **6**, we prepared a methyl complex $Ni(CH_3)(C_6F_5)$(dppen), **7**, and examined its thermolysis. The methyl complex is well expected to have a reactivity comparable to or even higher than the η^1-allyl complex with respect to the reductive elimination,[11] as is evident from the competitive thermolysis results on some Pt(IV),[13a] Pd(IV),[13b-d] and Au(III)[13e] complexes that simultaneously contain the methyl and the η^1-allyl ligands.

We have now found the rather low reactivity of **7** with regard to reductive elimination (first-order rate constant at 90 °C is 5.4 h^{-1}, $\Delta H^{\ddagger} = 98 \pm 2$ kJ/mol, $\Delta S^{\ddagger} = -32 \pm 15$ J/(Kmol)). Thus, it appears that the quite facile reductive elimination of the complex formed from **4** and diphosphines is much beyond the reactivity of the (η^1-allyl)nickel intermediate **6**, which was estimated by that of **7**.[14] We conclude that primarily the 18-electron, (η^3-allyl)nickel form is responsible for the highly reactive nature of the species formed by addition of diphosphines to **4** (Scheme II).

Scheme III



The palladium complexes analogous to **6**, namely **3**, also showed no dramatic increase of the rate of thermolysis[4a] when compared with that for the 16-electron η^3-allyl isomer **1** to such an extent as was found (10^8 times) upon comparing the reactivity of **5** with that of the 16-electron isomer **4**; compare, e.g., the first-order rate constant (h^{-1}, 40 °C in toluene) for **1a** (0.69) versus **3a** (0.058) and **3b** (0.092), and that for **1b** (0.11) versus **3c** (0.079) and **3d** (0.147). There is even a possibility that the intrinsic rate of the reductive elimination of the (η^1-allyl)palladium moiety is much slower than the observed rate of thermolysis employing **3**. In other words, a supposedly very reactive, 18-electron Pd(η^3-allyl)($C_6H_3Cl_2$)(dppe) complex, though very small in concentration, might have helped increase the observed rate from the intrinsic slow rate of the 16-electron η^1-allyl species (Scheme III). Consistent with this hypothesis, the methyl analogue Pd(CH_3)($C_6H_3Cl_2$-2,5)(dppe) was found to be much more reluctant to undergo reductive elimination than **3**.[15] Although we could not observe ^{1}H NMR evidence to support the transient formation of 18-electron (η^3-allyl)palladium complexes for the dichlorophenyl analogues, some fluxional aspects of the pentafluorophenyl analogues Pd(η^1-allyl)(C_6F_5)(diphos) reported before[5a] are consistent with the occurrence of such transients. Further details on these arguments will be reported elsewhere.

Conclusions. There is a difference in the ground-state structure of the allylnickel and -palladium complexes containing one aryl and one chelating diphosphine ligand. The nickel derivative takes a fluxional, 18-electron η^3-allyl

(11) This notion might look somewhat peculiar from a viewpoint of vast knowledge in organic compounds, showing that CH_3—X bonds (X = atoms and groups) are generally stronger than CH_2=$CHCH_2$—X bonds.[12a] Unfortunately, there have been available very few thermochemical data to assess the relative strength of the CH_3—M and CH_2=$CHCH_2$—M bonds. However, it seems worthy of note that the relative ease of reductive elimination of a metal-bound organic ligand is not necessarily correlated with the relative strength of the metal–ligand bond.[12b] Or it is even possible that the CH_2=$CHCH_2$—M bond is not much weaker than the CH_3—M bond as would be expected from the common trend described above. In this regard, it appears very intriguing that the experimentally estimated $PhCH_2$-Pd^{IV} bond strength was comparable to the CH_3-Pd^{IV} bond strength,[12c] as opposed to the considerably weaker $PhCH_2$-X bond strength compared to the CH_3-X bond strength.[12a]

(12) (a) Benson, S. W. *Thermochemical Kinetics*, 2nd ed., Wiley: New York, 1976; p 309. (b) Komiya, S.; Ozaki, S.; Shibue, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1555–1556. (c) Aye, K. T.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D.; Watson, A. A. *Organometallics* **1989**, *8*, 1518–1522.

(13) (a) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E.; Lavington, S. W. *J. Chem. Soc., Dalton Trans.* **1974**, 1613–1618. (b) Byers, P. K.; Canty, A. J.; Traill, P. R.; Watson, A. A. *J. Organomet. Chem.*, in press. (c) Brown, D. G.; Byers, P. K. Canty, A. J. *Organometallics* **1990**, *9*, 1231–1235. (d) Byers, P. K.; Canty, A. J. *J. Chem. Soc., Chem. Commun.* **1988**, 639–641. (e) Ozaki, S.; Komiya, S. *Abstracts Papers 56th Annual Meeting Chem. Soc. Jpn.*, Tokyo; 1988; Abst. No. 3IVB26.

(14) Participation into the rapid C–C coupling of the alternative 4-coordinated η^1-allyl species, having a structure considerably distorted from the regular square-planar geometry, though no precedence of this type of organonickel complexes has been known, remains to receive further experimental and theoretical scrutiny.

(15) Unpublished results.

structure, while the palladium derivative takes a 16-electron η^1-allyl isomeric form. This trend is consistent with both the greater tendency of the η^3-allyl–Pd bond to be converted to the η^1-allyl–Pd bond than the η^3-allyl–Ni bond[5b,8] and the smaller ability of the Pd atom to form the 5-coordinated 18-electron configuration than that of the Ni atom.[16] The unusually large increase in the reductive elimination rate upon increasing the electron count on Ni from 16 to 18 in the present case has precedence in dialkylnickel chemistry,[17] but no studies have revealed such a quantitative measure of the rate enhancement as was disclosed here. The contribution of another 18-electron type species Ni(η^1-allyl)(aryl)$(PR_3)_3$ appears unlikely at least for the combination of the ligand groups employed in the present study, for the rate of reductive elimination from **4** was not affected by the addition of phosphine. Finally, the present finding may be of special relevance to the better understanding and design of the nickel-catalyzed allylic transformations.[1,2,18]

Experimental Section

All manipulations of organonickel complexes were performed under dry argon by using a standard vacuum line technique. Solvents were purified in a standard manner immediately prior to use. Most of the starting materials were obtained from commercial sources.

^{1}H NMR spectra were obtained on a JEOL PS-100 spectrometer. ^{13}C and ^{31}P NMR spectra were obtained on a JEOL GSX-270 spectrometer. GLC analysis was done on a Hitachi 164 gas chromatograph.

Preparation of 4a. To a THF solution (75 mL) of 2,5-$C_6H_3Cl_2ZnCl$[4a] (17 mmol) cooled at −50 °C was added dropwise Ni(η^3-C_3H_5)(Br)(PPh_3) (3.84 g, 8.7 mmol) in THF (70 mL). The reaction mixture was allowed to warm to −20 °C. Stirring at this temperature was continued for 12 h, and then the solvent was removed under vacuum at the same temperature. The yellow residue thus obtained was triturated with cold methanol. The solids obtained were recrystallized from toluene/*n*-hexane in a refrigerator at ca. −10 °C to give yellow crystals of **4a**, 34%: mp 74 °C (dec). Anal. Calcd for $C_{27}H_{23}Cl_2PNi$: C, 63.83; H, 4.56. Found: C, 63.38; H, 4.54.

Preparation of 4b–d. A THF solution (20 mL) of $ZnCl_2$ (1.83 g, 13.4 mmol) was added to a THF solution (20 mL) of C_6F_5Li (13.4 mmol) cooled at −78 °C. To this solution was added, drop by drop, a THF solution (60 mL) of Ni(η^3-CH_2CMeCH_2)(Cl)(PPh_3) (4.60 g, 11.2 mmol) at −78 °C. The solution was gradually warmed to −20 °C, and the mixture was stirred at this temperature for 48 h. After methanol (1 mL) was added, solvents were evaporated under vacuum at 0 °C. The residue was washed with methanol and dried. The remaining solids were recrystallized from benzene/*n*-hexane to give yellow–orange crystalline materials of **4c**, 25%: mp 148 °C (dec). Anal. Calcd for $C_{28}H_{22}F_5PNi$: C, 61.92; H, 4.08. Found: C, 61.90; H, 4.13. ^{13}C NMR (CD_2Cl_2): δ 23.5 (s, Me), 62.6 (d, J_P = 6 Hz, CH_2=), 63.7 (d, J_P = 20 Hz, =CH_2), 124.7 (s, allyl center). ^{31}P NMR (CD_2Cl_2): δ (relative to external H_3PO_4) 35.7. Similarly prepared was **4b**: mp 127 °C (dec). Anal. Calcd for $C_{27}H_{20}F_5PNi$: C, 61.29; H, 3.81. Found: C, 61.24; H, 3.92. ^{13}C NMR ($CDCl_3$): δ 62.1 (d, J_P = 6 Hz, CH_2=), 63.5 (d, J_P = 17 Hz, =CH_2), 111.9 (s, allyl center). ^{31}P NMR ($CDCl_3$): δ 31.5 **4d**: mp 136 °C (dec). Anal. Calcd for $C_{28}H_{22}F_5PNi$: C, 61.92; H, 4.08. Found: C, 61.84; H, 4.04. ^{13}C NMR (CD_2Cl_2): δ 18.2 (s, Me), 55.9 (s, CH_2=), 82.4 (br, =CHMe), 113.5 (s, allyl center). ^{31}P NMR (CD_2Cl_2): δ 32.3.

When the addition of $ZnCl_2$ was omitted in the above preparative run for **4b**, workup of the reaction mixture afforded only a small amount (ca. 10%) of Ni$(C_6F_5)_2(PPh_3)_2$.[19] Anal. Calcd for $C_{48}H_{30}F_{10}P_2Ni$: C, 62.85; H, 3.30. Found: C, 62.38; H, 3.41.

Preparation of Ni$(CH_3)(C_6F_5)$(dppen), 7. A THF solution (5 mL) of MeLi (2.5 mmol) was added at 0 °C to a THF solution (30 mL) of Ni(C_6F_5)(Br)$(PPh_3)_2$ (2.0 g, 2.4 mmol), which was prepared from $NiBr_2(PPh_3)_2$ and 1 equiv of C_6F_5MgBr.[19] Stirring of the reaction mixture at 0 °C was continued for 24 h, and evaporation of the solvent under vacuum afforded crude products of *trans*-Ni$(CH_3)(C_6F_5)(PPh_3)_2$. This was allowed to react with an equimolar amount of dppen (each 0.82 mmol) in THF (15 mL) at room temperature for 1 h. The solvent was evaporated under vacuum, and the residue was washed with *n*-hexene. Recrystallization from benzene/*n*-hexane gave yellow solids of **7**, 15%: mp 132 °C (dec). Anal. Calcd for $C_{33}H_{25}F_5P_2Ni$: C, 62.21; H, 3.96. Found: C, 62.16; H, 4.02. ^{1}H NMR (C_6D_6): δ 0.76 (dd, J = 4.5, 10.5 Hz, Me).

Preparation of 3. Complexes **3b–d** were prepared in a manner similar to that described for **3a**.[4a] **3b**: mp 105 °C (dec). Anal. Calcd for $C_{35}H_{30}P_2Cl_2Pd$: C, 60.94; H, 4.38. Found: C, 61.06; H, 4.36. ^{1}H NMR (CD_2Cl_2): δ 2.26 (br, PdC*H*H), 2.58 (br, PdCH*H*), 3.9 (m, =CH_2), 5.64 (m, CH=). **3c**: mp 125 °C (dec). Anal. Calcd for $C_{36}H_{34}P_2Cl_2Pd$: C, 61.25; H, 4.86. Found: C, 61.34, H, 5.01. ^{1}H NMR (C_6D_6): δ 1.66 (s, Me), 1.5–2.0 (br, CH_2CH_2), 2.97 (m, $PdCH_2$), 4.32 (s, =C*H*H), 4.48 (s, =CH*H*). **3d**: mp 99 °C (dec). Anal. Calcd for $C_{36}H_{32}P_2Cl_2Pd$: C, 61.43; H, 4.58. Found: C, 61.12; H, 4.63. ^{1}H NMR (CD_2Cl_2): δ 1.09 (s, Me), 2.25 (br, PdC*H*H), 2.60 (br d, J = 9 Hz, PdCH*H*), 3.64 (s, =C*H*H), 3.80 (s, =CH*H*).

Thermolysis of 4a. The method of sample preparation for kinetic runs was the same as that described before for the kinetics for complex **1a**.[4a] At appropriate intervals, an aliquot (0.04 mL) was withdrawn by a syringe from each kinetic sample (1 mL; initial concentration of **4a** was 0.02 M) and poured into an acetone solution of HCl (ca. 5 equiv per Ni) under argon to quench unreacted **4a**. The resulting solution was analyzed by GLC, as was done previously.[4a]

Thermolysis of 4c. All of thermolyses employing **4c** in toluene-d_8 were performed in an NMR tube that was placed in a thermostated NMR probe. Increase of the coupling product and decrease of the complex were monitored by integration of the methyl resonance due to **4c** and the methyl (δ 1.59) and methylene (δ 3.10) resonances of CH_2=$CMeCH_2C_6F_5$. The initial concentration of **4c** was 0.1 M.

Formation and Thermolysis of 5. For the preparation of NMR samples of thermally unstable complexes **5**, an NMR tube (5 mm, 10 mm diameter) containing a deaerated toluene-d_8 or CD_2Cl_2 solution of **4** was fitted with a serum cap and cooled to −60 °C. To this solution was added a solution of dppe or dppen, drop by drop, with a hypodermic syringe. The tube was then quickly placed in a precooled NMR probe. Proceeding of the thermolysis of **5a** and **5c** was monitored by ^{1}H NMR spectroscopy in a manner similar to that described above.

Thermolysis of 7. This was performed in an NMR tube containing a C_6D_6 solution of **7** (0.1 M), and the reaction was followed by integration of the methyl resonances due to **7** and C_6F_5Me (δ 1.68). First-order rate constants (h^{-1}) are as follows: 5.79 (90 °C, no additive), 6.22 (90 °C, [dppen] = 0.3 M), 5.39 (90 °C, [PPh_3] = 0.5 M), 2.39 (82 °C, no additive), and 0.781 (71 °C, no additive).

Thermolysis of 3b–d. This was performed in the same way as that described for **3a**.[4a]

Acknowledgment. Partial support of this work by grants from the Ministry of Education, Science and Culture is acknowledged. We also thank Prof. A. J. Canty for informing us of his results prior to publication.

(16) (a) Jesson, J. P.; Meakin, P. *J. Am. Chem. Soc.* **1974**, *96*, 5760–5774. (b) Meakin, P.; Jesson, J. P. *Ibid.* **1974**, *96*, 5751–5759.

(17) (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.

(18) Yang, P. F.; Ni, Z. J.; Luh, T. Y. *J. Org. Chem.* **1989**, *54*, 2261–2262.

(19) Philips, J. R.; Rosevear, D. T.; Stone, F. G. A. *J. Organomet. Chem.* **1964**, *2*, 455–460.