have pointed out that in the interconversion of the various C_{4v} isomers (which we now recognize as belonging in the *nido*-B_5H_9 category) the intermediacy of a D_{3h} closo structure is strongly disfavored. Indeed, they propose the sequence $C_{4v} \rightarrow C_s \rightarrow C_{2v} \rightarrow C_s \rightarrow C_{4v}$ and we show below (Scheme V) how this can be applied to the M_3C_2 system.[34] It is clear from Scheme V that the overall effect of this rearrangement has the same result as does alkyne rotation; furthermore the molecules [A] and [B] are seen to be diastereomers rather than enantiomers. In conclusion, we have observed that tetrahedral M_2C_2 organotransition-metal clusters react with the two-electron donor $Fe(CO)_3$ and expand to give the square-based pyramidal (nido-octahedral) geometry. These M_3C_2 clusters are fluxional, and this phenomenon can be rationalized in terms of a formal rotation of the alkyne moiety relative to the metal triangle. The process is shown to be intramolecular and has an activation energy barrier in the range 60–70 kJ/mol. The data are consistent with a "modified windshield wiper"

motion as in the second Schilling–Hoffmann proposal and unequivocally eliminate the mechanism involving circumambulation about the periphery of the metal triangle.

Studies in progress will further elaborate the mechanisms of alkyne rotation and vertex interchanges as well as the orientation of alkynes in *closo*-M_3C_2 systems.

(34) A reviewer has pointed out that an edge-bridged tetrahedron (such as $Os_5H_2(CO)_{16}$, 74 electrons) represents an alternative and isoelectronic possibility for the square pyramid (such as $Os_5C(CO)_{15}$, 74 electrons); we note that the C_s structures in Scheme IV could be viewed as edge-bridged tetrahedral molecules.

Reductive Elimination of Aryl Carboxylates from Acyl(aryloxy)nickel(II) and -palladium(II) Complexes

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Acyl(*p*-cyanophenoxy)nickel(II) and -palladium(II) complexes, $M(COR)(OC_6H_4\text{-}p\text{-CN})L_2$ (M = Ni, Pd; L_2 = bpy, $(PEt_3)_2$), have been prepared by insertion reactions of CO into the metal–carbon bonds of the corresponding methylnickel(II) and -palladium(II) complexes. Addition of π-acids such as CO, maleic anhydride, and acrylonitrile selectively induces reductive elimination of *p*-cyanophenyl acetate from acylnickel(II) complexes, whereas thermolysis of the complexes mainly results in decarbonylation. In contrast, reductive elimination from the palladium analogue proceeds smoothly on thermolysis, and no apparent accelerating effect of added π-acids is observed. Kinetic studies of both reductive eliminations reveal that the former proceeds via an associative mechanism involving a five-coordinate intermediate, whereas the latter proceeds via two mechanisms, one being a dissociative pathway involving a three-coordinate species and the other being a direct reductive elimination from a four-coordinate species.

Introduction

Attack of external nucleophiles such as OH⁻ and RO⁻ on carbonyl, olefinic, and allylic ligands coordinated to transition metals constitutes one of the most important synthetic means for producing oxygen-containing organic compounds as catalyzed by transition-metal complexes.[1] In contrast, another conceptually possible approach for inducing C–O bond formation by a process involving reductive elimination (A) has received very little attention. In contrast, studies of reductive eliminations involving C–C bond formation from diorganotransition-metal complexes

(B), have been the subject of considerable mechanistic[2] and theoretical[2a,5] studies. Syntheses utilizing the reductive elimination process (B) catalyzed by nickel and palladium complexes have been well developed.[1] Only a few attempts have been reported for utilizing the reductive elimination

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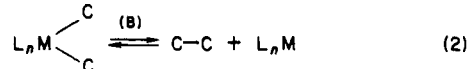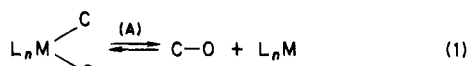
Table I. Yield, Melting Point, Analytical, and ^{1}H NMR Data for Methyl(aryloxy)nickel(II) and -palladium(II) Complexes

complex	yield,[a] %	mp, °C	anal. found (calcd)			NMR (ppm from Me$_4$Si)[b]		
			C	H	N	Pd–Me (J_{P-H} in Hz)	OC$_6$H$_4$X	others
2a, PdMe(OC$_6$H$_4$-*p*-CN)bpy	89	142[c] dec	55.1 (54.6)	4.2 (3.8)	10.1 (10.6)	0.85 (s)	6.97 (d, 9) 7.24 (d, 9)	
2b, PdMe(OC$_6$H$_4$-*p*-OMe)(PEt$_3$)$_2$	82	65–66	50.2 (50.0)	8.8 (8.4)		0.19 (t, 6)	7.05 (d, 9) 7.25 (d, 9)	3.62 (s)
2c, PdMe(OC$_6$H$_4$-*p*-Me)(PEt$_3$)$_2$	23	36–37	51.7 (51.7)	9.8 (8.7)		0.19 (t, 6)	7.25 (s)	2.44 (s)
2d, PdMe(OC$_6$H$_5$)(PEt$_3$)$_2$	84	44–47	50.9 (50.6)	9.0 (8.5)		0.18 (t, 6)	6.73 (t, 9) 7.40 (d, 9) 7.25 (d, 9)	
2e, PdMe(C$_6$H$_4$-*p*-CN)(PEt$_3$)$_2$	84	59–61	49.8 (50.5)	7.8 (7.8)	2.9 (2.9)	0.20 (t, 6)	7.05 (d, 9) 7.55 (d, 9)	
2f, PdMe(OC$_6$H$_4$-*p*-CN)(PMePh$_2$)$_2$	62	57–59	64.3 (63.8)	4.8 (5.2)	2.1 (2.2)	0.13 (t, 6)	6.56 (d, 9) 7.06 (d, 9)	
2g, PdMe(OC$_6$H$_4$-*p*-CN)(PEtPh$_2$)$_2$	90	112–113	65.0 (65.2)	5.7 (5.8)	2.0 (2.1)	0.18 (t, 6)	6.66 (d, 9) 7.16 (d, 9)	1.18 (q, 7) 2.1–2.4 (m)
1f, NiMe(OC$_6$H$_4$-*p*-CN)(PEt$_3$)$_2$	71	89–91	56.0 (56.1)	9.2 (8.7)	3.4 (3.3)	–0.96 (t, 8)	7.00 (d, 9) 7.32 (d, 9)	

[a] After recrystallization. [b] Solvent: CD$_2$Cl$_2$ (2a), acetone-d_6 (2b–g), C$_6$D$_6$ (1e). [c] Yellow color disappeared at this temperature, and it gradually turned to black till 180 °C. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

involving the C–O bond formation in organic synthesis.[3]

We have been interested in the reverse process of eq 1, namely, selective cleavage of C–O bonds[4] in alkenyl and aryl carboxylate as well as carbonates and reported that the acyl–O bond in aryl carboxylates can be readily cleaved by treatment with Ni(0) complexes.[4d]

$$L_nM\!\!\begin{array}{c}C\\ \diagup\\ \diagdown\\ O\end{array} \;\; \overset{(A)}{\rightleftharpoons} \;\; C\!-\!O \;+\; L_nM \qquad (1)$$

$$L_nM\!\!\begin{array}{c}C\\ \diagup\\ \diagdown\\ C\end{array} \;\; \overset{(B)}{\rightleftharpoons} \;\; C\!-\!C \;+\; L_nM \qquad (2)$$

This paper is concerned with reverse process of eq 3 and factors controlling the reductive elimination in which there

$$L_nNi^0 \;+\; RCOAr \;\;\rightleftharpoons\;\; L_nNi\begin{array}{c}\overset{O}{\parallel}\\ CR\\ \diagdown\\ OAr\end{array} \qquad (3)$$
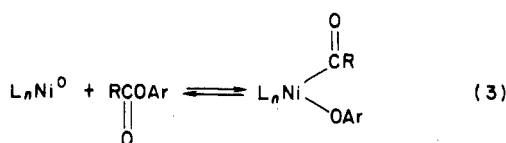
is C–O bond formation. In our studies of reductive elimination of alkanes from dialkylnickel and -palladium complexes conspicuous differences were observed between the behavior of nickel and palladium.[2c,f,h,i] The present study demonstrates some parallel trends between the reductive elimination patterns involving C–C and C–O bond formation via organonickel and -palladium complexes. A preliminary account of the present results has been reported.[4a]

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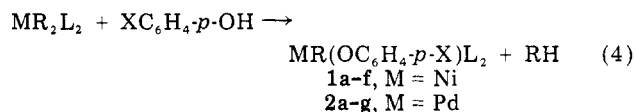
(3) Bäckvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 4959. Keinan, E.; Roth, Z. *J. Organomet. Chem.* **1983**, *48*, 1769.

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(5) (a) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857. (b) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181. (c) Pearson, R. G. *Acc. Chem. Res.* **1971**, *4*, 152. (d) Åkermark, B.; Johansen, H.; Roos, B.; Wahlgren, U. *J. Am. Chem. Soc.* **1979**, *101*, 5876.

Results and Discussion

Preparation of Methyl(aryloxy)nickel(II) and -palladium(II) Complexes. Since the route for preparation of the acyl(aryloxy)nickel or -palladium complexes via cleavage or aryl carboxylates leads to further decarbonylation and subsequent decomposition processes, reaction 3 cannot be employed for the preparation of acylnickel or -palladium aryloxides. Instead, we prepared series of alkyl(aryloxy)nickel(II), **1**, and -palladium(II), **2**, by by

$$MR_2L_2 \;+\; XC_6H_4\text{-}p\text{-OH} \longrightarrow$$
$$MR(OC_6H_4\text{-}p\text{-X})L_2 \;+\; RH \qquad (4)$$
$$\text{1a–f, M} = \text{Ni}$$
$$\text{2a–g, M} = \text{Pd}$$

1a, R = Me, L$_2$ = bpy, X = H; **1b**, R = Me, L$_2$ = bpy, X = CN; **1c**, R = Et, L$_2$ = bpy, X = CN; **1d**, R = Me, L$_2$ = (PEt$_3$)$_2$, X = H; **1e**, R = Me, L$_2$ = (PEt$_3$)$_2$, X = Ph; **1f**, R = Me, L$_2$ = (PEt$_3$)$_2$, X = CN; **2a**, R = Me, L$_2$ = bpy, X = CN; **2b**, R = Me, L$_2$ = (PEt$_3$)$_2$, X = OMe; **2c**, R = Me, L$_2$ = (PEt$_3$)$_2$, X = Me; **2d**, R = Me, L$_2$ = (PEt$_3$)$_2$, X = H; **2e**, R = Me, L$_2$ = (PEt$_3$)$_2$, X = CN; **2f**, R = Me, L$_2$ = (PMePh$_2$)$_2$, X = CN; **2g**, R = Me, L$_2$ = (PEtPh$_2$)$_2$, X = CN

treating dialkylnickel(II) and -palladium(II) complexes with equimolar amounts of the corresponding hydroxyarenes. The reactions proceed smoothly at room temperature with evolution of alkane, and we have prepared series of alkylnickel and -palladium aryloxides by these routes. These alkyl(aryloxy)nickel(II) and -palladium(II) complexes were subjected to reactions with carbon monoxide. Methyl(aryloxy)nickel(II) complexes **1a–f** are air sensitive, but the palladium(II) analogues **2a–g** are much less so. These complexes can be purified by recrystallization from suitable solvents and preparations of **1a–e** have been described previously.[4b] Table I summarizes the melting point, yield, analytical, and ^{1}H NMR data of these complexes. ^{1}H NMR spectra of complexes **1d–f** as well as of **2b–g** show M–Me signals as triplets due to coupling with two magnetically equivalent phosphorus nuclei, indicating the trans configuration of these complexes. The bidentate 2,2′-bipyridine ligand obviously gives cis complexes **1a–c** and **2a**.

Reactions of Methylnickel(II) and -palladium(II) Complexes with Carbon Monoxide. Results of the reactions of **1** and **2** with carbon monoxide are summarized in Table II. Methylnickel(II) complexes **1** reacted with an excess of CO in THF at room temperature to give Ni(CO)$_2$L$_2$ with liberation of quantitative yields of the

### Table II. Reactions of Methyl(aryloxy)nickel(II) and -palladium(II) Complexes with CO

complex	CO	temp,[d] °C	time, h	solv	product (mol/complex)	
					ester	complex
1a, NiMe(OPh)bpy	a	−78	10	THF	CH_3CO_2Ph (0.31)	$Ni(CO)_2bpy^c$
	b	rt	0.3	THF	CH_3CO_2Ph (1.00)	$Ni(CO)_2bpy^c$
1b, NiMe(OC_6H_4-p-CN)bpy	a	−78	10	THF	none	Ni(COMe)(OC_6H_4-p-CN)bpy (0.36)
1c, NiEt(OC_6H_4-p-CN)bpy	a	−78	4	THF	none	Ni(COEt)(OC_6H_4-p-CN)bpy (0.94)
	a	rt	1	THF	$C_2H_5CO_2C_6H_4$-p-CN (0.25)	$Ni(CO)_2bpy$ (0.36)
						NiEt(OC_6H_4-p-CN)bpy (0.67)
	b	rt	1	THF	$C_2H_5CO_2C_6H_4$-p-CN (0.80)	$Ni(CO)_2bpy^c$
1d, NiMe(OPh)(PEt_3)_2	b	rt	24	Et_2O	CH_3CO_2Ph (0.90)	$Ni(CO)_2(PEt_3)_2^c$
1e, NiMe(OC_6H_4-p-Ph)(PEt_3)_2	a	−78	10	Et_2O	$CH_3CO_2C_6H_4$-p-Ph (0.19)	$Ni(CO)_2(PEt_3)_2^c$
	b	rt	1	Et_2O	$CH_3CO_2C_6H_4$-p-Ph (0.88)	$Ni(CO)_2(PEt_3)_2^c$
1f, NiMe(OC_6H_4-p-CN)(PEt_3)_2	a	−78	10	THF	none	Ni(COMe)(OC_6H_4-p-CN)(PEt_3)_2
	b	rt	1	THF	$CH_3CO_2C_6H_4$-p-CN (0.90)	$Ni(CO)_2(PEt_3)_2^c$
2a, PdMe(OC_6H_4-p-CN)bpy	b	rt	5	THF	$CH_3CO_2C_6H_4$-p-CN (0.56)	$Pd(CO)_nbpy^c$
2b, PdMe(OC_6H_4-p-OMe)(PEt_3)_2	b	rt	5	acetone	$CH_3CO_2C_6H_4$-p-OMe (0.70)	$Pd(CO)_n(PEt_3)_m^c$
2c, PdMe(OC_6H_4-p-Me)(PEt_3)_2	b	rt	5	acetone	$CH_3CO_2C_6H_4$-p-Me (0.40)	$Pd(CO)_n(PEt_3)_m^c$
2d, PdMe(OPh)(PEt_3)_2	b	rt	5	acetone	CH_3CO_2Ph (0.20)	$Pd(CO)_n(PEt_3)_m^c$
2d, PdMe(OC_6H_4-p-CN)(PEt_3)_2	b	rt	5	acetone	none	Pd(COMe)(OC_6H_4-p-CN)(PEt_3)_2 (0.50)
2f, PdMe(OC_6H_4-p-CN)(PMePh_2)_2	b	rt	24	CH_2Ph_2	$CH_3CO_2C_6H_4$-p-CN (1.00)	$Pd(CO)_n(PMePh_2)_m^c$
2g, PdMe(OC_6H_4-p-CN)(PEtPh_2)_2	b	rt	24	CH_2Ph_2	$CH_3CO_2C_6H_4$-p-CN (1.00)	$Pd(CO)_n(PEtPh_2)_m^c$

[a] An equimolar amount of CO gas was brought in contact with monomethylmetal complex. [b] The reaction was carried out under an atmosphere of excess CO. [c] Formation of complex was confirmed by IR but the amount was not measured. [d] rt = room temperature.

corresponding aryl esters MeCOOAr. The reactions are

$$NiMe(OAr)L_2 + excess\ CO \xrightarrow{\text{room temp}}$$
$$\mathbf{1}$$
$$MeCOOAr + Ni(CO)L_2 \quad (5)$$
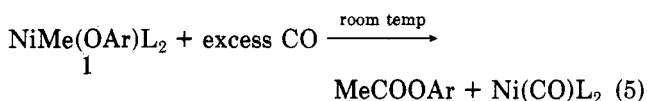
believed to proceed via insertion of CO into the alkyl-nickel bond to give acylnickel(II) species followed by reductive elimination of esters. Intermediate acyl(p-cyanophenoxy)nickel(II) complexes 3 having bpy or PEt_3 ligand(s) were isolated, without formation of esters, when complexes 1b, 1c, and 1f, containing an electron-withdrawing p-cyanophenoxy group, were treated with stoichiometric amounts of CO at −78 °C. Acylnickel(II)
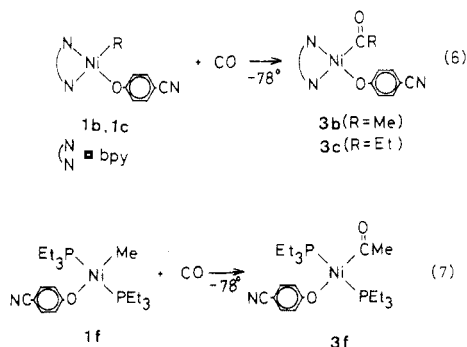
complexes 3b, 3c, and 3f are extremely air-sensitive but can be purified by recrystallization. The IR spectra of these complexes show a characteristic acyl ν(C=O) band at 1645 cm^{-1}. Singlets at 2.42 and 2.53 ppm due to Ni-CO*Me* are detected in the ^{1}H NMR spectra of 3b and 3f, respectively. The rates of formation of 3b and 3f were not affected by addition of free ligands such as bpy and PEt_3,

suggesting an associative insertion mechanism involving a five-coordinate intermediate NiMe(OC_6H_4-p-CN)-$(CO)L_2$.[6] On the other hand, isolation of the corresponding acyl intermediates failed for 1a, 1d, and 1e under similar conditions. In these cases, the corresponding carbonyl complexes $Ni(CO)_2L_2$ (L_2 = bpy and $(PEt_3)_2$) and aryl esters were detected in 20–30% yields and a part of the starting methylnickel(II) complex remained intact. The acyl intermediates formed in the reactions of 1a, 1d, and 1e appear to be unstable even at −78 °C and liberate esters and $Ni(CO)_2L_2$, probably by further interaction with CO (vide infra).

In contrast to the high reactivity of alkyl nickel(II) complexes toward carbon monoxide, the reactions of the palladium(II) analogues did not proceed at −78 °C even in the presence of an excess of CO. However, when reactions were carried out at room temperature in benzene solutions of 2a–2d, 2f, and 2g in the presence of an excess of CO, quantitative yields of the corresponding aryl esters were obtained in a few hours. The presence of the free tertiary phosphine ligand in the reaction mixture slightly retarded the reaction.[6] The resulting palladium complexes consisted of an equilibrium mixture of several palladium(0) carbonyl complexes, $Pd(CO)_nL_m$.[7] However, complex 2e

$$PdMe(OAr)L_2 + CO \rightarrow MeCOOAr + Pd(CO)_nL_m \quad (8)$$

$$L_2 = bpy,\ (PEt_3)_2,\ (PMePh_2)_2,\ (PEtPh_2)_2$$
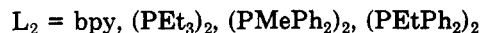
(6) Mechanisms of CO insertion into metal–carbon bond have been reviewed: (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (c) Kuhlman, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195.

(7) Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. 1.

Table III. Reactions of Acylnickel(II) and -palladium(II) Complexes

complex	additive (mol/L)	temp,[c] °C	time, h	solv	products (mol % complex)
3b	MAnh (ex)[a]	rt	4	THF	$MeCO_2C_6H_4$-p-CN (70), Ni(MAnh)bpy (77)
	thermolysis[a]	90	2	p-xylene	CO (10), MeCOMe (12)
3c	MAnh (38)[a]	rt	24	THF	$EtCO_2C_6H_4$-p-CN (62), Ni(MAnh)$_2$bpy (90)
	AN (ex)	rt	5	THF	$EtCO_2C_6H_4$-p-CN (60), Ni(AN)$_2$bpy
	EMA (ex)[a]	rt	6	none	$EtCO_2C_6H_4$-p-CN (31)
	CO (ex)[a]	rt	1	THF	$EtCO_2C_6H_4$-p-CN (79), Ni(CO)$_2$bpy (42)
	Na$_2$IrCl$_6$ (1)	rt	0.1	THF	$EtCO_2C_6H_4$-p-CN (33)
	thermolysis[a]	80–90	1	toluene	$EtCO_2C_6H_4$-p-CN (12), CO (17), C_2H_4 (12), C_2H_6 (4)
3f	MAnh (5.6)	rt	2	THF	$MeCO_2C_6H_4$-p-CN (56)
	Na$_2$IrCl$_6$ (1)	rt	1	acetone	$MeCO_2C_6H_4$-p-CN (50)
	thermolysis	150	3	none	$MeCO_2C_6H_4$-p-CN (11), CH$_4$ (8)
4e	CO (ex)	rt	24	C_6H_6	no reaction
	MAnh (ex)	rt	1	acetone	no reaction
	Na$_2$IrCl$_6$ (1)	rt	1	acetone	b
	thermolysis	180	1	CH$_2$Ph$_2$	$MeCO_2C_6H_4$-p-CN (68)
	thermolysis	35	50	Ph$_2$O	$MeCO_2C_6H_4$-p-CN (80)
	HOC$_6$H$_4$-p-Me (1)	rt	1	C_6H_6	$MeCO_2C_6H_4$-p-Me (60)
	dmpe (1)	rt	1	C_6H_6	$MeCO_2C_6H_4$-p-CN (50)
	dpe (1)	rt	1	C_6H_6	$MeCO_2C_6H_4$-p-CN (53)

[a] Data are taken from ref 4b. [b] IR spectrum of the residual solid after removal of volatile matters showed ν(C=O) band at 1675–1680 cm^{-1}. Abbreviations: MAnh, maleic anhydride; AN, acrylonitrile; EMA, ethyl methacrylate; dmpe, 1,2-bis(dimethylphosphino)ethane; dpe, 1,2-bis(diphenylphosphino)ethane; ex, excess. [c] rt = room temperature.

having *p*-cyanophenoxy group and PEt$_3$ ligands gave acylpalladium(II) intermediate **4e** on interaction with an excess of CO at room temperature. The reaction was accompanied by formation of a small amount of aryl ester. Increase of the CO pressure to 10 atm gave a pure acylpalladium(II) complex **4e** without formation of the ester.


$$\text{(9)}$$
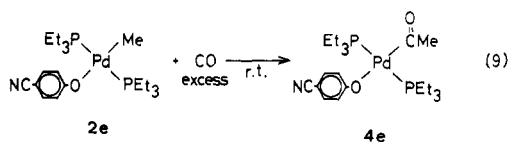
These results suggest that the excess of CO enhances the CO insertion into the Me–Pd bond, but reductive elimination is not accelerated, in contrast to the reaction of the acylnickel complex with CO.

Complex **4e** is less air sensitive than the nickel analogue **3f**. The IR spectrum of **4e** shows a characteristic ν(C=O) band at 1680 cm^{-1}. A triplet with a small coupling constant (J(P–H) = 1.1 Hz) at 2.48 ppm for the acyl group in the ^{1}H NMR spectrum of **4e** indicates the square-planar trans structure.

Reductive Elimination from Acyl(*p*-cyanophenoxy)metal(II) (M = Ni, Pd) Complexes. Results of the reactions of acyl(*p*-cyanophenoxy)nickel(II) and -palladium(II) complexes under various conditions are summarized in Table III.

Thermal Reductive Elimination. Thermolysis of the acylnickel complexes **3b** and **3f** in solution results in a decarbonylation reaction in which alkane and CO are liberated. For **3b**, formation of a small amount of acetone was also observed. A small amount of reductive elimination product (ester) also was formed for **3f**. The results indicate that the decarbonylation of the RCO ligand leading to a thermally unstable Ni–Me complex dominates over reductive elimination of ester. In contrast, the acetylpalladium analogue **4e** cleanly afforded the reductive elimination product on thermolysis without giving any decarbonylation product (eq 10).

$$\text{(10)}$$
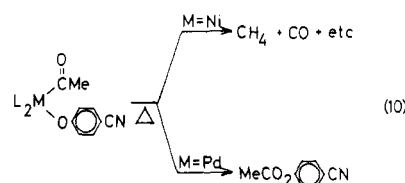
A kinetic study of the thermal reductive elimination from **4e** was carried out in order to obtain further insight into the thermolysis mechanism (eq 11). The rate of the

$$\text{(11)}$$
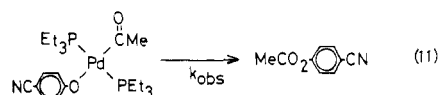
reductive elimination of *p*-cyanophenyl acetate from **4e** in C_6D_6 was followed by measuring the decrease in the methyl signal of **4e** or the increase in the methyl signal due to the ester by ^{1}H NMR (eq 12). The reaction was found to be first order in the concentration of remaining **4e**.

$$-\frac{d}{dt}[\mathbf{4e}] = k_{obsd}[\mathbf{4e}] \tag{12}$$

Figure 1 shows the dependence of the pseudo-first-order rate constant k_{obsd} on the concentration of free PEt$_3$ added. The k_{obsd} value decreases with an increase in the concentration of PEt$_3$, but it becomes constant at higher concentrations of PEt$_3$ (over 0.4 mol/L). The result suggests the existence of the two routes shown in Scheme I for the reductive elimination. One route involves the dissociation of a PEt$_3$ ligand to give a T-shaped intermediate from which reductive elimination takes place, and the other route is a direct reductive elimination of the ester from a four-coordinate species. Isomerization of the trans T-shaped species to the cis isomer during the reaction should be involved in the dissociative process. Such a dissociative mechanism for the reductive elimination leading to C–C bond formation has been proposed on the basis of the kinetics of thermolysis of alkylgold and -palladium com-
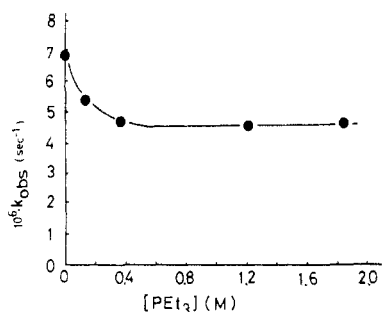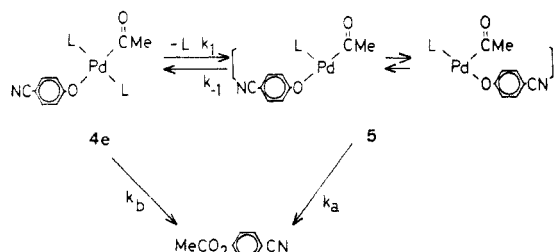
Figure 1. Dependence of k_{obsd} on the concentration of PEt_3 in the reductive elimination of $MeCO_2C_6H_4$-p-CN from **4e** in benzene at 35.0 °C.

Scheme I. Mechanism for the Thermal Reductive Elimination of Ester from 4e

plexes coordinated with tertiary phosphines[2a-e] and has been supported theoretically.[2a,5] A similar mechanism may be operative here.

Assumption of the steady-state approximation for the T-shaped intermediate, which is not detected by NMR during the reaction, gives the rate equation

$$-\frac{d}{dt}[4e] = \left(k_b + \frac{k_1 k_a}{k_{-1}[L] + k_a}\right)[4e]$$
$$= k_{obsd}[4e] \qquad (13)$$

$$k_{obsd} = k_b + \frac{k_1 k_a}{k_{-1}[L] + k_a} \qquad (14)$$

The rate equation thus obtained is consistent with the kinetic results, supporting the mechanism shown in Scheme I.

Addition of a bidentate ligand such as 1,2-bis(dimethylphosphino)ethane (dmpe) and 1,2-bis(diphenylphosphino)ethane (dpe) to a solution of **4e** at room temperature caused liberation of ester at a much faster rate (last two experiments in Table III). These chelating bis-(tertiary phosphines) of high coordinating abilities probably have displaced the two PEt_3 ligands and brought the acyl and p-cyanophenoxy ligands into adjacent positions suitable for their reductive elimination. The mechanism of direct reductive elimination from **4e** in the absence of the added ligand in Scheme I remained unsettled. The concerted path from a four-coorinate trans compound **4e** is considered to be symmetry forbidden,[5] so that the other types of channels for reductive elimination should be considered. An ionic process, in which an aryloxy anion externally attacks the acyl carbon to give the ester, is not plausible, since the addition of $NaOC_6H_4$-p-CN showed no apparent effect on the rate of reductive elimination. The fact that no apparent solvent effect was observed on changing the solvent polarity (benzene, diphenyl ether, and pyridine) is not compatible with an ionic mechanism. However, introduction of p-cresol to **4e** liberated $MeCOOC_6H_4$-p-Me instead of $MeCOOC_6H_4$-p-CN. This result may be interpreted by a priori aryloxy exchange
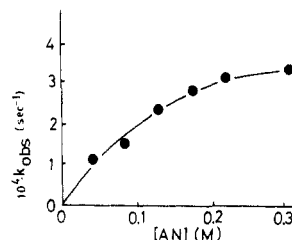
Figure 2. Dependence of k_{obsd} on the concentration of AN in the reductive elimination of $MeCO_2C_6H_4$-p-CN from **3c** in THF at 28.0 °C.

giving unstable $Pd(COMe)(OC_6H_4$-p-Me$)(PEt_3)_2$ to liberate the ester. UV irradiation of **4e**, which is expected to induce isomerization of the trans isomer to the cis,[8,9] showed no accelerating effect on the reductive elimination.

Reductive Elimination of Esters from Acyl(p-cyanophenoxy)metal Complexes Induced by π-Acids. As we noted previously,[4b] the reductive elimination from complexes **3b** and **3c** is markedly accelerated by addition of π-acids such as CO, maleic anhydride, and ethyl methacrylate. A similar accelerating effect of π-acids also was observed for the triethylphosphine complex **3f**. A one-electron oxidant,[10] $IrCl_6^{2-}$, also induced the reductive elimination from **3b** and **3f**. On the other hand, reductive elimination from the palladium analogue **4e** was not enhanced at all by the π-acids. Addition of high-pressure CO served only to accelerate the CO insertion into the Pd–C bond, and no enhancement in reductive elimination was observed (eq 15). The rate of the reductive elimi-

nation of ester from **3c** in the presence of acrylonitrile (AN) in THF was followed spectrometrically (eq 16). The absorption maximum at 482 nm for **3c** decreased with time, and instead a new peak at 440 nm, attributable to the reaction product $Ni(AN)_2bpy$,[11] gradually appeared. Isosbestic points at 395 and 460 nm were observed throughout the reaction. The rate of the reaction was first
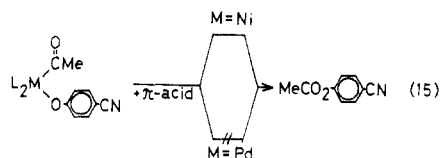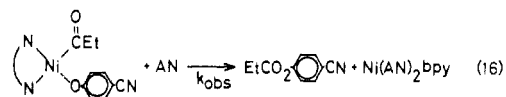
order in the concentration of **3c** until the reaction was 70–80% complete (eq 17). The pseudo-first-order rate

$$-\frac{d}{dt}[3c] = k_{obsd}[3c] \qquad (17)$$

constant k_{obsd} increases with increase in the concentration of acrylonitrile as shown in Figure 2. A reciprocal plot of both k_{obsd} and the concentration of acrylonitrile gives a straight line as seen in Figure 3. Addition of bpy ligand showed no retardation effect on the rate. The reaction mechanism shown in Scheme II is compatible with these kinetic data. Acrylonitrile reversibly coordinates to **3c** to

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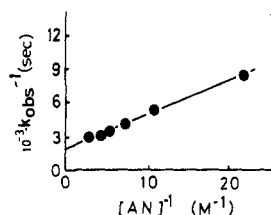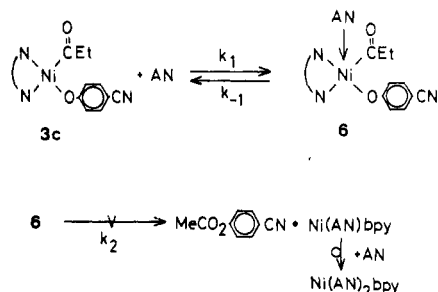
Figure 3. Reciprocal plot of both k_{obsd} and the concentration of AN in the reductive elimination of ester from **3c** in THF at 28.0 °C.

Scheme II. Mechanism for π-Acid Induced Reductive Elimination of Ester from 3c

give a five-coordinate species **6** from which reductive elimination takes place. The assumption of the preequilibrium in Scheme II is reasonable, since the coordinatively unsaturated 16-electron complex **3c** is capable to capture another ligand in solution.[11] The following rate equation is derived by assuming the reductive elimination process as a rate-determining step. In eq 18, [I] denotes the total

$$-\frac{d}{dt}[I] = \frac{k_2 K[AN]}{1 + K[AN]}[I]$$
$$= k_{obsd} \quad (K = k_1/k_{-1}) \tag{18}$$

$$\frac{1}{k_{obsd}} = \frac{1}{k_2} + \frac{1}{k_2 K[AN]} \tag{19}$$

concentration of **3c** and the five-coordinate intermediate **6** and K stands for preequilibrium constant k_1/k_{-1}. This equation is in agreement with the experimental results. Similar equilibria between dialkylnickel(II) and substituted olefins prior to reductive elimination were previously demonstrated.[2h,11]

Comparison of Reductive Elimination between Ni and Pd Complexes. The results obtained here are summarized below. (1) Acyl(aryloxy)metal(II) intermediates can be isolated when they carry an electron-withdrawing aryloxy group and strong donors as supporting ligands. Such a trend is compatible with the theoretical expectation that the electron-withdrawing property of the R group in an MR_2L_2-type complex makes the reductive elimination difficult and the stronger donor ligands L give a higher barrier for the reductive elimination reaction.[5]

(2) Thermal reductive elimination of ester from acyl-(aryloxy)palladium(II) complex proceeds via both dissociative and nondissociative routes, whereas decarbonylation dominates over reductive elimination in the thermolysis of the nickel analogues.

(3) π-Acids such as CO and olefins induce selective reductive elimination of esters from acyl(aryloxy)nickel(II) complexes via a five-coordinate intermediate. In contrast, no apparent accelerating effect of added π-acids was observed on the reductive elimination from the palladium(II) complex.

The sharp contrast in the reactivities of the Ni and Pd complexes may arise from the large difference of elec-

tron-donating ability of the metals. First, Ni, having a small ionization potential, acts as a good donor toward π-accepting ligands such as CO and olefins to form a five-coordinate intermediate from which a facile reductive elimination takes place.[12] Occurrence of the thermal decarbonylation reflects the strong bonding ability of nickel to CO. On the other hand, palladium has only a weak affinity toward CO and thermolysis of **4e** causes clean reductive elimination of an ester without decarbonylation. Very weak interaction of π-acids with palladium, due to relatively lower basicity of palladium, fails to form the five-coordinate intermediates needed to induce the reductive elimination. Therefore, thermal reductive elimination from the palladium complex dominates over decarbonylation.

The contrasting behavior of the nickel and palladium analogues both having the acyl and aryloxy ligands in the reductive elimination is reminiscent of the contrasting behavior of dialkylnickel and -palladium analogues in the reductive elimination on thermolysis and on interaction with π-acids. Namely, olefins having electron-withdrawing substituents induce a facile reductive elimination from $NiR_2(bpy)$,[2h] whereas little accelerating effect of π-acids has been observed in the reductive elimination from *cis*- and *trans*-PdR_2L_2.[2c] The similar contrasting patterns in reductive elimination of the nickel and palladium analogues having two alkyl groups on the one hand, and the acyl and aryloxo groups on the other, are intriguing. Involvement of similar controlling factors depending on the metal is suspected in these two types of reductive elimi-

Experimental Section

All manipulations were carried out under deoxygenated nitrogen or argon. Solvents were purified by usual methods under nitrogen. Phenols of reagent grade were purchased from Tokyo Kasei Co. Ltd. and used without further purification. Mono- and dialkylnickel(II) and mono- and dialkylpalladium(II) complexes were prepared according to literature methods.[4,7,13,14] GLC analyses were carried out by using Shimadzu 3BT, 3BF, 8APTF, and 8A gas chromatographs. ^1H NMR spectra were recorded on JEOL FX-100, FX-200, PMX-60, and MH-60 spectrometers. IR spectra were measured on Hitachi-295 and JASCO-A-302 spectrometers.

Kinetics. Reactions of nickel complex **3c** with acrylonitrile were monitored by the visible spectroscopy. To a quartz cell with a three-way stopcock containing a prescribed amount of **3c** was introduced THF, dried over K benzophenone ketyl, by trap-to-trap distillation. Immediately after the addition of a fixed amount of acrylonitrile into the cell by trap to trap distillation, the cell was placed in a thermostated cell holder and the reaction was followed spectrophotometrically. $10^4 k_{obsd}$ (s^{-1}) ([AN], mol/L) at 28.0 °C in THF: 1.16 (0.045), 1.78 (0.090), 2.38 (0.134), 2.87 (0.179), 3.13 (0.224), 3.48 (0.314).

Reductive elimination from **4e** was followed by ^1H NMR. To an NMR tube containing a fixed amount of **4e** was introduced benzene-d_6 (0.5 mL), dried over Na metal, by trap-to-trap distillation. The NMR tube was placed in a thermostated water bath after the NMR tube was sealed, and the ^1H NMR spectrum was periodically measured $10^6 k_{obsd}$ (s^{-1}) ([PEt$_3$], mol/L) at 35.0 °C in benzene-d_6: 6.91 (0), 6.84 (0.121), 4.67 (0.382), 4.56 (1.21), 4.65 (1.82). $10^6 k_{obsd}$ at 30.0 °C in benzene-d_6 in the absence of PEt$_3$: 7.27 (in pyridine), 7.22 (in CH$_2$Ph$_2$), 7.17 (in benzene).

Preparation of NiMe(OC$_6$H$_4$-p-CN)(PEt$_3$)$_2$, 1f. An equimolar amount of p-cyanophenol (487 mg) was added to an ether solution (20 mL) of NiMe$_2$(PEt$_3$)$_2$ (1.33 g, 4.09 mmol) at room temperature to give a yellow, homogeneous solution. Evolution

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of methane was observed. After 2 h, the yellow solution was concentrated to ca. 10 mL and chilled to −20 °C to afford yellow crystals. Recrystallization from ether gave pure material: yield 71%; mp 89–91 °C.

Other alkyl(aryloxy)nickel(II) and -palladium(II) complexes were prepared analogously. Yields, melting points, elemental analyses, and IR and ^{1}H NMR spectral data are summarized in Table I.

Reactions of Alkylnickel and -palladium Complexes with CO. Complex 1f (102 mg, 0.239 mmol) was dissolved in THF (2 mL). After evacuation, carbon monoxide (1 atm) was introduced. MeCOOC$_6$H$_4$-p-CN (0.197 mmol, 82%/Ni) was detected in the colorless solution after 1 day. The IR spectrum of the residual solid after volatiles were removed showed strong bands at 1910 and 1980 cm^{-1} attributable to ν(C≡O) of Ni(CO)$_2$(PEt$_3$)$_2$.[14]

Reactions of other alkylnickel and -palladium complexes are summarized in Table II.

Preparation of Ni(COMe)(OC$_6$H$_4$-p-CN)(PEt$_3$)$_2$, 3f. An equimolar amount of CO was introduced into a THF (5 mL) solution of 1f (229 mg, 0.535 mmol) under vacuum at −78 °C, by using a mercury manometer. More than 90% of CO gas was absorbed in 6 h. After 10 h, the reaction was stopped and the yellow solid obtained by removing THF *in vacuo* was recrystallized from hexane to give air-sensitive yellow crystals: yield 22%; mp 80–83 °C dec. Elemental analysis was not feasible because of its high air sensitivity, and the complex was identified by IR and NMR spectroscopy: IR ν(C≡N) 2200 cm^{-1} (vs), ν(C=O) 1645 (vs), ν(C—O) 1340 cm^{-1}; ^{1}H NMR (benzene-d_6) NiCOMe, 2.55 ppm (s, 3 H), PEt$_3$, 1–2 ppm (m, 30 H), OC$_6$H$_4$-p-CN, 7.03 ppm (d, J(H–H) = 9Hz, 2 H), 7.35 (d, J(H–H) = 9Hz), 2 H).

Preparation of *trans*-Pd(COMe)(OC$_6$H$_4$-p-CN)(PEt$_3$)$_2$, 4e.

Complex 2e (661 mg, 1.39 mmol) in benzene (10 mL) was placed in an autoclave (50 mL) under nitrogen. CO gas (ca. 10 atm) was introduced into the autoclave. After the reaction system was stirred at room temperature for 5 h, the solution was transferred into a Schlenk type flask. Removal of solvent afforded a colorless solid which was recrystallized from ether to give colorless crystals: yield 50%; mp 54–55 °C; IR ν(C≡N) 2180 cm^{-1} (vs), ν(C=O) 1670 (vs); ^{1}H NMR (acetone-d_6) PdCOMe, 2.39 ppm (t, J(P–H) = 1 Hz, 3 H), PEt$_3$, 1.16 (qui, J(P–H) = J(H–H) = 8 Hz, 18 H), 1.60 (m, 12 H), OC$_6$H$_4$-p-CN, 6.72 (d, J(H–H) = 9 Hz, 2 H), 7.25 (d, J(H–H) = 9 Hz, 2 H). Anal. Calcd: C, 50.1; H, 7.4; N, 2.8. Found: C, 50.7; H, 7.4; N, 2.8. In this preparation starting material 2e sometimes remained. Completion of the reaction was confirmed by monitoring the solution by ^{1}H NMR spectroscopy before performing isolation.

Communications

Intermediates in the Palladium-Catalyzed Reactions of 1,3-Dienes. 1. (η^3,η^3-Dodecatrienediyl)palladium, [Pd(η^3,η^3-C$_{12}$H$_{18}$)]

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Summary: Butadiene reacts with bis(dibenzylidene-acetone)palladium to give the title compound. The NMR spectra indicate that the C$_{12}$ chain in this molecule is arranged symmetrically around the palladium atom and has syn-substituted η^3-allyl groups and an uncomplexed cis double bond. Further reaction with bidentate ligands is accompanied by conversion of the η^3-allyl groups into the η^1-allyl form to give a 13-membered metallacycle. The significance of these complexes to the palladium-catalyzed linear trimerization of butadiene is discussed.

Although it has been known for over 20 years that donor ligand-free palladium catalysts convert butadiene into a mixture of isomers of the *linear* trimer dodecatetraene, there is little concrete information concerning the mechanism of this process. The original suggestion that an

(η^2,η^3,η^3-dodecatriendiyl)palladium species,[2,3] related to the nickel complex isolated from the *cyclotrimerization* of butadiene,[4] is involved was abandoned in favor of a mechanism involving a binuclear species following the isolation of a complex of this type (eq 1) which was, moreover, shown to be an active catalyst for the linear trimerization of butadiene.[5-7] We report here evidence which implies that the original suggestion was essentially correct.

Bis(dibenzylideneacetone)palladium, [Pd(dba)$_2$],[8] or the related bipyridine derivative [Pd(bpy)(dba)],[9] react with excess butadiene in ether at room temperature to give the

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