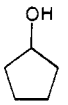
$$CpZr(CO)_2(dmpe)Cl + 2CH_2CH_2 \xrightarrow{-CO} CpZr[\eta^2\text{-}C(O)CH_2CH_2CH_2CH_2]Cl\cdot{}^1/_2(dmpe) \xrightarrow{2HCl}$$



$$+ CpZrCl_3(dmpe) \quad (6)$$

enolate-hydride complex $[CpZrClH(OC{=}CHCH_2CH_2CH_2)]\cdot{}^1/_2(dmpe)$ which could be expected on the basis of a similar cocyclization, obtained by prolonged photolysis of $Cp^*_2Zr(CO)_2$ solutions under an ethylene atmosphere.[17] Reaction 6 seems specific for ethylene, and attempts to react **3** with differently substituted olefins (propylene, isobutene, *cis*-2-butene, 2,3-dimethyl-2-butene) were unsuccessful.

A further investigation on the reactivity of complexes **3** and **4** is included in our continuing studies on these systems.

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Registry No. **1**, 114238-07-2; **2**, 116148-79-9; **3**, 116129-35-2; **3**-$^{13}C_2$, 116129-39-6; **4**, 116129-36-3; **4**-$^3C_2$, 116129-40-9; **5**, 116129-37-4; **6**, 115227-38-8; $CpZrCl_3(THF)_2$, 114238-08-3; dmpe, 23936-60-9; $CpHfCl_3(THF)_2$, 66349-82-4; $[CpFe(CO)_2]_2$, 12154-95-9; [CpFe(dmpe)(CO)][CpFe(CO)$_2$], 116129-38-5; $CpZrCl_3$(dmpe), 115227-37-7; butadiene, 106-99-0; ethylene, 74-85-1; cyclopentanol, 96-41-3.

Supplementary Material Available: Tables of anisotropic thermal parameters, atomic coordinates for the hydrogen atoms, and bond lengths and angles (4 pages); a listing of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of New Methyl(alkoxo)- and Methyl(thiolato)nickel and Methyl(alkoxo)- and Methyl(thiolato)palladium Complexes. CO and CS_2 Insertion into the Alkoxo–Palladium Bond

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Reactions of fluorinated alcohols ($HOCH(CF_3)_2$, $HOCH_2CF_3$, and $HOCH(CF_3)C_6H_5$) or aromatic thiols (HSC_6H_5 and HSC_6H_4-*p*-CH_3) with dialkylnickel and -palladium complexes ($NiMe_2$(bpy), $NiEt_2$(bpy) (bpy = 2,2′-bipyridine), $NiMe_2$(dpe), and $PdMe_2$(dpe) (dpe = 1,2-bis(diphenylphosphino)ethane)) give the corresponding monoalkyl complexes with an alkoxo or a thiolato ligand (NiMe(OR)(bpy), NiEt(OR)(bpy), MMe(OR)(dpe), and MMe(SAr)(dpe) (M = Ni, Pd; R = $CH(CF_3)_2$, CH_2CF_3, $CH(CF_3)C_6H_5$)). These complexes have been characterized by elemental analysis and NMR (^1H, $^{31}P\{^1H\}$, ^{19}F, and $^{13}C\{^1H\}$) spectroscopy. The methyl(alkoxo)nickel(II) and -palladium(II) complexes thus obtained react with carbon monoxide at normal pressure to give carboxylic esters in high yields. Reaction of carbon monoxide with NiMe(SAr)(dpe) (Ar = C_6H_5, C_6H_4-*p*-CH_3) also gives the corresponding carbothioic esters in good yields, while PdMe(SPh)(dpe) is unreactive with carbon monoxide under similar conditions. The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of the reaction mixture of $PdMe(OCH(CF_3)_2)$(dpe) with an equimolar amount of ^{13}CO at −60 °C show the formation of PdMe ($^{13}COOCH(CF_3)_2$)(dpe) produced through insertion of the carbon monoxide into the Pd–O bond. When the reaction temperature is raised to −20 °C, this alkoxycarbonyl complex undergoes reductive elimination to give 1,1,1,3,3,3-hexafluoro-2-propyl acetate. The reaction is accompanied by simultaneous decarbonylation of the alkoxycarbonyl ligand to regenerate $PdMe(OCH(CF_3)_2)$(dpe). The reaction of PdMe($OCH(CF_3)Ph$)(dpe) with carbon disulfide gives an isolable palladium complex, PdMe($SCSOCH(CF_3)Ph$)(dpe), formed by insertion of CS_2 into the Pd–O bond, while PdMe(SPh)(dpe) is unreactive with CS_2.

Introduction

In comparison with alkoxides of non-transition-metal elements and early transition metals,[1] examples of isolated late transition metals are still limited.[2-10] The chemistry of these late-transition-metal alkoxides merits study in its own right and also in view of the important roles these

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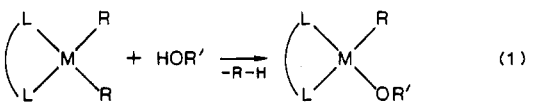
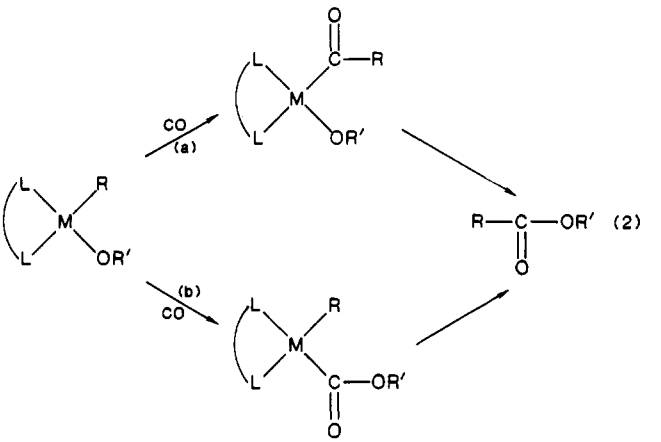
compounds are believed to play as intermediates in various metal-catalyzed synthetic organic reactions. The reactions in which these late-transition-metal alkoxides are involved include oxidation of alcohols.[11] hydrogenation of ketones,[12] condensation of aldehydes,[13] decarboxylation of allylic esters and carbonates,[14] and carbonylation of alcohols.[15] One generally believed reason for the paucity of the late-transition-metal alkoxides is their tendency to decompose through β-hydrogen elimination. Although some methoxides are known to eliminate formaldehyde,[9d] lending support for the explanation of the instability of the metal alkoxides in terms of readiness for β-hydrogen elimination, the scarcity of isolated late-transition-metal alkoxides still does not allow a general conclusion to be drawn regarding the cause of the instability.

We have previously observed that stable group 8 and 9 metal alkoxides resistant to β-hydrogen elimination were obtained on treatment of hydrides of cobalt(I), rhodium(I), and ruthenium(II) with acidic alcohols having fluorine substituents.[7] We have examined whether fluoroalkoxides of other late transition metals are similarly stable. The first part of this paper is concerned with the preparation of alkylnickel and -palladium complexes having these stable alkoxide groups with chelating supporting ligands by the following general route.



(1)

The second part of this paper deals with the reaction route of the alkylnickel and -palladium alkoxides in their CO and CS_2 insertions. The alkylmetal alkoxides prepared by eq 1 have two possible pathways for CO insertion (eq 2), one being the CO insertion into the metal-carbon bond (route a) and the other being the CO insertion into the metal–alkoxide bond (route b). Formation of carboxylic esters by reductive elimination may result from either pathway.



Our previous studies on reactions of methyl(aryloxo)-nickel(II) and -palladium(II) complexes showed that CO was inserted preferentially into the M–C bond to give acetyl(aryloxo)nickel and -palladium complexes which released aryl acetate by coupling of the acetyl group with the aryloxo groups. The reductive elimination was promoted by CO and other π-acids in the case of nickel whereas no promotion effect was observed for the acetylpalladium aryloxide.[16]

On the other hand, Bennett, Ros, Bryndza, and their respective co-workers successively reported insertion of CO into the Pt–O bond rather than into the Pt–C bond of $Pt(C_6H_9)(OMe)(dpe)$, $Pt(CF_3)(OMe)(PPh_3)_2$, $Pt(CH_2CN)(OCH_3)(Ph_2PCH{=}CHPPh_2)$, and PtMe(OMe)(dpe) to give platinum(II) complexes with a methoxycarbonyl ligand, PtR(COOMe)(L-L).[2,5,9b,c] These complexes, however, showed no tendency to undergo reductive elimination to the corresponding esters.

It was of interest to see which route the present nickel and palladium complexes would take in order to design a catalytic system for the preparation of carboxylic esters.

Results and Discussion

Preparation and Characterization of Alkylnickel and -palladium Complexes Having Alkoxo or Thiolato Ligands. We first attempted to isolate methylpalladium alkoxides by treatment of PdMeCl(dpe) with sodium methoxide or sodium 2-propoxide but obtained only some uncharacterized products. Fluorinated alcohols, on the other hand, gave isolable products. The reactions of dialkylnickel(II) and -palladium(II) complexes having a bpy or dpe ligand with fluorinated alcohols such as 1,1,1,3,3,3-hexafluoro-2-propanol, 2,2,2-trifluoro-1-phenylethanol, and 2,2,2-trifluoroethanol at room temperature gave the corresponding nickel and palladium complexes having both alkyl and alkoxo ligands as shown in eq 3–5. Similar complexes having both methyl and thiolato ligands are also prepared from the reaction of aromatic thiols such as benzenethiol and *p*-toluenethiol with $NiMe_2(dpe)$ and $PdMe_2(dpe)$. These complexes are stable at room temperature both in the solid state and in

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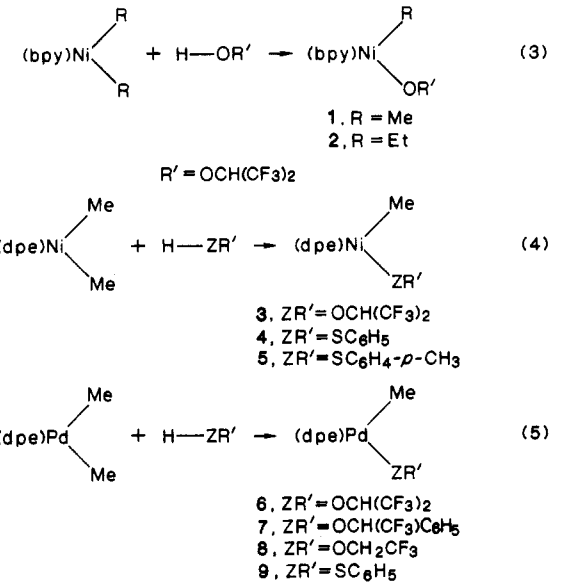
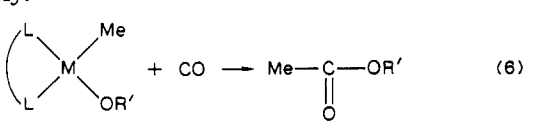


solution under nitrogen atmosphere. Tables I and II summarize the yields, melting points, and analytical and NMR data of these complexes. ^1H and $^{31}P\{^1H\}$ NMR spectra of **3–9** are consistent with the cis structures of the complexes having methyl and alkoxo (or thiolato) ligands. The $^{13}C\{^1H\}$ NMR spectrum of **6** shows signals due to the carbons of the alkoxo ligand and the methyl ligand with ^{13}C–^{19}F or ^{13}C–^{31}P coupling (Table II).

These alkylnickel and -palladium complexes having the fluorinated alkoxo ligands proved quite stable. Thermolysis products of hexafluoropropoxo complexes (**1**, **2**, and **6**), 2,2,2-trifluoro-1-phenylethoxo (**7**), and of 2,2,2-trifluoroethoxo complex (**8**) are summarized in Table III. Ketones expected in thermolysis via β-hydrogen elimination of these alkoxides were not observed except in thermolysis of **7** which produced trifluoroacetophenone in a minor amount. In the bpy-coordinated complexes **1** and **2**, the alkyl ligands were predominantly thermolyzed. In the thermolysis of the dpe-coordinated complexes, **6**, **7**, and **8**, the major thermolysis products were fluorinated alcohols. The source of hydrogen was not confirmed, but formation of ethylene and ethane from these methylpalladium complexes suggests involvement of a rather complex thermolysis route with participation of the methyl group in the thermolysis reaction. Reductive elimination of ethers from these alkylalkoxo complexes was not observed. These results suggest that the β-hydrogen elimination pathway is not a low-energy route at least in the thermolysis of the electronegative alkoxides.

Reactions of Nickel and Palladium Complexes Having Alkyl and Alkoxo (or Thiolato) Ligands with Carbon Monoxide. Results of the reactions of CO with complexes **1–9** at normal pressure are summarized in Table IV. Bipyridine-coordinated methyl- and ethylnickel complexes having the alkoxo ligand (**1**, **2**) react smoothly with CO at room temperature to give carboxylic esters in high yields with liberation of the bpy ligand, suggesting the formation of $Ni(CO)_4$ in the reaction mixtures. The dpe-coordinated methylnickel and -palladium complexes (**3**, **6–8**) react similarly to give the acetates and $Ni(CO)_2$(dpe) or a mixture of palladium(0) carbonyl complexes, respectively.[17]



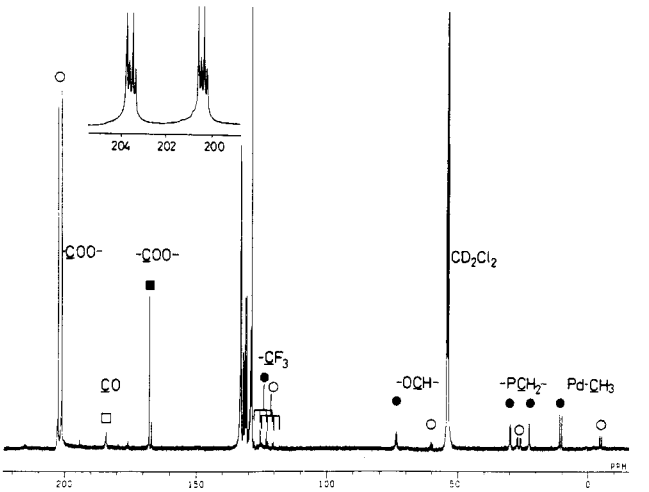
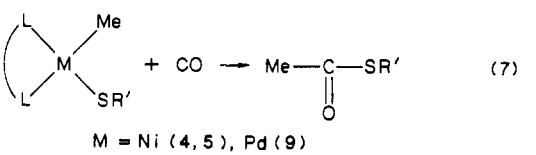


Figure 1. $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture of ^{13}CO with equimolar PdMe(OCH$(CH_3)_2$)(dpe) **6** at −60 °C in CD_2Cl_2. Signals with ●, ○, ■, and □ are due to **6**, PdMe(^{13}COOCH-$(CF_3)_2$)(dpe) (**10**), Me^{13}COOCH$(CF_3)_2$, and uncoordinated ^{13}CO, respectively. See ref 18 for discussion of the signals at 204–200 ppm.

The dpe-coordinated methylnickel complexes with thiolato ligands reacted smoothly at room temperature to give carbothioic esters whereas the reaction of the methyl(thiolato)palladium complex **9** was slow giving *S*-phenyl thioacetate in a 15% yield even after a prolonged reaction time to leave 75% of the starting complex **9**.



Reaction of CO with an equimolar amount of **6** at −60 °C was followed by NMR spectroscopy in order to identify the intermediate of the above reaction. The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture show signals due to PdMe(COOCH$(CF_3)_2$)(dpe) (**10**) in addition to signals arising from unreacted **6**. Figure 1 shows the $^{13}C\{^1H\}$ NMR spectrum obtained after the initial 3 h of reaction using ^{13}C-labeled CO. Signals due to carbons of PdCOO, CF_3, OCH, and $PdCH_3$ are observed at 202.0 (and 201.9),[18] 122.4, 60.2, and −5.0 ppm, respectively, with splitting due to ^{13}C–^{31}P or ^{13}C–^{19}F coupling (Table II). The other possible intermediate in ester formation, Pd(COMe)(OCH$(CF_3)_2$)(dpe), if present, would be expected to show signals due to carbons of CO and CH_3 group at about 240–210 ppm and 40–30 ppm, respectively, in the

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(18) The carbonyl carbon atom of **10** appears as two sets of doublets of doublets at 202.0 and 201.9 ppm, respectively, in the $^{13}C\{^1H\}$ NMR spectrum, while each of other carbon atoms appears as one set of signals. These spectroscopic features suggest the presence of two isomers with quite similar structures. Following formulae show two possible pairs of the isomers stemming from different conformations of the alkoxycarbonyl ligand.

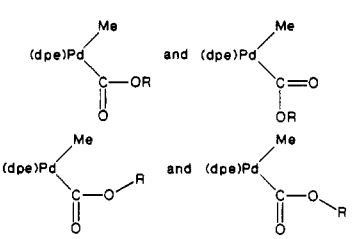


Table I. Yields, Melting Points, and Analytical Data of Complexes 1–9 and 11

complex	no.	yield (%)	color	mp (°C)[a]	anal.[b] C	H	N	S
NiMe(OCH(CF_3)$_2$)(bpy)	1	79	purple	142–145	42.7 (42.4)	2.9 (3.1)	7.0 (7.1)	
NiEt(OCH(CF_3)$_2$)(bpy)	2	87	purple	130–132	43.4 (43.8)	3.3 (3.4)	6.8 (6.8)	
NiMe(OCH(CF_3)$_2$)(dpe)	3	72	yellow	128–130	56.4 (56.4)	4.5 (4.4)		
NiMe(SPh)(dpe)	4	81	yellow	160–163	68.1 (68.2)	5.8 (5.6)		5.2 (5.5)
NiMe($SC_6H_4CH_3$)(dpe)	5	45	yellow	158–160	68.8 (68.6)	5.9 (5.8)		5.4 (5.4)
PdMe(OCH(CF_3)$_2$)(dpe)	6	80	white	139–142	52.0 (52.5)	4.2 (4.2)		
PdMe(OCH(CF_3)Ph)(dpe)	7	84	white	164–167	60.5 (60.5)	4.9 (4.8)		
PdMe(OCH_2CF_3)(dpe)	8	59	white	116–118	55.9 (56.3)	4.9 (4.7)		
PdMe(SPh)(dpe)	9	87	white	198–202	63.1 (63.0)	5.2 (5.1)		5.2 (5.1)
PdMe(SCSOCH(CF_3)Ph)(dpe)	11	75	yellow	125–128	56.0 (56.1)	4.3 (4.3)		

[a] Decomposed. [b] Calculated values are in parentheses.

Table II. NMR Data of Complexes 1–11[a]

complex	^{1}H[b] MCH_3 (MCH_2CH_3)	^{1}H[b] OCH	^{19}F[c]	^{31}P{^{1}H}[d]	^{13}C{^{1}H}[e] PdCOO (PdSCS)	^{13}C{^{1}H}[e] CF_3	^{13}C{^{1}H}[e] OCH	^{13}C{^{1}H}[e] PCH_2	^{13}C{^{1}H}[e] PdCH_3
1	−0.10 (s, 3 H)	3.65 (sep, 1 H) J_{FH} = 7 Hz	0.68 (d)						
2	0.72 (br, 5 H)	3.77 (sep, 1 H) J_{FH} = 7 Hz	0.64 (d)						
3	−0.24 (t, 3 H) J_{PH} = 5 Hz	4.30 (sep, 1 H) J_{FH} = 7 Hz	2.90 (d)	64.1 (d), 34.6 (d) J_{PP} = 6 Hz					
4	−0.23 (dd, 3 H) J_{PH} = 8, 4 Hz			65.5 (d), 52.7 (d) J_{PP} = 10 Hz					
5	0.52 (dd, 3 H) J_{PH} = 9, 4 Hz			65.4 (d), 52.4 (d) J_{PP} = 8 Hz					
6	0.85 (dd, 3 H) J_{PH} = 8, 2 Hz	5.38 (sep, 1 H) J_{FH} = 7 Hz	3.69 (d)	63.3 (d), 32.3 (d) J_{PP} = 25 Hz		124.0 (q) J_{CF} = 288 Hz	73.7 (sep) J_{CF} = 29 Hz	29.8 (dd) J_{CP} = 27, 10 Hz	22.4 (dd) J_{CP} = 34, 23 Hz	10.5 (dd) J_{CP} = 97, 3 Hz
7	0.37 (dd, 3 H) J_{PH} = 8, 3 Hz	5.22 (q, 1 H) J_{FH} = 6 Hz	−1.44 (d)	61.6 (d), 32.4 (d) J_{PP} = 23 Hz					
8	0.76 (dd, 3 H) J_{PH} = 8, 3 Hz	3.95 (q, 2 H) J_{FH} = 7 Hz	2.88 (t)	65.0 (d), 36.6 (d) J_{PP} = 27 Hz					
9	0.22 (dd, 3 H) J_{PH} = 7, 5 Hz			58.9 (d), 41.5 (d) J_{PP} = 25 Hz					
10[f]				56.3 (d), 45.7 (d)[g] J_{PP} = 22 Hz	202.0 (dd)[h] 201.9 (dd) J_{CP} = 183, 16 Hz	122.4 (q) J_{CF} = 282 Hz	60.2 (sep) J_{CF} = 35 Hz	27.1 (dd) J_{CP} = 27, 19 Hz	25.9 (dd) J_{CP} = 28, 16 Hz	−5.0 (dd) J_{CP} = 85, 5 Hz
11	0.69 (dd, 3 H) J_{PH} = 7, 5 Hz	6.89 (q, 1 H)[i] J_{FH} = 9 Hz	3.18 (d)	63.1 (d), 40.4 (d) J_{PP} = 25 Hz	222.0 (s)	127.4 (q) J_{CF} = 282 Hz	78.6 (q) J_{CF} = 32 Hz	30.3 (m)	25.6 (m)	5.7 (d)[i] J_{CP} = 98 Hz[j]

[a] Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; dd, doublet of doublets; m, multiplet; br, broad signal. [b] 100 MHz. Solvent: $(CD_3)_2CO$ (1, 2), C_6D_6 (4, 6, 8), CD_2Cl_2 (3, 5, 7, 9–11). [c] 94 MHz in CH_2Cl_2–CD_2Cl_2 (4:1). Ppm downfield from external CF_3COOH. [d] 40 MHz in CH_2Cl_2–CD_2Cl_2 (4:1). Ppm downfield from external PPh_3. [e] 125 MHz in CD_2Cl_2 at −60 °C. [f] Not isolated and measured as a mixture with 6 at −60 °C. Most signals in ^{1}H NMR spectrum are overlapped with those of 6 and are not assignable. [g] Splitting due to ^{13}C–^{31}P coupling is observed in the spectrum of ^{13}C-labeled compound (J_{PC} = 183 and 16 Hz, respectively). [h] Signals due to carbonyl carbon atom were observed by using ^{13}C-labeled compound. Two sets of the signals are observed probably due to the presence of isomers. See ref 13. [i] Measured at −60 °C. [j] Another J_{CP} is too small to be observed.

Table III. Thermolysis of Alkyl(alkoxo)nickel(II) and -palladium(II) Complexes[a]

complex	reactn temp (°C)	products (yield (%))[b]		
1	150	CH_4 (46)	C_2H_6 (16)	$HOCH(CF_3)_2$ (tr)
2	150	C_2H_4 (43)	C_2H_6 (32)	$HOCH(CF_3)_2$ (tr)
6	150	CH_4 (15)	C_2H_4 (2)	$HOCH(CF_3)_2$ (57)
7	150	CH_4 (12)	C_2H_4 (8)	$HOCH(CF_3)Ph$ (54)
			C_2H_6 (3)	CF_3COPh (7)
8	120	CH_4 (11)	C_2H_6 (10)	$HOCH_2CF_3$ (84)

[a] The reaction was carried out in diphenylmethane under vacuum. [b] tr = trace amount.

Table IV. Reactions of Carbon Monoxide with Alkyl(alkoxo (or thiolato))nickel(II) and -palladium(II) Complexes

	conditns[a]		products (yield (%))	
complex	solv	time (h)	ester	complex or ligand
1	THF	2.5	$CH_3COOCH(CF_3)_2$ (98)	bpy (100)
2	THF	2.5	$C_2H_5COOCH(CF_3)_2$ (97)	bpy (100)
3	THF	2.5	$CH_3COOCH(CF_3)_2$ (94)	$Ni(CO)_2(dpe)$ (88)
4	CH_2Cl_2	4	$CH_3COSC_6H_5$ (75)	$Ni(CO)_2(dpe)$ (75)
5	CH_2Cl_2	4	$CH_3COSC_6H_4CH_3$ (80)	$Ni(CO)_2(dpe)$[b]
6	THF	2	$CH_3COOCH(CF_3)_2$ (68)	$Pd(CO)_m(dpe)_n$[c]
7	THF	2	$CH_3COOCH(CF_3)$-C_6H_5 (89)	$Pd(CO)_m(dpe)_n$[c]
8	THF	2	$CH_3COOCH_2CF_3$ (74)	$Pd(CO)_m(dpe)_n$[c]
9	CH_2Cl_2	48	$CH_3COSC_6H_5$ (15)	

[a] The reaction was carried out under an atmosphere of excess CO. [b] Formation of the complex was confirmed by IR but the amount was not measured. [c] Composed of several palladium(0) carbonyl cluster complexes. See text.

$^{13}C\{^1H\}$ NMR spectra.[19] However, no signals assignable to this acetyl species were observed during the reaction.

Figure 2 shows the change of the amounts of **10** and **6** obtained from $^{31}P\{^1H\}$ NMR spectra in the course of the reaction. A gradual increase in the amount of **10** at the expense of **6** is observed under these reaction conditions. Attempts to isolate complex **10** from the reaction system of CO with **6** at low temperature were unsuccessful due to its thermal instability. Change of the $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture indicates a quite slow formation of $CH_3COOCH(CF_3)_2$ even at −60 °C. In the $^{31}P\{^1H\}$ NMR spectra several small signals also gradually grow. They may be assigned to several palladium carbonyl complexes with dpe ligands. When the reaction temperature is raised to −20 °C, an immediate decrease of **10** with an increase of **6** is observed in the $^{31}P\{^1H\}$ NMR spectrum. Several signals assignable to those of palladium(0) carbonyl complexes are also observed.

The NMR observation may be accounted for as follows. Complex **6** undergoes gradual insertion of CO into the Pd–O bond rather than into the Pd–C bond in the presence of an equimolar amount of CO at −60 °C to give complex **10** having an alkoxycarbonyl ligand. At this temperature reductive elimination of $CH_3COOCH(CF_3)_2$

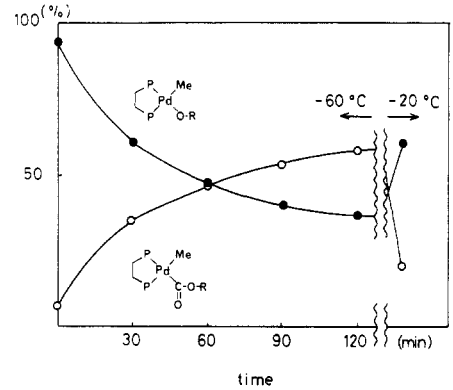
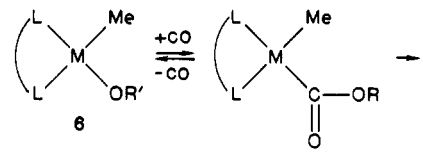


Figure 2. Reaction of CO with $PdMe(OCH(CF_3)_2)(dpe)$ (**6**). Time course of the amounts of **6** and $PdMe(COOCH(CF_3)_2)(dpe)$ (**10**) observed in $^{31}P\{^1H\}$ NMR spectra during the course of the reaction.

from **10** proceeds much more slowly than the formation of **10**. When the temperature is raised to −20 °C, reductive elimination of the ester occurs rapidly to give palladium(0) carbonyl complexes. Consumption of CO contained in the reaction mixture by this irreversible reaction makes **10** undergo spontaneous decarbonylation to regenerate **6**.



$$CH_3COOR + Pd(CO)_n(L\smile L)_m \quad (8)$$

$L\smile L$ = dpe; R = $CH(CF_3)_2$

Although reversibility of migratory insertion of CO into M–C bond has been well established,[16] there have been only a few reports of *reversible* insertion of CO into the M–O bond of metal alkoxide and decarbonylation of the alkoxycarbonyl ligand.[20] At present it is not possible to determine unambiguously whether insertion of CO into the Pd–O bond involves initial dissociation of the alkoxo ligand followed by its nucleophilic attack on the coordinated CO or whether the insertion proceeds through a mechanism including migratory insertion.[9c] NMR observation of the reaction mixture of CO and $PdMe(OCD(CF_3)_2)(dpe)$ in the presence of $HOCH(CF_3)_2$ did not give any clue regarding these mechanistic details of the reaction because signals due to –OCH– hydrogens of $HOCH(CF_3)_2$ and Pd–OCH-$(CF_3)_2$ in the ^1H NMR spectra appear at quite similar positions at −60 °C.

A similar NMR study on the reaction of CO with the methyl(alkoxo)nickel complex **3** was made to identify the intermediates in the formation of the esters. At −60 °C the formation of more than two species was observed in the $^{31}P\{^1H\}$ NMR spectra although their identities were not established by means of ^1H and $^{13}C\{^1H\}$ NMR spectroscopy due to the complexity of the spectra and due to rapid reductive elimination to give esters and $Ni(CO)_2(dpe)$ even at the low temperature.

Reaction of Carbon Disulfide with Methyl(alkoxo)palladium(II) Complex. Carbon disulfide is known to be inserted into the Pt–O bond of platinum(II) methoxo compounds, similarly to CO, giving platinum complexes with *O*-methyl dithiocarbonato ligands,[5] while palladium(II) complexes *trans*-$PdMeIL_2$ and $[PdMeL_3]^+$ (L = PMe_3)

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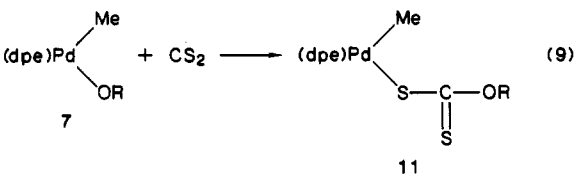
undergo insertion of CS_2 into Pd–C and Pd–P bonds to give $Pd(SCSMe)IL_2$ and $[PdMeL_2(SCSPMe_3)]^+$, respectively.[21]

The reaction of CS_2 with 7 gives PdMe(SCSOCH-(CF_3)Ph)(dpe) (11) as the sole product. This complex is



7 11

R = CH(CF3)Ph

stable at room temperature both in the solid state and in solution. Results of NMR measurement as well as elemental analysis are included in Tables I and II. ^1H and $^{13}C\{^1H\}$ NMR spectra of 11 at −70 °C show signals due to the methyl group coordinated to Pd with splittings due to ^1H–^{31}P and ^{13}C–^{31}P couplings. The signal of –SCSO– carbon appears as a singlet. Signals due to –CH–O– hydrogen of 11 in the ^1H NMR spectrum are at significantly lower field than those of the starting complex 7, while signals due to hydrogens of the methyl ligand in 7 and 11 appear at positions close to each other. The five-coordinated structure with π-bonded CS_2 ligand[22] for 11 can be excluded from the above NMR observations.

At room temperature the ^1H NMR signals of the methyl ligand in 11 are somewhat broadened and splitting of the signal due to ^1H–^{31}P coupling is unclear, indicating the presence of some fluxional behavior of the molecule on the NMR time scale.

Reaction of CS_2 with thiolato analogue 8 does not proceed at room temperature, and more than 90% of the unreacted 8 was recovered from the reaction mixture even after 48 h.

Experimental Section

All manipulations were carried out under nitrogen or argon. Solvents were purified by usual methods under nitrogen. 1,1,1,3,3,3-Hexafluoro-2-propanol, 2,2,2-trifluoroethanol, benzenethiol, and *p*-toluenethiol were purchased from Tokyo Kasei Co. Ltd. ^{13}CO (99% isotope purity) was purchased from CEA (Commissariat à l'énergie atomique). Dialkylnickel(II)[23] and dialkylpalladium(II)[24] complexes and 2,2,2-trifluoro-1-phenylethanol[7] were prepared according to the literature methods.

Elemental analyses were carried out by Dr. M. Tanaka and Mr. T. Saito of our laboratory by using a Yanagimoto CHN Autocorder Type MT-2 and Yazawa Halogen Analyzer. GLC analyses were carried out by using Shimadzu 3BT and 7AG gas chromatographs. NMR (^1H, ^{19}F, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$) spectra were recorded on JEOL FX-100 and GX-500 spectrometers by Dr. Y. Nakamura, Ms. R. Ito, and Ms. A. Kajiwara of our laboratory. IR spectra were recorded on a JASCO IR-810 spectrophotometer.

Preparation of Methyl(1,1,1,3,3,3-hexafluoro-2-propoxo)(2,2′-bipyridine)nickel (1) and Ethyl(1,1,1,3,3,3-hexafluoro-2-propoxo)(bipyridine)nickel (2). 1,1,1,3,3,3-Hexafluoro-2-propanol (220 mg, 1.3 mmol) was added to a solution of $NiMe_2$(bpy) (320 mg, 1.3 mmol) in THF (6 mL) at room temperature. The initial deep green solution turned to red-purple gradually on stirring at room temperature. Addition of hexane to the reaction mixture after 12 h caused precipitation of 1 as a red-purple solid, which was filtered and recrystallized from THF (420 mg, 79%).

2 was prepared analogously.

Preparation of Methyl(1,1,1,3,3,3-hexafluoro-2-propoxo)(1,2-bis(diphenylphosphino)ethane)nickel (3). 1,1,1,3,3,3-Hexafluoro-2-propanol (140 mg, 0.82 mmol) was added to a solution of $NiMe_2$(dpe) (400 mg, 0.82 mmol) in THF (10 mL) at room temperature. After the mixture was stirred for 4 h, the solvent was removed under reduced pressure to give 3 as a yellow solid which was recrystallized from a toluene–hexane (1:1) mixture (380 mg, 72%).

Preparation of Methyl(benzenethiolato)(1,2-bis(diphenylphosphino)ethane)nickel (4) and Methyl(4-methylbenzenethiolato)(1,2-bis(diphenylphosphino)ethane)nickel (5). Benzenethiol (140 mg, 1.3 mmol) was added dropwise to $NiMe_2$(dpe) (610 mg, 1.3 mmol) dispersed in toluene (5 mL) at −30 °C. When the reaction temperature was raised, the dimethyl complex dissolved gradually with evolution of methane, and the reaction mixture turned into a red solution. After the solution was stirred for 2 h at room temperature, 4 began to precipitate as a yellow solid. The reaction mixture was left at −20 °C for 12 h to cause complete precipitation of the product which was filtered, washed with Et_2O twice, and dried in vacuo (580 mg, 81%).

Complex 5 was obtained analogously.

Preparation of Methyl(1,1,1,3,3,3-hexafluoro-2-propoxo)(1,2-bis(diphenylphosphino)ethane)palladium (6), Methyl(2,2,2-trifluoro-1-phenylethoxo)(1,2-bis(diphenylphosphino)ethane)palladium (7), Methyl(2,2,2-trifluoroethoxo)(1,2-bis(diphenylphosphino)ethane)palladium (8), and Methyl(benzenethiolato)(1,2-bis(dipehnylphosphino)ethane)palladium (9). 1,1,1,3,3,3-Hexafluoro-2-propanol (200 mg, 1.2 mmol) was added to $PdMe_2$(dpe) (630 mg, 1.2 mmol) dispersed in toluene (10 mL) at room temperature. The white solid dissolved gradually on stirring. After the solution was stirred for 4 h, hexane was added to cause precipitation of 6 which was filtered and recrystallized from CH_2Cl_2–hexane (1:1) (640 mg, 80%).

Complexes 7–9 were prepared analogously.

Thermolysis of 1, 2, 6, 7, and 8. A solution of 7 (94 mg, 0.14 mmol) in diphenylmethane (2 mL) was heated at 150 °C under vacuum for 3 h. GLC analysis using propane and mesitylene as internal standards showed the presence of methane (10%), ethylene (14%), ethane (5%), phenyl trifluoromethyl ketone (7%), and 2,2,2-trifluoro-1-phenylethanol (37%) in the reaction mixture.

Thermolysis of the other complexes was carried out analogously.

Reaction of CO with 1-9. Complex 1 (90 mg, 0.23 mmol) was dissolved in THF (2 mL) at room temperature. After evacuation of the system CO was introduced at ambient pressure. The reaction mixture turned from purple to red immediately. After the solution was stirred for 2 h, volatile products were collected by trap-to-trap distillation. GLC analysis of the distillate showed the formation of 1,1,1,3,3,3-hexafluoro-2-propyl acetate (47 mg, 98%). The nonvolatile solid that remained in the reaction flask was revealed to be 2,2′-bipyridine (36 mg, 100%).

Reactions of CO with complexes 2–9 were carried out analogously. The results of these reactions are summarized in Table IV.

An NMR Study on the Reaction of Carbon Monoxide with 6. A solution of 6 (150 mg, 0.22 mmol) in CD_2Cl_2 (3 mL) was transferred to an NMR tube (10 mm, 20 cm) which was connected to a joint equipped with a nitrogen inlet. After evacuation of the system by use of a vacuum line (10^{-3} Torr), carbon monoxide (0.22 mmol), measured by means of a mercury manometer, was introduced into the tube with freezing the solution at −190 °C. The NMR spectrum was measured at −60 °C after the tube was sealed.

Reaction of CS_2 with 7. Carbon disulfide (37 mg, 0.47 mmol) was added dropwise to a colorless solution of 7 (280 mg, 0.40 mmol) in THF (10 mL) at room temperature to give a yellow solution immediately. After the solution was stirred for 1 h, the volume of solution was reduced to ca. 3 mL. Hexane was then added to the reaction mixture to cause precipitation of methyl(*O*-(2,2,2-trifluoro-1-phenylethyl) dithiocarbonato)(1,2-bis(diphenylphosphino)ethane)palladium (11) as a yellow solid which was filterd, washed with hexane, and dried in vacuo (230 mg, 75%).

Registry No. 1, 115981-38-9; 2, 115981-39-0; 3, 115981-40-3;

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4, 115981-41-4; 5, 115981-42-5; 6, 115981-43-6; 7, 115981-44-7; 8, 115981-45-8; 9, 115981-46-9; 10, 115981-47-0; 11, 115981-48-1; bpy, 366-18-7; $NiMe_2$(bpy), 32370-42-6; $NiEt_2$(bpy), 15218-76-5; $NiMe_2$(dpe), 31387-22-1; $PeMe_2$(dpe), 63455-39-0; $HOCH(CF_3)_2$, 920-66-1; $HOCH_2CF_3$, 75-89-8; $HOCH(CF_3)C_6H_5$, 340-04-5; HSC_6H_5, 108-98-5; HSC_6H_4-*p*-CH_3, 106-45-6; CH_4, 74-82-8; C_2H_4, 74-85-1; C_2H_6, 74-84-0; $CF_3COC_6H_5$, 434-45-7; $CH_3COOCH(CF_3)_2$, 6919-79-5; $CH_3CH_2COOCH(CF_3)_2$, 24499-62-5; $CH_3COSC_6H_5$, 934-87-2; $CH_3COSC_6H_4$-*p*-CH_3, 10436-83-6; $CH_3COOCH(CF_3)C_6H_5$, 84194-69-4; $CH_3COOCH_2CF_3$, 406-95-1.

Preparation of "Unnatural" Tellurium Analogues of Naturally Occurring Chromones and Flavones. The Control of Ipso vs Ortho Acylation, Selective Demethylation, and Olefin-Forming Condensation Reactions in Benzo[*b*]tellurapyranones

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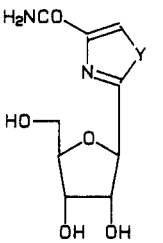
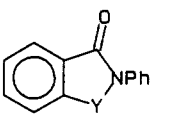
Several factors controlling the intramolecular acylations of β-(arylchalcogeno)cinnamoyl chlorides were examined. Aryltelluro groups were more highly activated toward electrophilic attack than the corresponding arylthio and arylseleno groups. Tellurium analogues of several naturally occurring, highly oxygenated chromones and flavones were prepared including eugenin (2-methyl-5-hydroxy-7-methoxy-4*H*-1-benzo[*b*]pyran-4-one), techtochrysin (2-phenyl-5-hydroxy-7-methoxy-4*H*-1-benzo[*b*]pyran-4-one), dimethylapigenin [2-(4-methoxyphenyl)-5-hydroxy-7-methoxy-4*H*-1-benzo[*b*]pyran-4-one], and trimethylluteolin [2-(3,4-dimethoxyphenyl)-5-hydroxy-7-methoxy-4*H*-1-benzo[*b*]pyran-4-one]. These compounds were prepared from the corresponding 5-methoxy-4*H*-1-benzo[*b*]tellurapyran-4-ones by reaction with boron trifluoride etherate to give difluoroboronate complexes of the 4*H*-1-benzo[*b*]tellurapyran-4-ones by demethylation at the 5-position and difluoroboronate complexation at the 5-oxo substituent and the 4*H*-1-benzo[*b*]tellurapyran-4-one carbonyl oxygen. The difluoroboronate complexes were isolable and represent novel heterocyclic structures. 5-Methoxy-4*H*-1-benzo[*b*]tellurapyran-4-thione (**36**) formed difluoroboronate complex **37** upon treatment with boron trifluoride etherate. Hydrolysis of the difluoroboronates gave the phenolic 5-hydroxy-4*H*-1-benzo[*b*]tellurapyran-4-ones. The difluoroboronate complex **34a**, bearing a 2-methyl substituent, was activated toward condensation reactions of the 2-methyl substituent with various aldehydes and ketones to give styryltellurachromones **38–41** allowing synthetic entry to the hormothamnione (**6**) skeletal framework. In 2-methyl-4*H*-1-benzo[*b*]tellurapyran-4-ones lacking a 5-methoxy substituent, the 2-methyl substituent was activated toward condensation reactions by reaction with ethyl fluorosulfonate. 2-Methyl-4-ethoxy-7-methoxy-4*H*-1-benzo[*b*]tellurapyrylium fluorosulfonate (**44**) reacted with various aldehydes and ketones to give styryl-4*H*-1-benzo[*b*]tellurapyrylium salts **45–48**. Both the difluoroboronate complexes and the 4-ethoxy-4*H*-1-benzo[*b*]tellurapyrylium salts could be hydrolyzed to the corresponding styrylchromones. 2-Methyl substituents in 4*H*-1-benzo[*b*]tellurapyrylium species were much more reactive in condensation reactions than the corresponding 4*H*-1-benzo[*b*]pyrylium species.

The biological activity of heterocyclic systems containing the heavier chalcogen atoms selenium and tellurium have been little explored. The recent literature contains examples of heterocyclic systems in which the heavier chalcogens impart a biological activity not observed with the oxygen and/or sulfur analogues. Tiazofurin [**1**, 2-(β-D-ribofuranosyl)-thiazole-4-carboxamide][1] and selenazofurin [**2**, 2-(β-D-ribofuranosyl)selenazole-4-carboxamide][2] have been shown to be effective antitumor agents in animals. Selenazofurin has been shown to possess broad-spectrum antiviral activity in cell culture experiments, as well.[3] The oxazole analogue **3** does not display such biological activity. 2-Phenyl-1,2-benzisoselenazol-3(2*H*)-one (**4**, ebselen) exhibits GSH-peroxidase-like activity in vitro while its sulfur analogue, **5**, is inactive.[4]

We have been interested in developing synthetic routes to selenium and tellurium analogues of the naturally occurring chromones and flavones in order to compare the effects of chalcogen substitution on biological activity. The chromones, flavones, pyranones, and related compounds are widespread in the plant kingdom from algae[5] to conifers.[6] Flavones and chromones have been found to be



1, Y=S
2, Y=Se
3, Y=O



4, Y=Se
5, Y=S

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