Preparation of Nickel Complexes with η^2-Coordinated Fluorinated Ketones from Dialkylnickel Complexes

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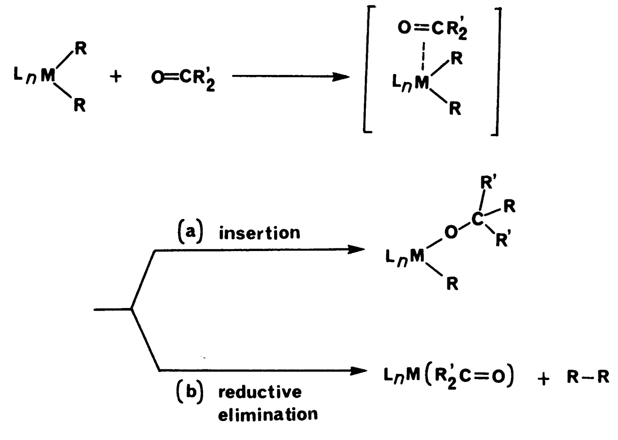
Synopsis. Reactions of hexafluoroacetone and 2,2,2-trifluoroacetophenone with dialkylnickel complexes cause extrusion of the alkyl ligands to give nickel complexes having an η^2-coordinated ketone and an auxiliary ligand such as bpy (2,2′-bipyridine) or dpe (1,2-bis(diphenylphosphino)ethane).

In comparison to a rich variety of η^2-olefin-coordinated transition metal complexes,[1] examples of η^2-ketone-coordinated transition metal complexes are still scarce.[2–5] We report here preparation and characterization of new ketone-coordinated nickel complexes derived from dialkylnickel complexes by reactions with fluorinated ketones.

Ketones with electron-withdrawing groups may cause two types of reactions with transition metal alkyls or hydrides. One is insertion of the carbonyl group in ketones into a metal–alkyl or metal–hydrogen bond to give transition metal alkoxides and the other is ketone coordination which induces reductive elimination of transition metal alkyls or hydrides. A similar effect of olefins with electron-withdrawing groups to promote reductive elimination of dialkylnickel complexes is well known.[6]

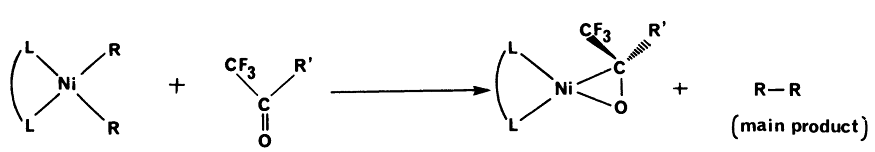


In our previous communication we have observed facile insertion of the carbonyl group in hexafluoroacetone and 2,2,2-trifluoroacetophenone into a metal–hydrogen bond of cobalt, ruthenium and rhodium hydride complexes to give stable alkoxides of these late transition metals.[7]

In the course of our recent study on the chemistry of nickel and palladium alkoxide complexes,[8] we examined reactions of fluorinated ketones with dialkyl nickel(II) complexes. We observed extrusion of the alkyl groups and formation of nickel complexes with the fluorinated ketones bonded in a side-on manner to the nickel center. Some of the ketone-coordinated nickel complexes prepared in the present study by treatment of dialkylnickel complexes with the fluorinated ketones have been previously prepared by displacement of olefin or tertiary phosphine ligands coordinated to Ni(0) center.[2–5] The present method provides an alternative route to the ketone-coordinated complexes, which have attracted less attention than the olefin-coordinated complexes.

Results and Discussion

Dialkylnickel complexes, $NiMe_2(bpy)$, $NiEt_2(bpy)$, and $NiMe_2(dpe)$ (dpe=1,2-bis(diphenylphosphino)ethane), react smoothly with hexafluoroacetone to give $Ni(\eta^2\text{-}(CF_3)_2CO)(bpy)$ **1** and $Ni(\eta^2\text{-}(CF_3)_2CO)(dpe)$ **3**. The reaction of $NiMe_2(dpe)$ with the fluorinated ketone gives mixtures of CH_4 and C_2H_6 as gaseous products, while similar reactions of $NiR_2(bpy)$ (R=Me, Et) give reductive elimination products R–R exclusively. Complexes **1** and **3** have been prepared from reactions of the ketone with $Ni(cod)_2$ (bis(1,5-cyclooctadiene)nickel) in the presence of the auxiliary ligands, bpy and dpe, respectively.[4] The products obtained in the present study show the IR spectra almost identical to those in the literature.[4] A similar reaction of $NiEt_2(bpy)$ with 2,2,2-trifluoroacetophenone gives a nickel–ketone complex $Ni(\eta^2\text{-}CF_3COPh)(bpy)$ **2** with



R = Me, Et.

1 L‿L = bpy, R' = CF_3 ;

2 L‿L = bpy, R' = Ph ;

3 L‿L = dpe, R' = CF_3 ;

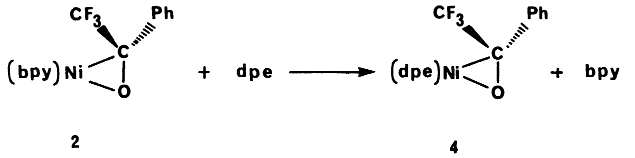
4 L‿L = dpe, R' = Ph .

Table 1. Reactions of Fluoro Ketones with Dialkylnickel Complexes

NiR_2L_2 (mmol)	Fluoro ketone (mmol)	Conditions[a]		Products (Yield/%)[b]	
		Temp	Time		
$NiMe_2(bpy)$ (0.36)	CF_3COCF_3 (0.36)	25 °C	1 h	C_2H_6 (92)	**1** (62)
$NiEt_2(bpy)$ (0.40)	CF_3COCF_3 (0.40)	25 °C	1 h	C_2H_6 (2), C_4H_{10} (85)	**1** (77)
$NiEt_2(bpy)$ (0.42)	CF_3COPh (0.42)	40 °C	1 h	C_4H_{10} (86)	**2** (63)
$NiMe_2(dpe)$ (0.40)	CF_3COCF_3 (1.00)	40 °C	10 h	CH_4 (23), C_2H_6 (42)	**3** (53)
$NiMe_2(dpe)$ (0.42)	CF_3COPh (2.00)	50 °C	18 h	CH_4, C_2H_6[c]	**4** (23)

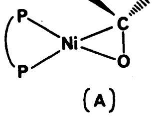
a) Reactions were carried out in THF under reduced pressure. b) Yields by GC for gaseous products. c) The formation was confirmed by GC, but the yields were not measured.

evolution of C_4H_{10}. Conversion of $NiMe_2(dpe)$ to $Ni(\eta^2\text{-}CF_3COPh)(dpe)$ **4** requires more severe conditions. Stirring a THF solution of $NiMe_2(dpe)$ with CF_3COPh for 18 h at 50 °C gave **4** in a 23% yield. Complex **4** can be independently prepared by reactions of the CF_3COPh-coordinated nickel complex with bipyridine ligand, **2**, with an equimolar amount of dpe in a higher yield. In general, dpe coordinates to a nickel center more tightly than bpy, and $NiMe_2(bpy)$ undergoes a facile ligand exchange with dpe to give $NiMe_2(dpe)$.[9] Products of these reactions are summarized in Table 1.

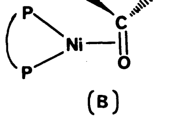


New complexes **2** and **4** obtained in these reactions were characterized by IR and NMR spectroscopy and elemental analysis as well as chemical reactions. IR spectrum of **2** shows a ν(C–F) band at 1140 cm^{-1} and a ν(C–O) band at 1080 cm^{-1}, the latter band being shifted by ca. 650 cm^{-1} lower than that of the uncoordinated ketone. ^{1}H NMR spectrum of **2** shows signals only in the aromatic hydrogen region, indicating the absence of alkyl ligand in the complex. Complex **2** reacts with an equimolar amount of I_2 to give 2,2,2-trifluoroacetophenone (83%) and $NiI_2(bpy)$.

The ^{1}H NMR of complex **4** shows signals due to hydrogens of dpe ligand and of the phenyl group in the coordinated ketone. $^{31}P\{^1H\}$ NMR spectrum shows two doublet signals, each of which is split into a quartet due to coupling with three fluorine atoms (see Experimental). $^{13}C\{^1H\}$ NMR spectrum of **4** shows signals due to the carbonyl carbon atom at δ=79.42 as a doublet of quartets by coupling with three fluorine and one phosphorus nuclei. The low value of the chemical shift of the signal and the low frequency of the ν(C–O) vibration in the IR spectrum suggest that complex **4** may be better formulated as a σ-bonded Ni(II) oxametallacycle (A) rather than a π-bonded Ni(0) complex (B).[10] These spectroscopic features indicate that complex **4** has a square planar coordination with a carbon, an oxygen, and two phosphorus ligating atoms around the nickel center.[11]



(A)



(B)

Experimental

All manipulations were carried out under nitrogen or argon atmosphere. Dialkylnickel complexes were prepared by the methods in the literature.[12,13] Hexafluoroacetone was purchased from PCR Inc. and introduced to the reaction flask by means of a vacuum line technique.[14] 2,2,2-Trifluoroacetophenone was purchased from Tokyo Kasei Co., Ltd.

Preparation of the Complexes 1, 2, and 3. To a THF (3 cm^3) solution of diethyl(bipyridine)nickel (110 mg, 0.40 mmol), hexafluoroacetone (66 mg, 0.40 mmol) was added at room temperature. Complex **1** was immediately precipitated as a red solid which was filtered, washed with hexane several times, and dried in vacuo (113 mg, 77%).

Complexes **2** and **3** were prepared analogously.

Complex 2: Mp 147—150 °C (decomp); ^{1}H NMR (CD_3COCD_3) δ=7.7—8.9 (m, $C_{10}H_{10}N_2$ and C_6H_5); ^{19}F NMR 12.6 ppm (downfield from external CF_3COOH, s). Found: C 54.7; H 3.1; N 6.9%. Calcd for $C_{17}H_{13}F_3N_2ONi$: C 54.2; H 3.4; N 7.4%.

Preparation of 4. A toluene (5 cm^3) solution of **2** (180 mg, 0.47 mmol) and dpe (90 mg, 0.47 mmol) was stirred for 1 h at room temperature to cause precipitation of a yellow solid of **4**, which was filtered and recrystallized from THF (52%).

Complex **4** was also obtained in a lower yield from the reaction of 2,2,2-trifluoroacetophenone with $NiMe_2(dpe)$ at 50 °C for 18 h.

Complex 4: Mp 153—156 °C (decomp); ^{1}H NMR (C_6D_6) δ=1.6—2.1 (4H, m, CH_2) and 7.0—8.3 (25H, m, C_6H_5); ^{31}P NMR (CD_2Cl_2) 58.16 ppm (downfield from external PPh_3 qd, J_{P-F}=4 Hz, J_{P-P}=51 Hz) and 51.56 ppm (qd, J_{P-F}=13 Hz, J_{P-P}=51 Hz); ^{19}F NMR (CD_2Cl_2) 12.8 ppm (downfield from external CF_3COOH, dd); ^{13}C NMR (CD_2Cl_2) δ=28.51 (dd, CH_2, J_{P-C}=18, 11 Hz), 24.40 (dd, CH_2, J_{P-C}=29, 11 Hz) 79.42 (qd, CO, J_{P-C}=27 Hz, J_{C-F}=33 Hz), and 117.10 (q, CF_3, J_{C-F}=292 Hz). Found: C 64.4; H 4.5%. Calcd for $C_{34}H_{29}F_3OP_2Ni$: C 64.7; H 4.6%.

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