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Preparation of Alkylnickel(II)-Phosphine Complexes by Reactions of Ni(acac)$_2$ with Alkylaluminums in the Presence of Tertiary Phosphine

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Synopsis. Four new alkylnickel(II)-phosphine complexes, NiR$_2$(PR'$_3$)$_2$ (R=CH$_3$, C$_2$H$_5$; PR'$_3$=triethylphosphine (PEt$_3$), tributylphosphine (PBu$_3$), 1,2-bis(diphenylphosphino)ethane(dpe)) and Ni(CH$_3$)(acac)(PEtPh$_2$) (PEtPh$_2$=ethyldiphenylphosphine), have been prepared by reactions of Ni(acac)$_2$ with AlR$_2$(OC$_2$H$_5$) in the presence of phosphine ligands.

Alkylnickel complexes are regarded as intermediates in important catalytic reactions such as isomerization and oligomerization of olefins and dienes.1) Although several groups have been engaged in research on the preparation and chemical properties of alkylnickel complexes,1a,2) the number of well-characterized alkylnickel complexes is still not large. We now report preparation of four new alkylnickel(II) complexes by reactions of Ni(acac)$_2$ (acac=2,4-pentanedionato) with alkylaluminums in the presence of tertiary phosphines (L).

Results and Discussion

Reactions of Ni(acac)$_2$ with AlR$_2$(OEt) below −30 °C in the presence of phosphine ligands give NiR$_2$L$_2$, NiR(acac)L, zero-valent nickel complexes, or Ni–Al binary complexes depending on the alkylaluminum and phosphine ligand employed,

$$\mathrm{Ni(acac)_2 + AlR_2(OEt) + L \xrightarrow[\mathrm{Et_2O}]{-30\,^{\circ}\mathrm{C\ or\ below}} NiR_2L_2,\ NiR(acac)L,\ NiL_4,\ Ni\text{–}Al\ complex} \quad (1)$$

R	L	Product
Me	PEt$_3$	NiMe$_2$(PEt$_3$)$_2$ **1**
Et	PEt$_3$	Ni-Al binary complex **2**
Me	PBu$_3$	NiMe$_2$(PBu$_3$)$_2$ **3**
Me	dpe	NiMe$_2$(dpe) **4**
Et	dpe	NiEt$_2$(dpe)·(Et$_2$O)$_{0.5}$ **5**
Me	PEtPh$_2$	NiMe(acac)(PEtPh$_2$) **6**
Me	PMePh$_2$	Ni(PMePh$_2$)$_4$ **7**
Me	P(OEt)$_3$	Ni-Al binary complex **8**
Me or Et	P(OPh)$_3$	Ni(P(OPh)$_3$)$_4$ **9**

Me=CH$_3$, Et=C$_2$H$_5$, Bu=*n*-C$_4$H$_9$, Ph=C$_6$H$_5$, acac=2,4-pentanedionato, dpe=1,2-bis(diphenylphosphino)ethane

Among the complexes listed above, the dimethylnickel complex, **4**,2g) and zero-valent nickel complexes, **7**3) and **9**,4) have been prepared by other researchers through different pathways. The comparison of the products obtained using the phosphine ligands listed above reveals that subtle differences in electronic and steric effects of the phosphine ligands exerts a pronounced influence on the course of alkylation reaction. Properties of the complexes are described below.

NiR$_2$L$_2$: Dialkylnickel(II) complexes **1**, **3**, and **5** have relatively low thermal stabilities, the thermal decomposition proceeding gradually even at room temperature in a solid, with evolution of CH$_4$ and C$_2$H$_6$ from the dimethyl complexes and C$_2$H$_6$ and C$_2$H$_4$ from **5**. The absence of butane in the thermolysis product of **5** contrasts with the results of thermolysis of NiEt$_2$(2,2'-bipyridine), which liberates mainly butane during the thermolysis.2a,2c) The low thermal stabilities of the dialkyl complexes not only require the researchers to carry out the preparation and workup below −30 °C, but also prevent characterization of the complexes by microanalysis. Thus characterization of NiR$_2$L$_2$ was performed mainly on the basis of macroanalysis of Ni, the amount of RH released on acidolysis with H$_2$SO$_4$, and spectroscopy (IR and NMR). As for **3**, we characterized it by the amount of RH released on the acidolysis and by ^{1}H NMR spectroscopy, due to its high instabilities. As for **1** and **5**, their chemical reactivities with active hydrogen compounds5) and CO6) support the proposed structures. All the dialkyl complexes are free of aluminum, as proved by qualitative analyses.

Table 1 summarizes spectroscopic data of the new complexes prepared by Reaction 1. IR spectra show signals due to R and L ligands. In the ^{1}H NMR spectrum, the dimethyl complexes **1** and **3** give rise to the Ni–CH$_3$ signal at higher magnetic field than TMS; similar results were reported for dimethylnickel complexes.2) The triplet pattern (J(^{1}H–^{31}P)=8 Hz) of the Ni–C$\underline{\mathrm{H}}_3$ signal of **1** at −70 °C reveals that **1** has a *trans* configuration. The ^{1}H–^{31}P spin-spin coupling, however, is not observable at −60 °C or above, presumably due to rapid exchange between PEt$_3$ in **1** and free PEt$_3$ partly liberated from **1**. The Ni–C$\underline{\mathrm{H}}_2$– signal of **5** is located at higher magnetic field than the Ni–CH$_2$–C$\underline{\mathrm{H}}_3$ signal, as is found for NiEt$_2$(2,2'-bipyridine).2b)

NiMe(acac)(PEtPh$_2$) **6**: Complex **6** has higher thermal stabilities than the dialkylnickel complexes. The IR spectrum of **6** shows ν(C=O) bands at 1590 and 1520 cm^{-1} characteristic of a bidentate acac ligand. ^{1}H-NMR spectrum shows two singlets for the two CH$_3$ groups of the acac ligand, indicating **6** has a

TABLE 1. IR AND NMR DATA OF NEW ALKYLNICKEL(II) COMPLEXES

Complex	IR ν/cm^{-1}	^{1}H-NMR		
		Solvent	Temp/°C	Chemical shift δ[a]
1	2970 1160 770	C_6H_6	25	-0.70(6H, s, br, Ni-CH_3) 1.04(18H, m, br, P-CH_2-$C\underline{H}_3$) 1.52(12H, q, 7 Hz, P-$C\underline{H}_2$-)
		Toluene-d_8	-70	-0.60(6H, t, 8 Hz, Ni-$C\underline{H}_3$) 0.96(18H, qui, 8 Hz, P-CH_2-$C\underline{H}_3$) 1.40(12H, m, br, P-$C\underline{H}_2$-)
3		Pyridine	-30	-0.50(6H, s, br, Ni-CH_3) 1.0(18H, t, 6 Hz, P$(CH_2)_3C\underline{H}_3$) 1.5—1.9(36H, m, P$(C\underline{H}_2)_3$)
5	2900 2810 1430 695	Pyridine	25	0.48(4H, q, 8 Hz, Ni-$C\underline{H}_2$-) 1.55(6H, t, 8 Hz, Ni-CH_2-$C\underline{H}_3$) 2.2(4H, P-$C\underline{H}_2$) 4.2(2H, O($C\underline{H}_2CH_3)_2$)
6	2950 1590 1520 1390	C_6H_6	25	-0.10(3H, s, Ni-$C\underline{H}_3$) 0.9—1.3(3H, m, P-CH_2-$C\underline{H}_3$) 1.60(3H, s, acac-$C\underline{H}_3$) 1.80(3H, s, acac-$C\underline{H}_3$) 1.7—2.1(2H, m, P-CH_2-) 5.3(1H, s, acac-CH)

a) s: Singlet, t: triplet, q: quartet, qui: quintet, m: multiplet, br: broad.

square planar structure like that known for NiEt(acac)(PPh_3)[7] and NiR(acac)(PCy_3).[8]

Binary Complexes Containing Nickel and Aluminium Components: The Ni(acac)$_2$/AlEt$_2$(OEt)/PEt$_3$ and Ni(acac)$_2$/AlMe$_2$(OEt)/P(OEt)$_3$ systems afford yellow crystalline complexes. The complexes contain both nickel and aluminum. Electric conductivities of solutions of the complexes reveal that they have ionic structures. Their IR spectra show characteristic bands of aluminate anion at *ca.* 650 cm^{-1}. ^{1}H NMR spectra show signals not only due to R groups and L ligands but also one due to Al-O$C\underline{H}_2CH_3$ group at about 3.7 ppm. These results suggest that the complexes have ionic structures like $[CoR_2(2,2'\text{-bipyridine})_2]^+[AlR_4]^-$, which were isolated from Co(acac)$_3$/AlR$_3$/2,2′-bipyridine systems.[9] The ^{1}H NMR spectrum of **8** is consistent with the structure: $[NiMe(P(OEt)_3)_3]^+[AlMe_3OEt]^-$.

Experimental

General. Manipulation of complexes, analysis, and measurement of IR and NMR spectra were carried out as reported.[2a–2c,5–7]

Preparation of Complexes. *NiR_2L_2*: AlMe$_2$(OEt) (13 cm^3, 100 mmol) was added to a mixture of Ni(acac)$_2$ (6.0 g, 23 mmol) and PEt$_3$ (8.0 cm^3, 54 mmol) in Et$_2$O (60 cm^3) at −60 °C. Stirring the mixture at −30 °C for 10 h gave a brown homogeneous solution, which was condensed to *ca.* 20 cm^3. Cooling the solution to −78 °C gave brown needles (6.1 g, 84%). The brown needles were separated by filtration, washed repeatedly with Et$_2$O at −78 °C, and recrystallized from Et$_2$O to obtain 4.4 g (60%) of **1**. Mp 35 °C (dec). Found: Ni, 18.0%. Calcd for NiMe$_2$(PEt$_3$)$_2$: Ni, 18.1%. CH$_4$/**1** (acidolysis with H$_2$SO$_4$) = 1.8.

Complex **3** was obtained analogously from a mixture of Ni(acac)$_2$ (5.0 g, 19 mmol), PBu$_3$ (9.3 cm^3, 37 mmol), and AlMe$_2$(OEt) (11 cm^3, 88 mmol); the reaction time was 5 h and the temperature was −40 °C; yield = 14%. Mp 0 °C (dec): CH$_4$/**3** (acidolysis) = 2.0.

AlEt$_2$(OEt) (24 cm^3, 150 mmol) was added to a mixture of Ni(acac)$_2$ (6.5 g, 25 mmol) and dpe (10 g, 25 mmol) in 100 cm^3 of Et$_2$O at −50 °C. Stirring the mixture for 10 h at −20 °C gave a yellowish orange precipitate, which was separated by filtration, washed repeatedly with Et$_2$O, and dried in a vacuum to obtain **5** (yield = 12%). Mp 50 °C (dec). Found: Ni, 10.3%. Calcd for NiEt$_2$(dpe)(Et$_2$O)$_{0.5}$: Ni, 10.6%. C$_2$H$_6$/**5** (acidolysis) = 2.0.

Complex **4** was prepared analogously and characterized by comparing its NMR data with those reported in the literature.

*NiMe(acac)(PEtPh$_2$) **6***: AlMe$_2$(OEt) (14 cm^3, 110 mmol) was added to a mixture of Ni(acac)$_2$ (7.3 g, 28 mmol) and PEtPh$_2$ (14 cm^3, 57 mmol) in Et$_2$O (60 cm^3) at −70 °C. Stirring the mixture at −40——25 °C for 10 h gave a brown solution and a yellow precipitate. After condensing the solution to *ca.* 20 cm^3, the yellow precipitate was separated by filtration, washed with Et$_2$O, and dried in vacuum to yield 3.5 g (35%) of **6**. Mp 80 °C (dec). Found: C, 62.1; H, 6.5; Ni, 15.2%. Calcd for NiMe(acac)(PEtPh$_2$): C, 62.3; H, 7.0; Ni, 15.1%. CH$_4$/**6** (acidolysis) = 1.0.

Ni–Al Complexes: AlMe$_2$(OEt) (5.0 cm^3, 44 mmol) was added to a mixture of Ni(acac)$_2$ (2.6 g, 10 mmol) and P(OEt)$_3$ (3.4 cm^3, 20 mmol) in Et$_2$O (45 cm^3) at −50 °C. Stirring the mixture at −10 °C for 10 h gave a brown hoogeneous solution, which was condensed to *ca.* 30 cm^3. Coolming the solution to −78 °C gave transparent brown prisms. After washing with a mixture of Et$_2$O and hexane, the complex was recrystallized from Et$_2$O to yield 2.0 g of **8**. ^{1}H NMR (acetone-d_6, −60 °C): $\delta = -0.98$ (9H, s, Al-$C\underline{H}_3$), −0.90 (3H, s, Ni-CH_3), 1.18 (3H, Al-O$CH_2C\underline{H}_3$), 1.30 (27H, t, 7 Hz, P-O$CH_2C\underline{H}_3$), 3.70 (2H, q, 7 Hz, Al-O$C\underline{H}_2CH_3$), 4.20 (18H, q, 7Hz, P-O$C\underline{H}_2CH_3$). Equivalent conductivity: 35% of the equivalent conductivity of KI in acetone at −72 °C. Complex **2** was prepared analogously.

Ni(0)-Complexes: Complexes **7** and **9** were prepared under similar conditions to those adopted to prepare **1**—**6** and **8**. They were characterized by elemental analysis.

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