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Preliminary communication

PHENYL(ACETYLACETONATO)NICKEL(II) COMPLEXES WITH TERTIARY PHOSPHINE LIGANDS

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Summary

Preparation and NMR spectra of novel phenyl(acetylacetonato)nickel(II) complexes with phosphines as ligands are reported.

Employment of alkylaluminum compounds in combination with transition metal acetylacetonates in the presence of appropriate ligands provides a convenient route to various isolable alkyl-transition metal complexes [1]. This method often shows advantages in its ease of separation of products as compared to conventional methods utilizing transition metal salts and alkylating agents such as Grignard and alkyllithium reagents where removal of metal salts formed sometimes presents troublesome problems. The reaction between the transition metal acetylacetonate and an alkylaluminum compound obviously proceeds through an exchange reaction of the acetylacetonato group with the alkyl substituent, and some intermediate transition metal complexes having both alkyl and acetylacetonato groups have been isolated [2-4]. However, the preparation of a corresponding aryl-transition metal complex has not been reported. We report here the preparation of novel phenyl(acetylacetonato)nickel(II) complexes with tricyclohexylphosphine (PCy_3), triphenylphosphine, and triethylphosphine. Unlike aryl complexes of the type *trans*-$[NiArX(PR_3)_2]$ or *trans*-$[NiAr_2(PR_3)_2]$, the stability of which was ascribed to an *ortho*-substitution effect [5], the phenyl complexes obtained in the present work exhibit marked stability even without *ortho*-substituents. The acetylacetonato chelate may be playing an important role in the stabilization of the complex with a transition metal-to-carbon σ-bond.

Treatment of nickel(II) acetylacetonate with an equimolar amount of triphenylaluminum etherate ($AlPh_3 \cdot Et_2O$)* in the presence of a slight

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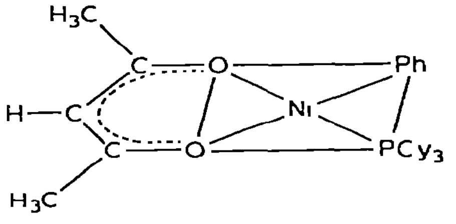
*Triphenylaluminum etherate, $AlPh_3 \cdot Et_2O$, was prepared from PhMgBr and $AlCl_3$ [6]. Anal. Found: Al, 8.37. $C_{22}H_{25}OAl$ calcd.: Al, 8.12%. On acidolysis, benzene (104% on the basis of the formula) and diethyl ether (79%) were detected.

excess of PCy_3 in diethyl ether at −20° under nitrogen yielded [NiPh(acac)(PCy_3)] (I) (yield 55%). This can be recrystallized from tetrahydrofuran to give a yellow crystalline powder which is considerably stable to air. M.p. under nitrogen: 155.5-158.0° (dec.). (Found: C, 68.0; H, 8.3; Ni, 11.7. $C_{29}H_{45}O_2PNi$ calcd.: C, 67.6; H, 8.8; Ni, 11.4%). On acidolysis of I by dry HCl, formation of benzene (100% on the basis of the above formula) and acetylacetone (84%) was detected by means of GLC. The ^1H NMR (Table 1) and IR spectra of the complex also were consistent with the square planar structure.



(I)

Similarly a brown complex, [NiPh(acac)(PPh_3)] (II), was obtained by the use of PPh_3 in place of PCy_3 (yield 40%). Although this compound, being very sensitive to air, has not been obtained analytically pure, the ^1H NMR (Table 1) and IR spectra of the complex recrystallized from tetrahydrofuran were consistent with the above formula.

When nickel acetylacetonate was allowed to react with $AlPh_3 \cdot Et_2O$ in the presence of 2 equivalents of PEt_3 in diethyl ether at room temperature, a five-coordinate phenyl complex, [NiPh(acac)(PEt_3)$_2$] (III), was obtained in a yield of 52%. This was recrystallized from dichloromethane and diethyl ether in the presence of PEt_3 to give red crystals, m.p. under argon: 63.0-65.5°. Found: Ni, 12.8. $C_{23}H_{42}O_2P_2Ni$ calcd.: Ni, 12.5%). Acidolysis of

TABLE 1

^1H NMR SPECTRA OF THE PHENYL COMPLEXES OF NICKEL(II) [a,b]

Compound		[NiPh(acac)(PCy_3)]	[NiPh(acac)(PPh_3)]	[NiPh(acac)(PEt_3)$_2$]
Solvent		C_6D_6	C_6D_6	CD_2Cl_2
acac	CH_3	8.25 (s)	8.28 (3, s)	8.20 (6, s)
		8.30 (s)	8.62 (3, s)	
	CH	4.60 (1, s)	4.70 (1, s)	4.60 (1, s)
PhNi	*ortho*	1.8-2.0 (2, m)	2.2-2.6 (m) [c]	2.5-2.7 (2, m)
	meta and *para*	2.6-2.9 (3, m)	3.1-3.2 (3, m)	3.1-3.3 (3, m)
PR_3		7.7-9.1 (three blocks of m)	2.2-2.6 (m) [c] (*ortho*-Ph)	8.86 (18, t) (CH_3)
			2.9-3.1 (9, m) (*meta* and *para*-Ph)	7.4 (12, (br), s) (PCH_2)

[a] 100 MHz at 25°, tetramethylsilane as an internal standard. [b] Chemical shifts are in τ values. Figures in parentheses are peak intensity and multiplicity: s, singlet; t, triplet; m, multiplet; and (br), broad. [c] *ortho* protons of Ph—Ni and PPh_3 are not distinguishable. Overall relative peak intensity of this area was 8.

III with dry HCl yielded benzene (100%) and acetylacetone (95%) as analyzed by GLC. The ^{1}H NMR spectrum of III (Table 1) in which methyl protons of acac are equivalent suggests that two phosphine ligands occupy *cis* positions of square pyramidal configuration with an apical phenyl group. The possibility, however, of a bipyramidal configuration with two phosphines at apical positions cannot be excluded. Variable temperature NMR spectra of III at room temperature and —70° showed no indication of splitting of the methyl resonances in the acetylacetonato ligand. Further ^{1}H and ^{31}P NMR studies are in progress.

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