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Preliminary communication

Synthesis of new complexes containing Al–X–Ni bonds: Reactions of dicyclooctadienylnickel(0) with Me_2AlSPh, Et_2AlPPh_2 and $(Me_2AlSCH_2)_2$

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Recently, several new complexes containing aluminium–transition metal bonding have been described, including $[Fe_2(\pi\text{-}C_5H_5)_2(CO)_4 \cdot 2AlEt_3]$ [1], $[\pi\text{-}C_5H_5Mo(CO)_3 \cdot AlMe_3]$ [2], $[(\pi\text{-}C_5H_5)_2WH_2 \cdot AlMe_3]$ [3], $[\pi\text{-}C_5H_5(CO)_3W(AlR_2)]$ [4], $[\pi\text{-}C_5H_5Ti(Et_2AlC_5H_4)]_2$ [5], and $[(R_2Al)Mo(\pi\text{-}C_5H_5)(CO)_2L]$ [6]. In these complexes, the Lewis acidity of the aluminium atom is satisfied either by the oxygen atom of the basic ligand (CO) or by a transition metal having a non-bonding electron pair. In contrast, the reactions of organoaluminium compounds containing Al–hetero atom (N,O,S,P) bonds described in our previous paper[7], suggest that R_2AlSPh or R_2AlPPh_2 should act as a "basic ligand" toward appropriate transition metals.

In this communication, we report the synthesis of the complexes containing the new linkage (Al–X–Ni), which was produced according to equation (1), in which COD denotes cyclooctadiene.

$$2\,R_2AlX + Ni(COD)_2 \longrightarrow (R_2AlX)_2Ni(COD) + COD \qquad (1)$$

(I) $R = Me$, $X = SPh$
(II) $R = Et$, $X = PPh_2$
(III) $(R_2AlX)_2 = (Me_2AlSCH_2)_2$

All reactions were carried out under dry argon. Dimethylaluminium phenylthiolate (0.696g, Me_2AlSPh (m.p. 216°, dec.) NMR in benzene: τ 10.15) in benzene (10 ml) was added dropwise to a benzene solution of the freshly prepared $Ni(COD)_2$ (0.611g) cooled to 0–5°. The colour of the solution changed immediately from yellow to black. The small amount of black precipitate was removed after the mixture had been kept at 15° for 4h, and the filtrate was concentrated under reduced pressure to give 92% of free cyclooctadiene, along with a dark-brown solid (I) (0.562g), which was unstable in air and on heating. This solid was identified as $(Me_2AlSPh)_2Ni(COD)$ by analysis (Found: active methyl groups (Me*), 4.15; Al, 11.93; and Ni, 11.30. Calcd.: Me*, 4.00/mole; Al, 11.40; Ni, 11.78%). IR(Nujol); 1580m cm^{-1}. The NMR spectrum showed three broad peaks, centred at τ 10.2, 7.8 and 4.9.

Product(II) was obtained in low yield (29%) from the reaction between $Ni(COD)_2$ and Et_2AlPPh_2, and was a fairly stable brown solid (Found: Et*, 3.69; Ni, 7.43. Calcd.: Et*, 4.00/mole; Ni, 8.30%). The NMR spectrum showed broad but clear signals at τ 9.10, 8.55, 7.93 and 5.70, in an intensity ratio 2/3/2/1.

Both (I) and (II) were shown to be monomeric in benzene: mol. wt.: I, found 362 (calcd. 373); II, found 669 (calcd. 707).

Bis(dimethylaluminium) ethanedithiolate, $Me_2AlSCH_2CH_2SAlMe_2$, which forms white crystals, m.p. 169–170°, and is slightly soluble in benzene (NMR peaks in benzene: τ 10.25 and 7.29 at 75°) should be a more effective ligand. Treatment with an equimolar amount of $Ni(COD)_2$ gave the expected black solid in 77% yield. This was less stable than the starting materials, and ignited spontaneously in air; analysis showed it to be $(Me_2AlSCH_2)_2Ni(COD)$ (III) (Found: Me*, 3.91; Al, 14.12; Ni, 16.69. Calcd.: Me*, 4.00/mole; Al, 14.48; Ni, 15.73%). Its NMR spectrum could not be measured due to its paramagnetism, which suggests the configuration around the nickel atom in this complex (III) must be tetrahedral. Cryoscopic molecular weight measurements could not be carried out because it is practically insoluble in benzene; this insolublility suggests that it has a polymeric structure.

In contrast to the behaviour of $Ni^0(COD)_2$, $Ni(Acac)_2$ did not react with Me_2AlSPh to give an Al–X–Ni complex, and instead three products(IV)–(VI) were obtained, according to equation (2).

$$2\,Me_2AlSPh + Ni(Acac)_2 \longrightarrow \underset{(IV)}{Me_2Al(Acac)} + \underset{(V)}{Al(Acac)_3} + \underset{(VI)}{[Ni(SPh)_2]_n} \qquad (2)$$

Compound(IV): b.p. ~ 40°/0.6mm Hg, 51% yield, NMR, τ 10.40, 8.40 and 4.96 in benzene. Compound(V): white needle-shaped crystals, m.p. 193–195°, 27% yield based on aluminium, NMR, τ 8.33 and 4.81 in benzene. (VI): red-brown solid, insoluble in benzene, 86% yield based on nickel. (Anal. found: Ni, 20.7. Calcd.: Ni, 21.2%.)

Reaction (2) is reminiscent of reaction (3) which was carried out by Abel *et al.*[8].

$$Me_2Sn(SPh)_2 + Ni^{II}Cl_2 \longrightarrow Me_2SnCl_2 + [Ni(SPh)_2]_{6\text{-}n} \qquad (3)$$

The reaction between $Ni^{II}(\pi\text{-}C_5H_5)_2$ and Me_2AlSPh in benzene solution at 75° for 24 h gave $[Ni(\pi\text{-}C_5H_5)(SPh)]_2$, as black crystals, m.p. 118–123°, in a yield of 16%, along with dimethylaluminium cyclopentadienide; the NMR spectrum of the latter indicates that the Al—cyclopentadienyl bonding is of the σ-type. It could not be obtained pure.

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