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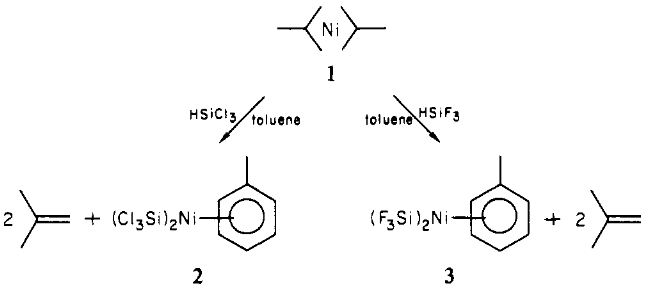
Communications

Conversion of (π-Allyl)nickel Complexes to (π-Arene)nickel Complexes

Sir:

In the past 8 years the only method of preparation of π-arene derivatives of Ni(II) has been through the techniques of metal atom/vapor chemistry.[1,2] We have now discovered a convenient, classical solution-phase procedure that promises to greatly expand the number of different X_2Ni–η^6-arene derivatives available.

We have found that the reaction of diallylnickel or bis(2-methylallyl)nickel with active hydrogen compounds such as $HSiCl_3$ and $HSiF_3$ proceeds smoothly to generate 2 mol of propene (or 2-methylpropene) to produce $(Cl_3Si)_2Ni$ and $(F_3Si)_2Ni$. In the presence of toluene these coordinatively unsaturated Ni(II) derivatives bind in an η^6-fashion to yield $(Cl_3Si)_2Ni(\eta^6$-toluene) and $(F_3Si)_2Ni(\eta^6$-toluene).



Actually reactions of allylnickel derivatives with active hydrogen sources have not been exploited. Our preliminary experiments suggest that this procedure will be general for nickel as well as other metals.

The chemistry of **2** and **3** is being explored. As with other such derivatives of Ni(II),[2] the arene is highly labile, and multiple coordination sites on Ni can be readily made available by loss of the arene. Complex **3** exhibits especially good stability and can even be sublimed.

Procedure. Preparation of Bis(2-methylallyl)nickel (1).[3] To a 2-methylallylmagnesium chloride suspension/solution at 0 °C, prepared from 2-methylallyl chloride (6.6 mL, 6 mmol) and magnesium (1.7 g, 7 mmol) with a piece of iodine as initiator in 100 mL of diethyl ether at 0 °C, was slowly added $NiBr_2$ (5.5 g, 2.5 mmol) over a period of 30 min. The bis(2-methylallyl)nickel (**1**) was formed continuously. After the yellowish mixture was stirred at 0 °C for an additional 2 h, light orange crystalline **1** was separated by slow vacuum distillation at room temperature and was trapped at −30 °C. Complex **1** was dissolved in 30 mL of toluene for the following experiment.

Preparation of (η^6-Toluene)bis(trichlorosilyl)nickel(II) (2). To complex **1** in toluene solution at −196 °C was slowly added $HSiCl_3$ (10 mL, 10 mmol) in 20 mL of toluene solution. The solution was warmed to room temperature during a period of 4 h, resulting in a dark red solution. The solvent was removed under vacuum at room temperature yielding a yellow-orange powder. The solid was washed with pentane (3 × 15 mL) and then dried under vacuum (8.7 g, yield 83% based on $NiBr_2$); mp 138–140 °C (lit.[2] mp 140 °C). The IR and NMR spectra were identical with that of an authentic sample.[2]

Preparation of (η^6-Toluene)bis(trifluorosilyl)nickel(II) (3). Trifluorosilane was prepared from the reaction of $HSiCl_3$ (10 mL, 10 mmol), SbF_3 (53.7 g, 30 mol), and $SbCl_5$ (3 mL, as catalyst) at room temperature for 3 h.[4] The resultant products were distilled through two traps (−93 °C, toluene slush; −130 °C, pentane slush). The first trap condensed $HSiCl_3$, $HSiCl_2F$, and $HSiClF_2$, and the second trap condensed $HSiF_3$ as well as SiH_4 and HCl as side products. The second trap was isolated and evacuated for 30 min at −130 °C (1.0 torr) to remove both side products.

The $HSiF_3$ was distilled onto complex **1** in toluene solution that was frozen with liquid nitrogen. The solution was warmed to room temperature during a period of 8 h, resulting in a light orange solution and a black powder. A light yellow solid precipitated with the black powder upon vacuum removal of solvent. The solid was extracted four times with 15-mL portions of toluene, each portion filtered, and solvent removed again. The resultant light yellow solid was washed with pentane (3 × 5 mL) and then dried under vacuum at room temperature (1.30 g, yield 16% based on $NiBr_2$); mp 95 °C. IR, NMR, and mass spectra matched exactly those reported earlier where **3** was prepared by a metal atom technique.[5]

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Registry No. 1, 12261-14-2; **2**, 80410-01-1; **3**, 88083-21-0; $NiBr_2$, 13462-88-9; $HSiCl_3$, 10025-78-2; $HSiF_3$, 13465-71-9; 2-methylallyl chloride, 563-47-3; diallylnickel, 12077-85-9.

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