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Preliminary communication

REDUCTIVE SUBSTITUTION OF NICKELOCENE; INTERCEPTION OF A MONOHYDRIDO INTERMEDIATE IN THE HYDROGENATION OF 2,3,4,5-TETRAPHENYLCYCLOPENTADIENONE (TETRACYCLONE)

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Summary

Reductive substitution* of nickelocene with tetracyclone affords bis(tetracyclone)nickel(0) (1), η^3-1,2,3,4-tetraphenyl-5-ketocyclopentenylcyclopentadienylnickel (2) and *trans*-1,2,3,4-tetraphenylcyclopenten-1-one-5 (3); evidence is presented that 2 is an intermediate in the formation of 3 from 1.

Cases of interception of intermediates in hydrogenation reactions are rare. Very recently, Astruc and coworkers [1] have provided examples of an alkene-substituted organometallic system where the monohydrogenated alkene portion is electronically stabilized to the extent that it can be isolated and characterized, i.e., the transition metal acts as an electron sink for the extra electron density. Here we report a complementary example of this phenomenon wherein the monohydrido intermediate is likely formed prior to formation of the transition metal complex, i.e., the intermediate is intercepted by the transition metal to produce an isolable complex. In the process two separate displacement of C_5H_5 rings from a metallocene [2] as well as a novel hydride transfer from a complexed C_5H_5 ring are inferred.

When nickelocene and tetracyclone are heated in a sealed thick wall glass tube at 170°C for 30 minutes bis(η^4-tetracyclone)nickel (1) (49.0%), η^3-1,2,3,4-tetraphenyl-5-ketocyclopentenylcyclopentadienylnickel (2) (3.2%) and *trans*-1,2,3,4-tetraphenylcyclopenten-1-one-5 (3) (6.0%) are obtained (Scheme 1) [3]. The identity of known 1 was confirmed by IR, ^{1}H NMR and ^{13}C NMR spectroscopy [4]. Elucidation of the structure of the novel, air sensitive monohydrido nickel complex 2 was made on the basis of its elemental analyses, IR, ^{1}H NMR, ^{13}C

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*For a definition of "reductive substitution" cf. the communication on p. C21—C25.

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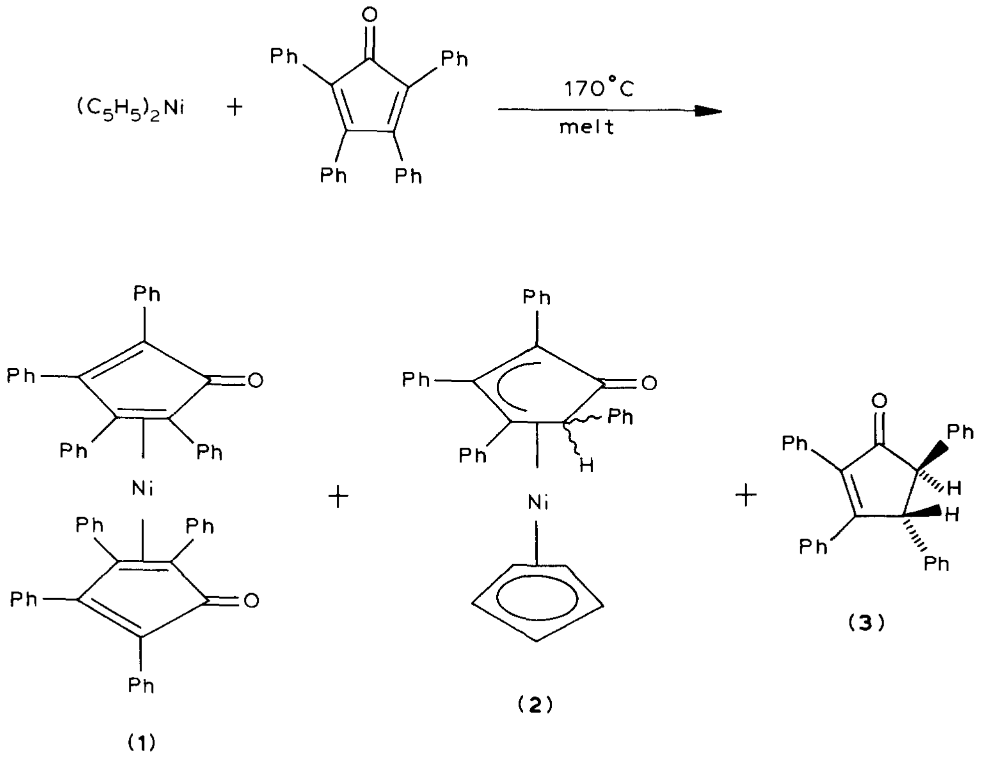

SCHEME 1

NMR and mass spectrum; a compelling piece of evidence for the structural assignment is the observation of molecular weight ions for **2** at 508 and 510 corresponding to the two isotopes of nickel in $Ph_4C_5OHNiC_5H_5$. The structure of the *trans*-2,3-dihydrotetracyclone (**3**) was verified by comparison of its ^1H NMR and physical constants with published data [5].

The isolation of complex **2** is intriguing because of the possibility that **2** may be an intermediate in the reduction of tetracyclone to the dihydro derivative **3**. Treatment of equimolar amounts of **2** and nickelocene under the requisite conditions produced **3** in 62% yield. Thermal decomposition of **2** alone under an inert atmosphere produced **3** in 42% yield. This data suggests that both intra- and inter-molecular hydrogen transfer routes are operating in the production of the dihydro compound **3** from the monohydrido intermediate **2**.

A likely pathway for the formation of intermediate **2** from nickelocene involves first a $\pi \to \sigma$ ($\eta^5 \to \eta^1$) rearrangement of a cyclopentadienyl ring [6] followed by hydride transfer from this electron rich system to the α-carbon of the tetracryclone moiety; the resulting π-allyl system subsequently performs a ligand substitution reaction on nickelocene (involving a second $\eta^5 \to \eta^1$ rearrangement) as first described by Ustynyuk [7]. A second hydrogen transfer reaction can occur interannularly, within **2**, or intermolecularly between **2** and nickelocene to form the ultimate reduction product **3**.

To our knowledge, this is the first demonstration of the reducing capabilities of a cyclopentadienyl ring. Further details of this transformation are being investigated.

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3 Separation of **1**, **2** and **3** was accomplished by chromatography on alumina or silica gel. Rapid chromatography on silica gel afforded improved yields of slightly air-sensitive compound **2**. An analytical sample was isolated in 4.1% yield using this technique: ^{1}H NMR ($CDCl_3$) (δ(ppm)); 4,92s (1) (allylic H of the 5-ketocyclopentenyl ring), 5.28s (5) (C_5H_5), 7.14—7.51m (20) (C_6H_5). Spectral data for **2** did not provide sufficient information to determine whether the allylic H is *exo* or *endo*.

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