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Preliminary communication

SYNTHESIS OF 5,7-DIHYDRODIBENZO[*c,e*] METALLEPINS VIA A NEW DI-GRIGNARD OR DILITHIUM REAGENT

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Summary

Thermally robust metallacycles $[M(\eta\text{-}C_5H_5)_2L]$ ($L = [(2\text{-}CH_2C_6H_4)_2]^{2-}$, M = Ti, Zr, Hf) and $[SnPh_2L]$ have been obtained from the newly developed reagents, $L[MgCl(thf)_n]_2$ and $L[Li(tmeda)]_2$, as has the silylated derivative, $[2\text{-}(Me_3SiCH_2)C_6H_4]_2$. A new radical anion of 9,10-dihydrophenanthrene derived from the reaction of lithium and LCl_2 or LBr_2 in thf has been detected.

We draw attention to two Main Group organometallic reagents, the di-Grignard, II, and the organo-dilithium complex, III, as sources of the dianion, $[(2\text{-}CH_2C_6H_4)_2]^{2-}$. The di-Grignard reagent derived from *o*-bis(chloromethyl)benzene was recently prepared [1] and shown to be a useful precursor for a wide variety of *o*-xylidene metallacycles [2]. Reagents II and III (the latter having no counterpart in *o*-xylidene chemistry) should have a similar potential. In principle, the ligand $[(2\text{-}CH_2C_6H_4)_2]^{2-}$ is capable of unusual bonding configurations similar to those for the closely related, extensively studied benzyl group [3], and like the *o*-xylidene system, the derived alkylmetal complexes are stabilized towards β-hydrogen elimination. Additional important features are (i) the ligand has a flexible bite associated with torsion along the biphenyl axis, and is thus potentially capable of accommodating a wide variation in heteroatom size and (ii), the associated organometallic compounds are unusual examples of metallacycloheptadiene derivatives.

Generation of II is unexpected given that intramolecular cyclization generally occurs with formation of 9,10-dihydrophenanthrenes (V) [4] and that a previous attempt to prepare a di-Grignard based on this system was unsuccessful [5]. However, in view of the successful synthesis of the previously inaccessible di-Grignard reagent of *o*-bis(chloromethyl)benzene [1] formation of II is not

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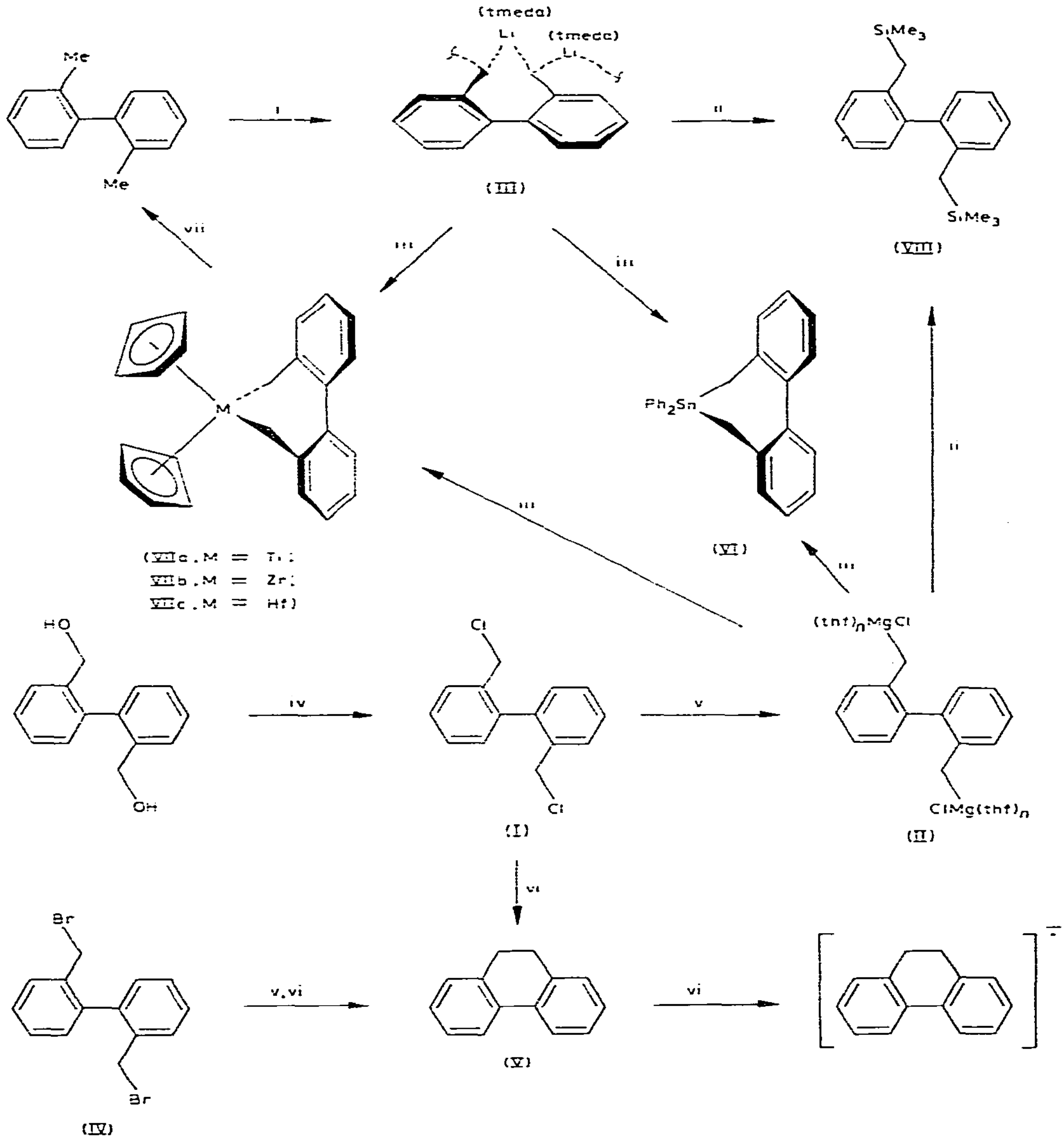

SCHEME 1

Reagents and conditions: i, $LiBu^n$ (ca. 1.6 *M* in n-C_6H_{14} 2 mol) + tmeda ($Me_2NCH_2CH_2NMe_2$) 2 mol, 12 h at 20°C; ii, $ClSiMe_3$, 0°C; iii, $SnPh_2Cl_2$ or $M(\eta\text{-}C_5H_5)_2Cl_2$, OEt_2, 30°C (thf, 20°C with II); iv, conc. HCl/H_2SO_4; v, Mg, thf, 20°C; vi, Li, thf, 20°C; vii, > 180°C.

surprising and the optimum conditions were found to be identical with those for that Grignard reagent as was the choice of halide (yields of II, typically > 90%). Under the same conditions bis(2-bromomethyl)biphenyl afforded the intramolecular cyclization product, V, which was also obtained from reactions of IV or I in thf with lithium powder. An added feature of the latter reactions is the formation of a new radical anion (dark green solution, g_{av} = 2.0044, H-hyperfine coupling unresolved). Dilithiation of di-*o*-tolyl (Scheme 1) gave an organodilithium complex (III) in high yield (94%) as a crystalline solid, which means that exact stoichiometries of highly pure starting materials can be used in further reactions. In the solid it possesses a polymeric structure (Scheme 1) as shown by an X-ray structure determination [6]. The ability to selectively dilithiate di-*o*-tolyl offers a more direct route to $[(2\text{-}CH_2C_6H_4)_2]^{2-}$. In contrast, for *o*-xylidene there is little selectivity under similar conditions [7]. This difference can be attributed to the fact that in the biphenyl derivatives there is only one charge associated with each potentially resonance stabilizing benzene ring.

Production of bis(2-trimethylsilylmethyl)biphenyl (VIII), by treating II and III with $ClSiMe_3$, and the transmetallation reactions involving II and III to form the metallacycles, 5,7-dihydrodibenzo[*c*,*e*]metallepins (VI and VII, Scheme 1) demonstrate the potential of these reagents. All the new compounds, I, III, VI—VIII*, have been characterized by analysis and spectral data**, and the structure of the stannepin VI has been unambiguously established by an X-ray study [6].

For metallacycle rings up to and including six atoms in metallacyclohexanes, β-hydrogen elimination will be disfavoured because of the difficulty in achieving a low M—C—C—H dihedral angle. However, for a more flexible seven membered ring, β-hydrogen elimination is reasonably facile, as e.g. with $[(PPh_3)_2\text{-}\overline{Pt\{CH_2(CH_2)_4CH_2}\}]$ [8], and consequently for enhanced stability it is imperative for the chelating alkyl to be free from β-hydrogens. This is the case with the transition metal metallacycles VII, which are remarkably thermally robust, being sublimable in vacuo (160°C/0.1 mmHg) and decomposing only slowly above 180°C to generate di-*o*-tolyl, presumably formed by cyclopentadienyl hydrogen abstraction, rather than by reductive elimination to yield V. The related complexes $[M(\eta\text{-}C_5H_5)_2(CH_2Ph)_2]$ are less stable (e.g. the compound with M = Ti decomposes in benzene at 30°C) [9]. This difference in stability suggests that alkylmetals with chelating alkyl groups ("linked" benzylalkyls) are more stable than those involving unidentate ligands. Compounds VII are resistant towards CO insertion (20°C/1 atm) whereas with the analogous *o*-xylidene complexes carbonylation readily occurs [2a]. This difference may be related to the larger steric requirements in the present case, hindering access to the metal centre.

Another example of a metallacycloheptadiene (an unsymmetrical one) is a proposed intermediate in the acetylene insertion reaction of $[\overline{Co(\eta\text{-}C_5H_5)(PPh_3)(CH{=}CHCH_2CH_2})]$ into $[Co(\eta\text{-cycloocta-1,3-diene})(\eta\text{-}C_5H_5)]$ [10].

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*I, white, m.p. 46°C; III, yellow, m.p. (dec.) 102°C; VI, white, m.p. 189°C; VIIa, yellow, m.p. 168°C; VIIb, orange, m.p. 165°C; VIIc, yellow, m.p. 162°C; VIII, colourless liquid, b.p. 120°C/0.1 mmHg.

**VI and VII are rigid on the NMR time scale since the methylene protons are non-equivalent, anisochronous, giving rise to an AB quartet.

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