

Review

Pentafulvene complexes of group four metals: Versatile organometallic building blocks



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ABSTRACT

A survey of the chemistry of pentafulvene complexes of group four metals is presented. Different synthetic procedures are discussed, leading to mono- and bis(η^5 : η^1 -pentafulvene)metal complexes. Due to Umpolung of the coordinated pentafulvene ligand the C_{exo} -atom become strong nucleophilic and a broad range of element–H activation reactions are investigated. This review covers the bond activation reactions of molecular hydrogen, N–H and C–H bond splitting reactions leading to titanium hydrides, imides and hydrazides as well as titanaaziridines, employing pentafulvene titanium complexes. A new concept of the preparation of tridentate Cp,O,P - and Cp,N,P - ligands is presented. These ligands are used for the preparation of electrophilic cationic group four metal complexes. In the case of cationic Cp,N , P -titanium complexes frustrated Lewis pair (FLP) reactivity is found.

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1. Introduction

The stabilisation of low valent transition metal complexes by strong π -acceptor ligands has fascinated chemists for a long time [1]. On the one hand, carbonyl ligands are dominating the modern inorganic chemistry and a broad range of applications [2]. On the other hand, the synthesis of the ferrocene molecule marked the starting point of the organometallic chemistry employing π -coordinated ligands [3,4]. With these concepts the formation of η^6 -coordinated arene complexes, following the 18-electron rule, like $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ and $(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}$ become comprehensible [5–7]. It was found, that pentafulvenes, as the nonvalence isomer of benzene, display a rich organometallic chemistry [8]. They are fascinating cross-conjugated ligands, offering a broad range of coordination modes, from η^2 , η^4 up to η^6 , to many transition metals (Scheme 1) [9–12].

By using the arene complexes $(\eta^6\text{-arene})_2\text{M}$ (M: Ti, Mo, W) and the pentafulvene ligand $\text{C}_5\text{H}_4=\text{CPh}_2$ an exchange of the arene molecule by the stronger π -acceptor leads to $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{CPh}_2)_2\text{Ti}$ and $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{CPh}_2)(\eta^6\text{-arene})\text{M}$ (M: Mo, W) complexes [13]. In contrast to the classic metal vapour techniques, an upscaling of the synthetic protocols and an expansion of the chemical scope become possible by a reductive complexation route in the case of group four metals.

2. Scope

This review will summarize the effective use of suitable pentafulvenes ligands, sodium or magnesium as reducing agents, and various group four metal precursors to generate, $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{CR}_2)_2\text{M}$ (M: Ti, Zr [14–16]), $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{CR}_2)(\eta^5\text{-C}_5\text{R}_5)\text{MX}$ (M: Ti, Zr, Hf; X: Cl, R: H, Me) [17] and $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{CR}_2)(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}$ [18] complexes in a very good yield and on a multigram scale. The resulting $\pi\text{-}\eta^5$: $\sigma\text{-}\eta^1$ coordination mode is attributed to a strong π -back-donation from the metal to the fulvene moiety. This coordination involves a change of the polarity (“Umpolung”) of the exocyclic carbon atom of the fulvene ligand (C_{exo}) [19]. This Umpolung leads to a strong nucleophilic character of the C_{exo} centre compared to its electrophilic reactivity in the free ligand as used in the heydays of the pentafulvene chemistry in the early 1970s [20,21]. For the $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{CR}_2)_2\text{M}$ (M: Ti, Zr) complexes, a broad range of subsequent reactions, like electrophilic attacks [22–24], haptotropic shifts [25,26], insertion reactions of multiple bond containing substrates (e.g. nitriles, isonitriles, imines or carbonyl compounds) [16,27–29], and E–H bond activations are found. In particular, the

unprecedented N–H/C–H [15,30,31] as well as the double C–H bond activation reactions at comparatively mild conditions [32] are evidence for the special reactivity of the $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{CR}_2)_2\text{Ti}$ complexes when compared to classic metallocene methyl complexes like $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^1\text{-CH}_3)_2$ (Fig. 1). The latter appear to be inert in most of the reactions mentioned above, caused by strong kinetic hindrance, leading to carbene mediated reaction pathways [33].

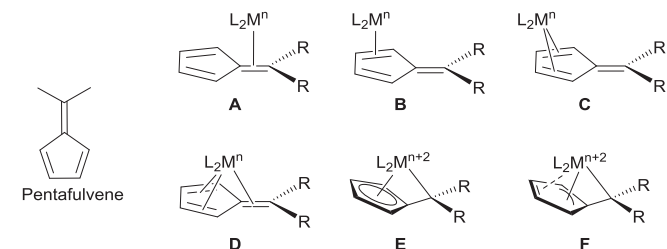
Due to the weak $\text{M}^+ \dots \text{C}_{\text{exo}}$ interaction, the $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{CR}_2)_2\text{M}$ complexes of group four metals can also be understood as the first examples of heteroatom free organometallic frustrated Lewis pairs, compared to the broad range of heteroatom containing Lewis pairs [34,35]. In the case of Cp_2TiMe_2 Ti–CH₃ bond length of 2.181(2) and 2.170(2) Å are found [36] compared with the Ti–C_{exo} distances of the fulvene ligand in $(\text{Fv})_2\text{Ti}$ complexes, exhibiting distances in the range of 2.341 up to 2.410 Å [14].

3. The organic chemistry of fulvenes

Fulvenes are cyclic cross-conjugated molecules with an odd number of carbon atoms in the ring. According to the size of the ring skeleton they are named triafulvens (a), pentafulvens (b), heptafulvens (c) and nonafulvens (d) (Fig. 2). Recent investigations demonstrate that the parent compounds are characterized by typically olefinic properties [21].

Pentafulvenes were discovered in 1900 and the intensive colors, depending on the substitution patterns (yellow to red), of these compounds are responsible for the name of the whole substance family [37]. Compared to benzene, its isomeric pentafulvene has a high-energy HOMO and a comparably low-energy LUMO. This accounts for the long-wavelength UV absorption of fulvenes, being responsible for the color of these derivatives. Looking at the high-energy HOMO and the low-energy LUMO of fulvenes compared to aromatic systems, it is qualitatively understood that the thermal stability of unsubstituted fulvenes is very low. Such fulvenes undergoes an easy Diels–Alder dimerization. [21] Based on their dipole moments, as well as on their reactivity patterns, fulvenes could occupy an intermediate position between open-chain olefinic and aromatic compounds [20]. Exocyclic substituents might increase the dipolar character and favor aromatic substitution over olefinic addition, thus increasing the aromatic character of the pentafulvenes as shown in Scheme 2.

Due to this dipolar character of pentafulvenes a broad range of nucleophiles can be added to the C_{exo} -position. This is illustrated in Scheme 3 for the addition of organo lithium reagents, a well-



Scheme 1. Different coordination modes of pentafulvenes: neutral η^2 -exo (A), neutral η^2 -endo (B), neutral η^4 (C), neutral η^6 (D), dianionic $\pi\text{-}\eta^5$: $\sigma\text{-}\eta^1$ (E), dianionic $\pi\text{-}\eta^2$: $\pi\text{-}\eta^3$: $\sigma\text{-}\eta^1$ (F).

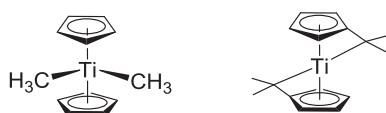


Fig. 1. Cp_2TiMe_2 (Petasis reagent, left) compared to $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{CR}_2)_2\text{Ti}$ (Fv_2Ti) complexes (right).

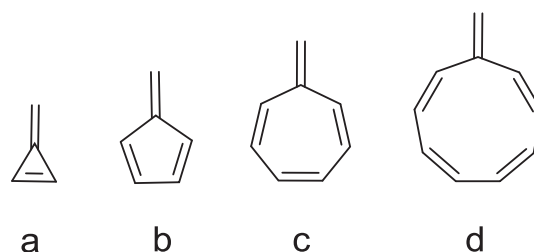
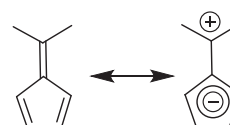


Fig. 2. Fulvenes of different ring size.



Scheme 2. Dipolar character of pentafulvenes.

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