Unsaturated dodecahedranes–metal complexation

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Abstract

The propensity of highly pyramidalized unsaturated dodecahedranes (1, 11, 13) for metal complexation has been tested; structures, complexing strengths and reversibility have been analyzed by IR, 1H, 13C, 31P, 195Pt NMR, Mößbauer measurements and crystal structure analysis. © 2000 Elsevier Science Ltd. All rights reserved.

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Ever since we have worked on the synthesis of pentagonal dodecahedranes, 1 unsaturated ones 1–6 such as monoene 1, diene 2, 3 triene 3, tetraene 4, pentaene 5, 2 hexaene 6, and ultimately decaene 7 — the smallest fullerene 4 — have been high on our agenda. 5 The consequences of the enormous strain and reactivity, the geometrical/stereoelectronic prerequisites/limitations of in-plane homoconjugation (σ-homoaromaticity) in the neutral olefins as well as in their ions were just two topics of interest. 6 In this context, with a great variety of halogenated dodecahedranes available, 3–5 preparative protocols were explored which would bring about β-cis-eliminations and rapid (reversible) protection of the newly formed, extremely reactive C=C double bonds by, e.g., metal complexation. Pertinent results are reported in this letter. 7

The olefins 1–7 — due to the high olefinic pyramidalization the HOMOs are slightly raised and the LUMOs significantly lowered — are, in principle, good ligands for d 10 metals (Pt, Pd, Ni); steric protection of their C=C double bonds by the allylic hydrogen atoms — responsible, inter alia, for the astonishing thermal stability of 1 and 2 — should not be prohibitive (cf. the related olefins studied by Borden et al. 8 ). In fact, with Pt(PPh) 3(C 2 H 4 ) (12) monoene 1 (HOMO: −7.94 eV (exp.), −8.84

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eV (AM1); LUMO: +0.40 eV (AM1)) reacted smoothly to give the yellowish-beige crystalline 1:1 complexes 14 and 15, respectively (Scheme 1). To be noted, reagent 12—through whatever mechanism—neatly effected cis-elimination of Br from 1,2-dibromide 10, hence highly oxygen-sensitive 1 could be complexed in-situ (85%). Such a procedure could also be followed in the case of 13 when the bases used (e.g., NaOCH₃) for its generation from the bissec precursor 9 were found to be tolerated by 12 and the metal complex formed. Diene 11 with an excess of 12 yielded the 1:2 complex 17 (>80%); with 1 equivalent of 12 it yielded a mixture of 11 and 17, rather than the 1:1 complex 16. With Pd(PPh₃)₄ and Ni(PPh₃)₄ both 1 and 13 reacted smoothly (THF, room temperature) to give the crystalline, air-sensitive complexes 18/19 and 20/21 (>80% after crystallization).

As exemplified with bisadduct 17 (Fig. 1) the ¹H and ¹³C chemical shifts are typically influenced by the complexation, the former C–C double bonds are elongated by ca. 0.11 Å, pyramidalization is increased by ca. 7° (d₁C–C (av.)=1.328 Å, φ (av.)=43.5° (B3LYP/6-31G*)), and the carbon cage is only moderately distorted (crystal structure analysis). As in reference systems, the coupling constant ¹J₁Pt–C with 366 Hz for 15 and 365 Hz for 17 is nearly twice that in 12 (194 Hz); ¹J₁Pt–P on the other hand, with 3365 Hz for 15 and 3380 Hz for 17, is significantly smaller than in 12 (3740 Hz). Still, δ₁P=32.6 for 17 is at a higher field than for 12 (δ₁P=34.1). High back-donation (Pt→π* olefin) and a stronger σ-donation (π olefin→6s (Pt)) are indicated by the large ¹J₁Pt–C-coupling constants and reduced metal–phosphine interactions (¹J₁Pt–P). Oxidation of platinum is expressed for 17 with δ₁Pt=–418 compared with δ₁Pt=–555 for 12; the acceptor quality of the carbon cage is roughly that of tricyanoethylene (δ₁Pt=–424, TCNE: δ₁Pt=–363). A more quantitative estimate of the thermodynamic stability became possible for 15 (E_diss=50–66 kcal mol⁻¹) when in exchange experiments with Pt(PPh₃)₃(cis-stilbene) (E_diss=43.3±4.2 kcal mol⁻¹), Pt(PPh₃)₃(trans-stilbene) (E_diss=50.2±8.8 kcal mol⁻¹), and Pt(PPh₃)₃(TCNE) (E_diss=66.2±8.8 kcal mol⁻¹) cis- and trans-stilbene were displaced, but not, however, TCNE. For the Borden reference olefins (φ=48–60°) dissociation energies of 35.1–58.3 kcal mol⁻¹ had been reported. As a reversible protecting measure, complexation with [Fe(CO)₄] or [Mo(CO)₅] seemed most promising. Monoenes 1/13 reacted smoothly at room temperature with Fe(CO)₅ in a large excess to give the complexes 22/23 (ca. 75% after crystallization) as solids that were stable for days in air and in solution (CHCl₃, benzene); in addition, with less than 1 equivalent of Fe(CO)₅ the 2:1 complexes
24-25 were formed. Analogously, from diene 11 the 1:2 complex 30 was obtained in the form of a brown solid after crystallization (EtOH). With Mo(CO)₆ complexation occurred much slower; only after refluxing in benzene with equivalent amounts of 1 or 13 was transformation into the complexes 26/27 complete (~65% after crystallization; no further complexation to give 28/29). Under these conditions diene-diester 11 was not complexed but instead was totally dimerized (31). In-situ complexation of 1 could be accomplished when treatment of 1,2-dibromide 10 with Fe₂(CO)₉ caused neat Br₂ elimination and instantaneous complexation with in-situ-generated [Fe(CO)₄] to yield complex 22 (>80%). From the latter, under mild oxidative conditions (Ce(NO₃)₄/CH₃OH/THF, room temperature), ligand 1 was conveniently regained. The Mo complex 26, although not, however, the Fe complex 22, was cleaved by Br₂ to give dibromide 10 — this type of metal substitution, being of preparative interest in view of the complications involved in the cis-1,2-addition of Br₂ to unsaturated dodecahedranes (Scheme 2). The IR spectra of 22/23 display four CO signals (22: 2077, 2043, 1994, 1972 cm⁻¹) that manifests local C₂ᵥ symmetry, equatorial orientation of the dodecahedral ligand, and strong π-donation. This latter effect is also expressed in the MS fragmentation pattern with (22) F=0.32 (0.27 for Fe(CO)₅(styrene), 0.34 for Fe(CO)₄(C₂H₄)). The Mößbauer spectrum of 23 consists of a symmetrical doublet with strong quadrupole splitting — in line with local C₂ᵥ symmetry and a strong ligand field. The IsₐFe value is expectedly smaller than for Fe(CO)₅ (IsₐFe=−0.06 mm s⁻¹) and Fe(CO)₅(C₂H₄) (IsₐFe=0.00 mm s⁻¹), an indication of a higher acceptor quality at a similar symmetry (∆Eₐ(Fe(CO)₅(C₂H₄))=1.79 mm s⁻¹). By these criteria fullerene C₆₀ is a stronger acceptor (IsₐFe=−0.26 and ∆Eₐ=1.58 mm s⁻¹).
Investigations are underway as to whether in-situ generation and complexation can be utilized for the isolation/identification of polyunsaturated dodecahedrane by treatment of polybrominated dodecahedrane ([C_{20}H_{8-12}Br_{12-8}]_{5,7}) with Fe_{2}(CO)_{9}.

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References

9. Crystallographic data for 17 have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge (e-mail: deposit@chemcrys.cam.ac.uk) on quoting the deposition number CCDC 136717.
15. With AgX and CuX (X=Br, NO$_3$) the olefins 1 and 13 only form complexes with X being weakly coordinating (e.g. not BF$_4^-$, B(C$_6$H$_5$)$_4^-$). These complexes, with an unknown coordination state of the metals and held together primarily by $\sigma$-donation of the olefins, are relatively unstable. Exposure of the Ag complexes to KI leads back to 1.
19. For the adduct (CCTI-13) obtained from 13 and the Vaska-complex IrCICO(PPh$_3$)$_2$ (CCTI) $\nu_{C=O}$=1990 cm$^{-1}$ and Mößbauer $\Delta E_Q$ (Is) values of 4.73 (−0.195) mm s$^{-1}$ were measured (F. E. Wagner) placing the $\pi$-acceptor strength of 13 below that of C$_6$O (CCTI–C$_6$O: $\nu_{C=O}$=2014 cm$^{-1}$; 2.71 (−0.259) mm s$^{-1}$) and TCNE (CCTI–TCNE: $\nu_{C=O}$=2060 cm$^{-1}$; 1.87 (−0.194) mm s$^{-1}$).