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TETRAHEDRON
LETTERS

Unsaturated dodecahedranes–metal complexation

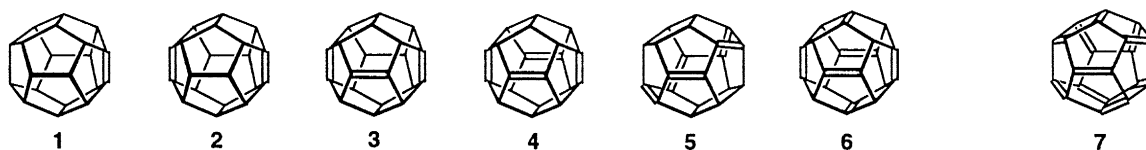
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Abstract

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.

Keywords: dodecahedranes; unsaturation; pyramidalization; metal complexation; Mößbauer.

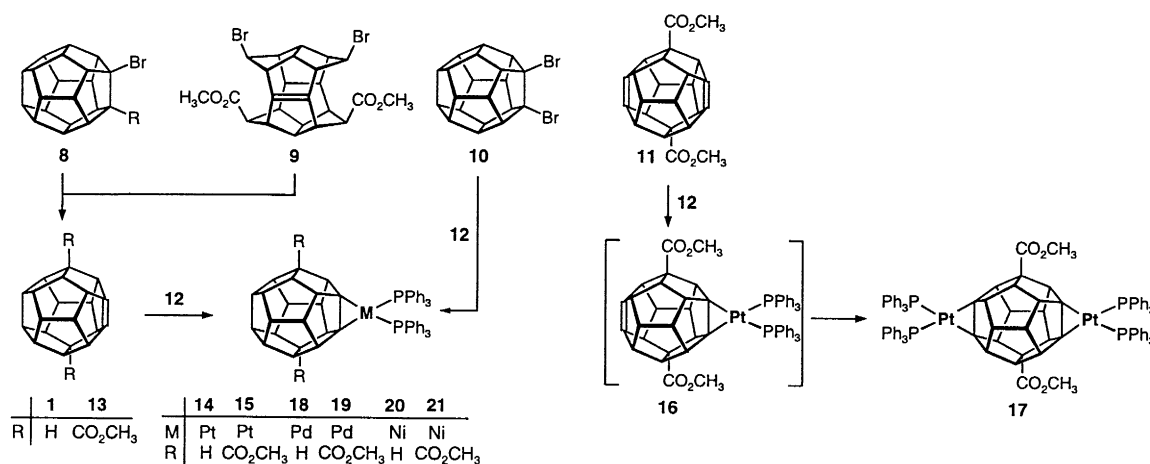


Ever since we have worked on the synthesis of pentagonal dodecahedranes,¹ unsaturated ones^{1–6} such as monoene **1**, diene **2**,³ triene **3**, tetraene **4**, pentaene **5**,² hexaene **6**, and ultimately decaene **7**—the smallest fullerene⁴—have been high on our agenda.⁵ The consequences of the 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 d¹⁰ 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**³—should not be prohibitive (cf. the related olefins studied by Borden et al.⁸). In fact, with Pt(PPh)₃(C₂H₄) (**12**) monoene **1** (HOMO: –7.94 eV (exp.), –8.84

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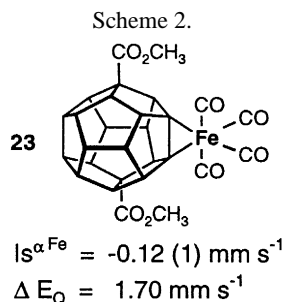
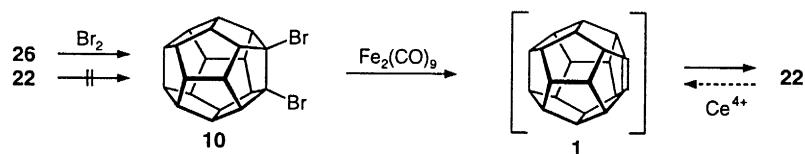
eV (AM1); LUMO: +0.67 eV (AM1)) and its 1,6-diester derivative **13** (HOMO: $-7.72/8.40$ ($n+n-$, exp.), -8.85 eV (AM1); LUMO: +0.40 eV (AM1))⁶ reacted smoothly to give the yellowish-beige crystalline 1:1 complexes **14** and **15**, respectively (Scheme 1). To be noted, reagent **12**—through whatever mechanism—neatly effected *cis*-elimination of Br₂ 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 bisseco 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).



Scheme 1.

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° ($d_{C=C}$ (av.)=1.439 Å, ϕ (av.)=50.1°; **11**: $d_{C=C}$ =1.328 Å, ϕ =43.5° (B3LYP/6-31G*)), and the carbon cage is only moderately distorted (crystal structure analysis⁹). As in reference systems,⁸ the coupling constant ¹J_{Pt-C} with 366 Hz for **15** and 365 Hz for **17** is nearly twice that in **12** (194 Hz); ¹J_{Pt-P} on the other hand, with 3365 Hz for **15** and 3380 Hz for **17**, is significantly smaller than in **12** (3740 Hz). Still, δ_P =32.6 for **17** is at a higher field than for **12** (δ_P =34.1). High back-donation (Pt→ π^* _{olefin}) and a stronger σ -donation (π _{olefin}→6s (Pt)) are indicated by the large J_{Pt-C} coupling constants and reduced metal–phosphine interactions (J_{Pt-P}). Oxidation of platinum is expressed for **17** with δ_{Pt} =-418 compared with δ_{Pt} =-555 for **12**; the acceptor quality of the carbon cage is roughly that of tricyanoethylene (δ_{Pt} =-424, TCNE: δ_{Pt} =-363).¹⁰ A more quantitative estimate of the thermodynamic stability became possible for **15** (E_{diss} =50–66 kcal mol⁻¹) when in exchange experiments¹¹ 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.^{8,12}

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);¹³ in addition, with less than 1 equivalent of Fe(CO)₅ the 2:1 complexes



Investigations are underway as to whether in-situ generation and complexation can be utilized for the isolation/identification of polyunsaturated dodecahedranes by treatment of polybrominated dodecahedranes ($[C_{20}H_{8-12}Br_{12-8}]^{5,7}$) with $Fe_2(CO)_9$.

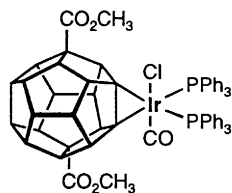
Acknowledgements

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