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LETTERS

## Unsaturated dodecahedranes–metal complexation

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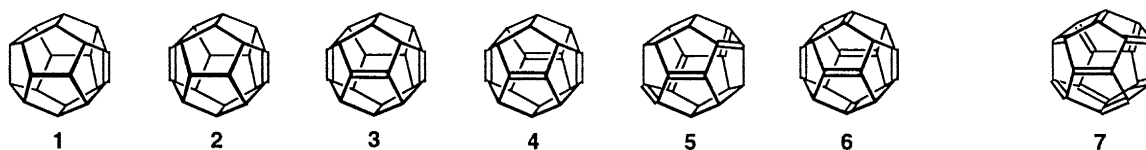
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### Abstract

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, <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>195</sup>Pt NMR, Mößbauer measurements and crystal structure analysis. © 2000 Elsevier Science Ltd. All rights reserved.

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

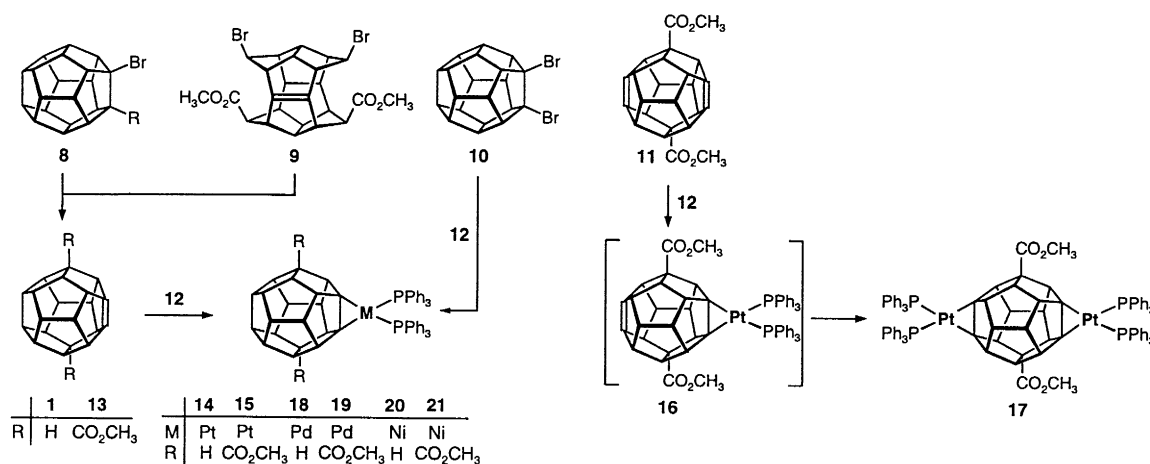


Ever since we have worked on the synthesis of pentagonal dodecahedranes,<sup>1</sup> unsaturated ones<sup>1–6</sup> such as monoene **1**, diene **2**,<sup>3</sup> triene **3**, tetraene **4**, pentaene **5**,<sup>2</sup> hexaene **6**, and ultimately decaene **7**—the smallest fullerene<sup>4</sup>—have been high on our agenda.<sup>5</sup> The consequences of the enormous strain and reactivity, the geometrical/stereoelectronic prerequisites/limitations of in-plane homoconjugation ( $\sigma$ -homoaromaticity) in the neutral olefins as well as in their ions were just two topics of interest.<sup>6</sup> In this context, with a great variety of halogenated dodecahedranes available,<sup>3–5</sup> preparative protocols were explored which would bring about  $\beta$ -*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.<sup>7</sup>

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<sup>10</sup> 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**<sup>3</sup>—should not be prohibitive (cf. the related olefins studied by Borden et al.<sup>8</sup>). In fact, with Pt(PPh)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>) (**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))<sup>6</sup> 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<sub>2</sub> 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. NaOCH<sub>3</sub>) 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(PPh<sub>3</sub>)<sub>4</sub> and Ni(PPh<sub>3</sub>)<sub>4</sub> 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 <sup>1</sup>H and <sup>13</sup>C 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,  $\phi$  (av.)=50.1°; **11**:  $d_{C=C}$ =1.328 Å,  $\phi$ =43.5° (B3LYP/6-31G\*)), and the carbon cage is only moderately distorted (crystal structure analysis<sup>9</sup>). As in reference systems,<sup>8</sup> the coupling constant <sup>1</sup>J<sub>Pt-C</sub> with 366 Hz for **15** and 365 Hz for **17** is nearly twice that in **12** (194 Hz); <sup>1</sup>J<sub>Pt-P</sub> on the other hand, with 3365 Hz for **15** and 3380 Hz for **17**, is significantly smaller than in **12** (3740 Hz). Still,  $\delta_P$ =32.6 for **17** is at a higher field than for **12** ( $\delta_P$ =34.1). High back-donation (Pt→ $\pi^*$ <sub>olefin</sub>) and a stronger  $\sigma$ -donation ( $\pi$ <sub>olefin</sub>→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  $\delta_{Pt}$ =-418 compared with  $\delta_{Pt}$ =-555 for **12**; the acceptor quality of the carbon cage is roughly that of tricyanoethylene ( $\delta_{Pt}$ =-424, TCNE:  $\delta_{Pt}$ =-363).<sup>10</sup> A more quantitative estimate of the thermodynamic stability became possible for **15** ( $E_{diss}$ =50–66 kcal mol<sup>-1</sup>) when in exchange experiments<sup>11</sup> with Pt(PPh<sub>3</sub>)<sub>3</sub>(*cis*-stilbene) ( $E_{diss}$ =43.3±4.2 kcal mol<sup>-1</sup>), Pt(PPh<sub>3</sub>)<sub>3</sub>(*trans*-stilbene) ( $E_{diss}$ =50.2±8.8 kcal mol<sup>-1</sup>) and Pt(PPh<sub>3</sub>)<sub>3</sub>(TCNE) ( $E_{diss}$ =66.2±8.8 kcal mol<sup>-1</sup>) *cis*- and *trans*-stilbene were displaced, but not, however, TCNE. For the Borden reference olefins ( $\phi$ =48–60°) dissociation energies of 35.1–58.3 kcal mol<sup>-1</sup> had been reported.<sup>8,12</sup>

As a reversible protecting measure, complexation with [Fe(CO)<sub>4</sub>] or [Mo(CO)<sub>5</sub>] seemed most promising. Monoenes **1/13** reacted smoothly at room temperature with Fe(CO)<sub>5</sub> 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 (CHCl<sub>3</sub>, benzene);<sup>13</sup> in addition, with less than 1 equivalent of Fe(CO)<sub>5</sub> the 2:1 complexes

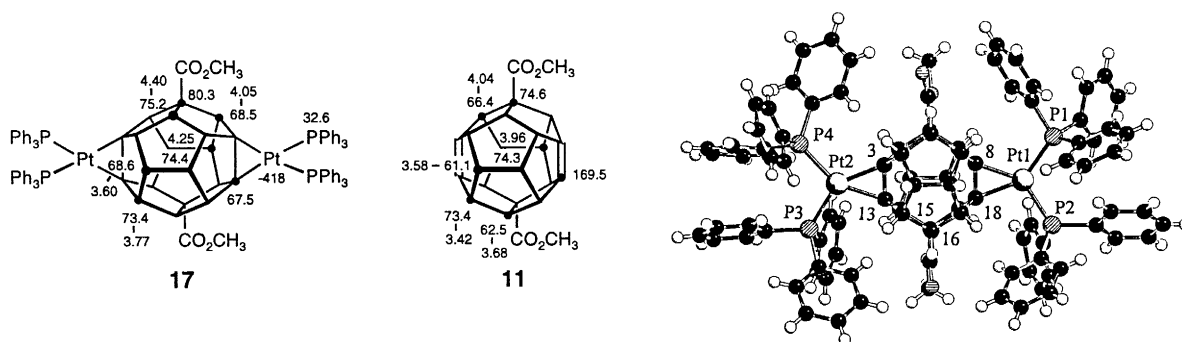
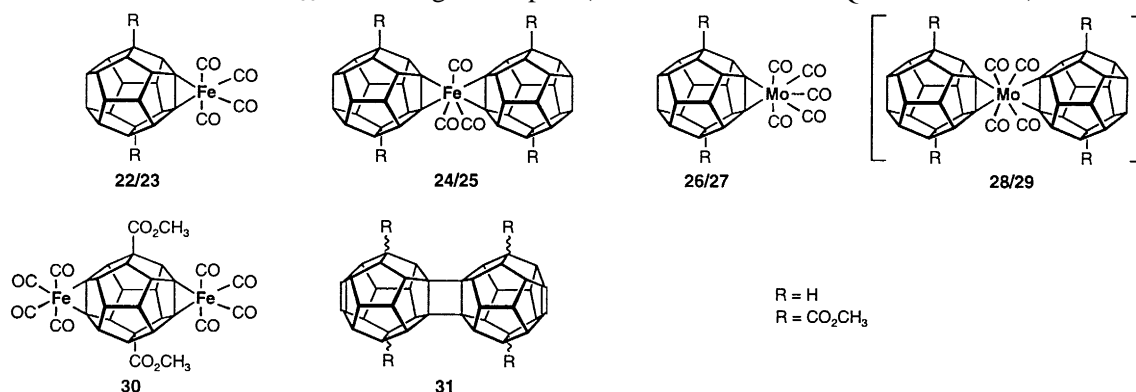
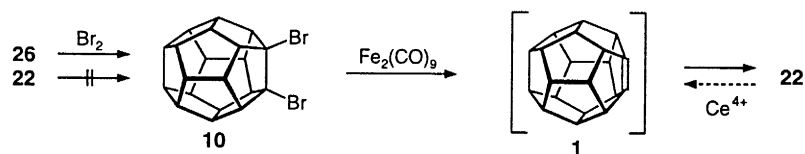


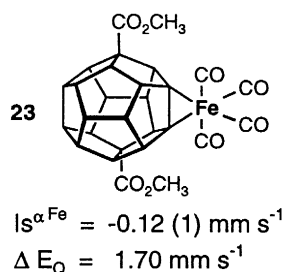
Fig. 1. <sup>1</sup>H, <sup>13</sup>C NMR assignments and crystal structure analysis (Schakal plot) of **17** (**11** for comparison). Selected distances and angles: C3=C13=1.434 Å, C8=C18=1.444 Å, C3–Pt2=2.116(8) Å, C8–Pt1=2.104(8) Å, C18–Pt1=2.100(8) Å, C13–Pt2=2.102(8) Å, C15–C16=1.590(12) Å, P1–Pt1=2.268(2) Å, P2–Pt1=2.290(2) Å, P3–Pt2=2.294(2) Å, P4–Pt2=2.286(2) Å, C13–C3–Pt2=69.5°, C8–Pt1–C18=40.2°, C8–Pt1–P1=105.0°, C18–Pt1–P1=144.4°, C13–Pt2–C3=39.8°,  $\Phi$  (C3)=51.2°,  $\Phi$  (C13)=50.0°,  $\Phi$  (C8)=49.6°,  $\Phi$  (C18)=51.7°<sup>9</sup>

**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)<sub>6</sub> 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**).<sup>14</sup> In-situ complexation of **1** could be accomplished when treatment of 1,2-dibromide **10**<sup>3</sup> with Fe<sub>2</sub>(CO)<sub>9</sub> caused neat Br<sub>2</sub> elimination and instantaneous complexation with in-situ-generated [Fe(CO)<sub>4</sub>] to yield complex **22** (>80%). From the latter, under mild oxidative conditions (Ce(NO<sub>3</sub>)<sub>4</sub>/CH<sub>3</sub>OH/THF, room temperature), ligand **1** was conveniently regained.<sup>15</sup> The Mo complex **26**, although not, however, the Fe complex **22**, was cleaved by Br<sub>2</sub> 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 Br<sub>2</sub> to unsaturated dodecahedranes (Scheme 2).<sup>3,7</sup> The IR spectra of **22/23** display four CO signals (**22**: 2077, 2043, 1994, 1972 cm<sup>-1</sup>) that manifests local C<sub>2v</sub> symmetry, equatorial orientation of the dodecahedral ligand, and strong  $\sigma$ -donation. This latter effect is also expressed in the MS fragmentation pattern<sup>16</sup> with (**22**)  $F=0.32$  (0.27 for Fe(CO)<sub>4</sub>(styrene), 0.34 for Fe(CO)<sub>4</sub>(Cl<sub>2</sub>CCH<sub>2</sub>)). The Mößbauer spectrum of **23** consists of a symmetrical doublet with strong quadrupole splitting—in line with local C<sub>2v</sub> symmetry and a strong ligand field. The  $I_s^{\alpha\text{Fe}}$  value is expectedly smaller than for Fe(CO)<sub>5</sub> ( $I_s^{\alpha\text{Fe}}=-0.06$  mm s<sup>-1</sup>) and Fe(CO)<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>) ( $I_s^{\alpha\text{Fe}}=0.00$  mm s<sup>-1</sup>), an indication of a higher acceptor quality at a similar symmetry ( $\Delta E_Q$  (Fe(CO)<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>))=1.79 mm s<sup>-1</sup>). By these criteria fullerene C<sub>60</sub> is a stronger acceptor ( $I_s^{\alpha\text{Fe}}=-0.26$  and  $\Delta E_Q=1.58$  mm s<sup>-1</sup>).<sup>17-19</sup>





Scheme 2.



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  $Fe_2(CO)_9$ .

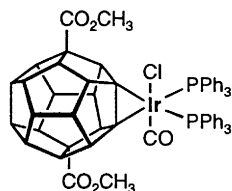
## Acknowledgements

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