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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 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 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 2^3 —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); ${}^{1}J_{Pt-P}$ 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 $\rightarrow \pi^*_{olefin}$) and a stronger σ -donation ($\pi_{olefin} \rightarrow 6s$ (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). A more quantitative estimate of the thermodynamic stability became possible for 15 ($E_{\rm diss}$ =50-66 kcal mol⁻¹) when in exchange experiments¹¹ with $Pt(PPh_3)_3(cis\text{-stilbene})$ ($E_{diss}=43.3\pm4.2~\text{kcal mol}^{-1}$), $Pt(PPh_3)_3(trans\text{-stilbene})$ ($E_{diss}=50.2\pm8.8$ 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

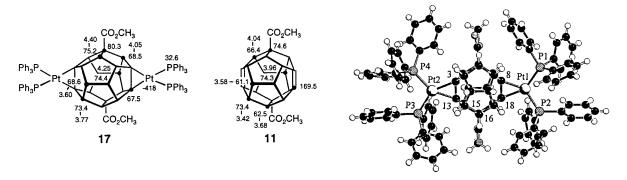
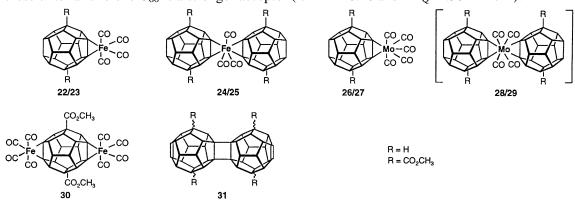


Fig. 1. 1 H, 13 C NMR assignments and crystal structure analysis (Schakal plot) of **17** (**11** for comparison). Selected distances and angles: C3=C13=1.434 Å, C8=C18=1.444 Å, C3-Pt2=2.116(8) Å, C8-Pt1=2.104(8) Å, C18-Pt1=2.100(8) Å, C13-Pt2=2.102(8) Å, C15-C16=1.590(12) Å, P1-Pt1=2.268(2) Å, P2-Pt1=2.290(2) 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°, Φ (C3)=51.2°, Φ (C13)=50.0°, Φ (C8)=49.6°, Φ (C18)=51.7°9

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).¹⁴ In-situ complexation of 1 could be accomplished when treatment of 1,2-dibromide 10^3 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.¹⁵ 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).^{3,7} The IR spectra of 22/23 display four CO signals (22: 2077, 2043, 1994, 1972 cm⁻¹) that manifests local C_{2v} symmetry, equatorial orientation of the dodecahedral ligand, and strong σ -donation. This latter effect is also expressed in the MS fragmentation pattern¹⁶ with (22) F=0.32 (0.27 for Fe(CO)₄(styrene), 0.34 for Fe(CO)₄(Cl₂CCH₂)). The Mößbauer spectrum of 23 consists of a symmetrical doublet with strong quadrupole splitting—in line with local C_{2v} symmetry and a strong ligand field. The $Is^{\alpha Fe}$ value is expectedly smaller than for Fe(CO)₅ (Is $^{\alpha Fe}$ =-0.06 mm s⁻¹) and Fe(CO)₄(C₂H₄) (Is $^{\alpha Fe}$ =0.00 mm s⁻¹), an indication of a higher acceptor quality at a similar symmetry (ΔE_Q (Fe(CO)₄(C₂H₄))=1.79 mm s⁻¹). By these criteria fullerene C_{60} is a stronger acceptor (Is $\alpha^{Fe} = -0.26$ and $\Delta E_{O} = 1.58$ mm s⁻¹). ^{17–19}



26 Br₂
Br
Br
Fe₂(CO)₉
Scheme 2.

CO₂CH₃

$$Is^{\alpha Fe} = -0.12 (1) \text{ mm s}^{-1}$$

$$\Delta E_{O} = 1.70 \text{ mm s}^{-1}$$

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 $Fe_2(CO)_9$.

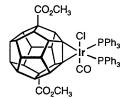
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References

- 1. Prinzbach, H. In *Organic Synthesis: Modern Trends*; Chizhov, O., Ed.; Blackwell: Oxford 1987, p. 23. Fessner, W.-D.; Prinzbach, H. In *Cage Hydrocarbons*; Olah, G. A., Ed.; Wiley: New York, 1990, p. 353.
- McEwen, A. B.; Schleyer, P. v. R. J. Org. Chem. 1986, 51, 4357. Fokin, A. A.; Jiao, H.; Schleyer, P. v. R. J. Am. Chem. Soc. 1998, 120, 9364.
- 3. Weber, K.; Fritz, H.; Prinzbach, H. *Tetrahedron Lett.* **1992**, *33*, 619. Melder, J.-P.; Pinkos, R.; Fritz, H.; Wörth, J.; Prinzbach, H. *J. Am. Chem. Soc.* **1992**, *114*, 10 213. Pinkos, R.; Melder, J.-P.; Weber, K.; Hunkler, D.; Prinzbach, H. *J. Am. Chem. Soc.* **1993**, *115*, 7173. Bertau, M.; Leonhardt, J.; Weiler, A.; Weber, K.; Prinzbach, H. *Chem. Eur. J.* **1996**, 2, 570. Melder, J.-P.; Weber, K.; Weiler, A.; Sackers, E.; Fritz, H.; Hunkler, D.; Prinzbach, H. *Res. Chem. Intermed.* **1996**, 7, 667.
- 4. Prinzbach, H.; Weiler, A.; Landenberger, P.; Wahl, F.; Wörth, J.; Scott, L. T.; Gelmont, M.; Olevano, D.; Issendorff, B. v., to be published.
- Prinzbach, H.; Weber, K. Angew. Chem., Int. Ed. Engl. 1994, 33, 2239. Pinkos, R.; Weiler, A.; Voss, T.; Weber, K.; Wahl, F.; Melder, J.-P.; Fritz, H.; Hunkler, D.; Prinzbach, H. Liebigs Ann./Recueil 1997, 2069. Scheumann, K.; Sackers, E.; Bertau, M.; Leonhardt, J.; Hunkler, D.; Fritz, H.; Wörth, J.; Prinzbach, H. J. Chem. Soc., Perkin Trans. 2 1998, 1195.
- Weber, K.; Prinzbach, H.; Schmidlin, R.; Gerson, F.; Gescheidt, G. Angew. Chem., Int. Ed. Engl. 1993, 32, 875. Martin, H.-D.; Mayer, B.; Weber, J.; Prinzbach, H. Liebigs Ann. 1995, 2019. Weber, K.; Lutz, G.; Knothe, L.; Mortensen, J.; Heinze, J.; Prinzbach, H. J. Chem. Soc., Perkin Trans. 2 1995, 1991. Prinzbach, H.; Gescheidt, G.; Martin, H.-D.; Herges, R.; Heinze, J.; Prakash, G. K. S.; Olah, G. A. Pure Appl. Chem. 1995, 67, 673.
- 7. Dissertation, T. Oßwald, University of Freiburg, 1999. Dissertation, K. Weber, University of Freiburg, 1993.
- 8. Hrovat, A.; Borden, W. T. J. Am. Chem. Soc. 1988, 110, 4710. Borden, W. T. Chem. Rev. 1989, 89, 1095. Nicolaides, A.; Smith, J. M.; Kumar, A.; Barnhart, D. M.; Borden, W. T. Organometallics 1995, 14, 3475.

- 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.
- 10. Pellizer, G.; Graziani, M.; Lenarda, M.; Heaton, B. T. Polyhedron 1983, 2, 657.
- 11. Simoes, J. A. M.; Beauchamps, J. L. Chem. Rev. 1990, 90, 629.
- 12. Uddin, J.; Dapprich, S.; Frenking, G.; Yates, B. F. Organometallics 1999, 18, 457.
- 13. Fe(CO)₄(C₆₀) decomposes within 24 h in solution. See: Douthwaite, R. E.; Green, M. L. H.; Stephens, A. H. H.; Turner, J. F. C. *J. Chem. Soc.*, *Chem. Commun.* **1993**, 1522.
- 14. Dissertation, A. Weiler, University of Freiburg, 1997. Dissertation, T. Voss, University of Freiburg, 1995.
- 15. With AgX and CuX (X=Br, NO₃) the olefins $\bf 1$ and $\bf 13$ only form complexes with X being weakly coordinating (e.g. not BF₄⁻, B(C₆H₅)₄⁻). These complexes, with an unknown coordination state of the metals and held together primarily by σ -donation of the olefins, are relatively unstable. Exposure of the Ag complexes to KI leads back to $\bf 1$.
- Koerner v. Gustorf, E. Z. Naturforschg. 1966, 21b, 42. Koerner v. Gustorf, E.; Henry, M. C.; McAdoo, D. J. Liebigs Ann. Chem. 1967, 707, 190.
- 17. Yamada, Y.; Tominga, T. J. Radioanal. Nucl. Chem. Letters 1994, 188, 83. J. Radioanal. Nucl. Chem. Letters 1995, 188, 95.
- 18. Christides, C.; Devlin, E.; Simopoulos, A.; Evans, D. J.; Meidine, M. F.; Paul, R. L. J. Phys. Chem. 1994, 98, 11 666.
- 19. For the adduct (CCTI-13) obtained from 13 and the Vaska-complex IrClCO(PPh₃)₂ (CCTI) $\nu_{C=O}$ =1990 cm⁻¹ and Mößbauer ΔE_Q (Is) values of 4.73 (-0.195) mm s⁻¹ were measured (F. E. Wagner) placing the π-acceptor strength of 13 below that of C₆₀ (CCTI-C₆₀: $\nu_{C=O}$ =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).²⁰



20. Vértes, A.; Gál, M.; Wagner, F. E.; Gütlich, P.; Tuczek, F. Inorg. Chem. 1993, 32, 447.