DPPA may open up a host of interesting synthetic possibilities and create added flexibility in synthesis. The investigation is continued along a broad front to determine the full range of ability in synthetic chemistry and to clarify the underlying reaction mechanisms.[14]

[14] The exact mechanistic details of the peptide formation must remain speculative at this time. The intermediacy of the carboxylic acid azide is tentative, and it seems attractive to consider a concerted process.

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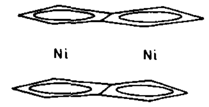
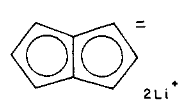
Sandwiches of Iron and Cobalt with Pentalene

Sir:

Of the few compounds in which a transition metal is sandwiched between the rings of a pair of nonbenzenoid aromatic hydrocarbons, the simplest is bis(pentalenylnickel) (I) which forms when dilithium pentalenide[1] (II) reacts with nickel chloride.[2] With ferrous chloride



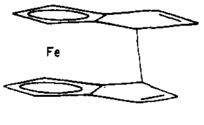
I



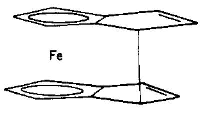
II

a structurally different product results, consisting of two molecules of pentalene and only one of iron. Cobalt analogs of both structures can also be made, and we are reporting here the preparation of these iron and cobalt compounds.

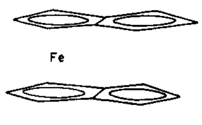
Bis(pentalenyl)iron was prepared by stirring dilithium pentalenide (5.4 mmol) in tetrahydrofuran (THF, 60 ml) with a slurry of ferrous chloride[3] (6.4 mmol) at −78° for 1 hr and at room temperature for 4 hr. After quenching with water, removal of solvent at reduced pressure, extraction with pentane, sublimation (50°, 0.02 mm) of the pentane-soluble extract, and recrystallization from hexane, we obtained an 18% yield of an orange-red crystalline solid, mp 127–128°, whose formula is two molecules of pentalene plus one of iron.[4] Its proton nmr spectrum shows a four-proton AB quartet, $|J| = 5.6$ Hz, at τ 3.14 and 3.85,[5] where olefinic protons resonate, and multiplets for the remaining protons at 6.01 and 6.3. The spectrum implies that the structure of the molecule is either III or IV and



III



IV

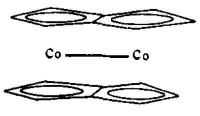


V

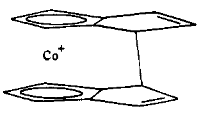
appears to exclude alternative structures, such as V, that lack a new carbon–carbon bond. The closest precedent is the structure of bis(azulene)iron, which has a four-carbon bridge between two ferrocene rings.[6,7] Although the two pentalene rings are presumably united by a carbon–carbon bond, in the molecule's mass spectrum, while the parent ion is the most abundant, the next most abundant (88% as intense at 75 eV) is pentalene cation, $C_8H_6^+$, in which that carbon–carbon bond is absent.[8,9]

The same reaction with cobaltous chloride does not give an analogous product, but gives bis(pentalenylcobalt) (VI), instead. When dilithium pentalenide (9.6 mmol) in THF (10 ml) was stirred with a slurry of cobaltous chloride (10.8 mmol) and THF (30 ml) for 1 hr at room temperature, the solvent distilled, and the residue sublimed at 150° (10^{-3}–10^{-4} mm), we obtained in 4.3–10% yield bis(pentalenylcobalt) (VI), a green-black solid that does not melt below 270°.[10] The structure was assigned on the basis of the mass spectrum,[11] which shows the parent peak as the most abundant ion, the proton nmr spectrum, which consists of a triplet at τ 5.84 and doublet at 6.33, $|J| = 2.2$ Hz, in the intensity ratio 4.16:7.84, and the ir spectrum, which is remarkably similar to that of the nickel analog I.[2,12]

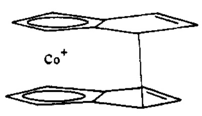
However, oxidizing VI with hydrogen peroxide removes a cobalt atom giving a bis(pentalenyl)cobalticinium ion, which can be isolated as the hexafluorophosphate in 21% yield,[13] and which is isoelectronic and presumably isostructural with bis(pentalenyl)iron. The similarity of the two structures is indicated by the similarity of their proton nmr spectra, the cobalticinium ion like the iron analog showing a four-proton AB quartet, $|J| = 5.5$ Hz, in the olefin region and appropriate resonances around τ 5 for the remaining eight protons.[15] The structure of this ion is thus either VII or VIII. The cobalticinium hexafluorophosphate is an orange solid that does not melt, but darkens when



VI



VII



VIII

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[1] (a) T. J. Katz and M. Rosenberger, *J. Amer. Chem. Soc.*, **84**, 865 (1962); (b) T. J. Katz, M. Rosenberger, and R. K. O'Hara, *ibid.*, **86**, 249 (1964).

[2] T. J. Katz and N. Acton, *ibid.*, **94** 3281 (1972).

[3] If ferric chloride is used in place of ferrous chloride, the yield is 12%.

[4] *Anal.* Calcd for $C_{16}H_{12}Fe$: C, 73.88; H, 4.65; Fe, 21.47. Found: C, 73.83; H, 4.77; Fe, 21.59.

[5] Intensities: 2.12, 2.10, 1.86, 5.96. The solvent was CS_2. The peaks at τ 3.85 are each split into 2.0-Hz doublets.

[6] (a) E. O. Fischer and J. Müller, *J. Organometal. Chem.*, **1**, 464 (1964); (b) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 716 (1969).

[7] Simple two-atom bridged ferrocenes are known; *cf.* H. L. Lentzer and W. E. Watts, *Tetrahedron*, **27**, 4343 (1971).

[8] The only other peaks of greater intensity than 20% of the base peaks [*m/e* 260 (100%), 261 (21%), 262 (4%)] are *m/e* 56 (Fe^+, 37%), 158 ($C_8H_6Fe^+$, 47%), and 202[2] ($C_{16}H_{10}^+$, 27%).

[9] The uv spectrum in *n*-hexane shows the following: λ_{max} 465 nm (ϵ 520), 290 (sh), 246 (9100), 217 (11,400).

[10] *Anal.* Calcd for $C_{16}H_{12}Co_2$: C, 59.65; H, 3.76; Co, 36.59. Found: C, 59.06; H, 4.04; Co, 34.80.

[11] Peaks of greater than 5% intensity at 75 eV: *m/e* 43 (8%), 59 (Co^+, 7%), 102 ($C_8H_6^+$, 9%), 161 ($C_8H_6Co^+$, 11%), 202 ($C_{16}H_{10}^+$, 6%),[1] 263 [$(C_8H_6)_2Co^+$, 11%], 264 (7%), 322 (P^+, 100%), 323 (P^+, 18.5).

[12] The visible spectrum in argon-purged benzene shows a maximum at 369 nm (ϵ 4230) and a tail out to 850 nm.

[13] The elemental analysis, like that of other cobalticinium hexafluorophosphates,[14] was poor. However, the tetraphenylborate was analyzed successfully for C and H. *Anal.* Calcd for $C_{40}H_{32}CoB$: C, 82.48; H, 5.54. Found: C, 82.88; H, 5.41. The analyst's results for Co were inconsistent: calcd, 10.12; found, 11.39, 8.09. Analyses were by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.

[14] J. E. Sheats and M. D. Rausch, *J. Org. Chem.*, **35**, 3245 (1970).

[15] In CD_3CN: AB quartet, $|J| = 5.5$ Hz at τ 2.78 and 3.04, the high-field lines split further into 1.7-Hz doublets (3.86 H) and multiplets at 4.63 (4.14 H), 5.07 (2.07 H), and 5.35 (1.93 H).

heated above *ca.* 265°. It is soluble in acetone and acetonitrile, but only sparingly in chloroform.[16]

An interesting property of the bis(pentalenylcobalt) molecule VI is that it is diamagnetic. Bis(*as*-indacenylcobalt) in contrast is paramagnetic.[17] The implication is that there is a cobalt–cobalt bond in the former and not in the latter, presumably because a bond of normal length (2.5 Å)[18] can be accommodated in the pentalene system,[2] but would be stretched in the *as*-indacene cystem.[19] The iron complex, III or IV, when crystalline is moderately stable in air although it begins to decompose after several hours. Air destroys solutions rapidly. The cobalt complex VI is similarly stable. The cobalticinium compound, VII or VIII, is stable in air both as a solid and in solution.[22]

Thus, at least two kinds of transition metal complexes of pentalene can be formed: those like I or VI in which two metals are sandwiched between a pair of rings, and those like bis(pentalenyl)iron (III or IV) or bis(pentalenyl)cobalticinium ion (VII or VIII), in which one of these metals is removed and the remaining free valencies[23] at carbon unite.

Acknowledgment. We are grateful to the U. S. Army Research Office-Durham for its support under Grant No. DA-ARO(D)-31-124-G1119.

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(16) λ_{max} (CH_3CN) 310 nm (ϵ 6030), 367 (ϵ 3320).

(17) Unpublished experiment in this laboratory by Dr. N. Acton.

(18) M. C. Baird, *Progr. Inorg. Chem.*, **9**, 1 (1968).

(19) The distance between the two iron atoms in bis(*as*-indacenyliron) is 3.887 Å[20] and between the two nickel atoms in bis(*as*-indacenylnickel) 4.40 Å.[21]

(20) R. Gitany, I. C. Paul, N. Acton, and T. J. Katz, *Tetrahedron Lett.*, 2723 (1970).

(21) Prepared by us and X-rayed in the laboratory of Professor Iain C. Paul (unpublished experiments).

(22) Cobalticinium salts are much more resistant to oxidation than are ferrocenes. The simple salts withstand boiling nitric acid, potassium permanganate, and ozone [E. O. Fischer and G. E. Herberich, *Chem. Ber.*, **94**, 1517 (1961)].

(23) J. Thiele, *Justus Liebigs Ann. Chem.*, **306**, 87 (1899).

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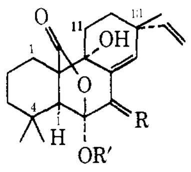
Structures of Fungal Diterpene Antibiotics LL-S491β and -γ

Sir:

We report the isolation and structural elucidation of two novel pimarane diterpenes LL-S491β (**1**) and -γ (**2**) from fermentations of the fungus *Aspergillus chevalieri* (Lederle culture S491). LL-S491β displays significant antibacterial activity against certain gram-positive organisms and LL-S491γ exhibits antiviral activity against *Herpes simplex*. Both compounds possess strong antiprotozoal activity against *Tetrahymena pyriformis*. The isolation of these metabolites is especially noteworthy in that diterpenes appear to be of limited distribution among fungi[1] and the only other pimarane examples have been the virescenols, the glycosides[2] of which also show antibacterial activity.



1, R = O; R′ = H
2, R = β-OH, α-H; R′ = H
3, R = O; R′ = Ac

A pimarane or closely related skeleton[3] for LL-S491β (**1**), $C_{20}H_{26}O_5$, mp 180–185°, $[\alpha]_D$ +112.4° (MeOH), is suggested by the very characteristic eight-line nmr[4] pattern at δ 5.02–5.65 (2 H) and a four-line system at 5.84 (1 H) typical of vinyl protons of a C_{13} vinylidene grouping.[5] Three tertiary C-Me's are indicated by signals at δ 1.09 (3 H, s) and 1.20 (6 H, s), and a doublet in the ir at 1370 cm^{-1} in the spectrum of **1**, **2**, and many of their derivatives suggest that two C-Me's are geminal.[6] Hydroxy, γ-lactone, ketone, and double bond functionalities are indicated by ir bands at 3500, 1755, 1710, and 1620 cm^{-1}, respectively. Two 1 H exchangeable nmr signals at δ 1.90 and 5.25 resonate as sharp singlets indicative of two tertiary hydroxyl groups. Pyridine-catalyzed acetylation of **1** gave monoacetate **3**, containing a broad 1785-cm^{-1} ir band suggestive of a γ-lactol acetate system. The nmr of **3** is devoid of the C_6OH signal at δ 5.25 but the C_9OH proton signal shifts to 2.15.

A uv maximum at 241 nm (ϵ 5850)[7] in the spectrum of **1** supports the presence of an α,β-unsaturated ketone (1710 cm^{-1}) which is cisoid because of the strong intensity of the 1620-cm^{-1} ir absorption.[8] The H_{14} signal resonates at δ 6.86 (J ± 1 Hz)[9] consistent with this view. The unusually high ketone frequency is undoubtedly due to electronic interactions with the nearby oxygen functions and has ample precedent in certain picrotoxinin derivatives.[11]

Borohydride reduction of **1** gave LL-S491γ (**2**), mp 190–195°, $[\alpha]_D$ +69.3° (MeOH), which has only end

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(1) W. B. Turner, "Fungal Metabolites," Academic Press, New York, N. Y., 1971, p 235.

(2) N. Cagnoli-Bellavita, P. Ceccherelli, R. Mariani, J. Polonsky, and Z. Baskevitch, *Eur. J. Biochem.*, **15**, 356, (1970), and references therein; N. Cagnoli-Bellavita, German Offen. 2,100,918 (1971); *Chem. Abstr.*, **75**, 130094*t* (1971).

(3) R. McCrindle and K. H. Overton in "Rodd's Chemistry of Carbon Compounds," S. Coffey, Ed., Vol. II, Part C, Elsevier, London, 1969, Chapter 14.

(4) Satisfactory analyses (high-resolution mass spectral and in some cases elemental) were obtained for all compounds reported; uv spectra were taken in methanol, ir in KBr discs, and nmr spectra in deuteriochloroform at 100 MHz. We thank W. F. Fulmor and L. Brancone and associates for the spectral and analytical data, Dr. G. Van Lear for the mass spectra, and P. Mullen of the Stamford Laboratories for the CD curves. We also wish to thank A. Shay, M. Dann, and associates for the large scale fermentations and initial processing, Dr. H. Tresner for the identification of the culture, and A. Dornbush, Dr. H. Lindsay, H. Lindh, and staffs for the biological testing.

(5) E. Wenkert and P. Beak, *J. Amer. Chem. Soc.*, 83, 998 (1961); see also R. M. Carman, *Aust. J. Chem.*, **16**, 1104 (1963).

(6) K. Nakanishi, "Infrared Spectroscopy-Practical," Holden-Day, San Francisco, Calif., 1962, p 22.

(7) The uv spectrum in basic solution reveals a bathochromic shift of the maximum to 263 nm (ϵ 4600) (reversible on addition of acid) which represents the α-diketone chromophore. No evidence for the diosphenol chromophore was observed in the basic spectrum although prolonged exposure to base caused considerable degradation. The existence of the ketonic form to the apparent exclusion of the enolic structure is reminiscent of the chemistry of xanthoperol and 6,7-diketo-5-isodeoxypodocarponitrile: E. Wenkert and B. G. Jackson, *J. Amer. Chem. Soc.*, **80**, 211 (1958).

(8) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

(9) Spin-decoupling experiments have shown the splitting to be due to a proton in the methylene envelope. This is most likely the C_{12} equatorial hydrogen as this would allow for W-type coupling (see ref 10).

(10) S. Sternhell, *Quart. Rev., Chem. Soc.*, 23, 236 (1969).

(11) R. M. Carman, G. Hassan, and R. B. Johns, *J. Chem. Soc.*, 130 (1959). See also Y. Mazur and F. Sondheimer, *Experientia*, **16**, 181 (1960), and references therein.