This noble metal is made of "base" atoms: atoms of platinum are reactive.

This might have been anticipated as follows. The high boiling point of the metal (>3800°) is evidence of very strong interaction forces. Large interaction forces saturate the combining capacity of an atom. Under these circumstances, the chemical reactivity of the bulk substance bears little resemblance to the chemical reactivity of the atoms. As evidence, the reaction at −196° of carbon atoms with various substrates[2] was not predictable from the chemical properties of graphite or diamond, boiling point ~4200°. As a rough rule of thumb, the higher the boiling point of an element the less is the similarity in chemical properties of the atoms and the bulk element.

By a method similar to that employed in studying carbon atoms,[3] platinum atoms (evaporated from a tungsten filament at 1950°) were generated under high vacuum and were deposited simultaneously with a large excess of substrate on the walls of the vessel which were cooled to −196°. The flight to the walls was collision free, the first encounters of the platinum atoms with substrate being on the cold walls. Reaction products are separated from the large excess of substrate after completion of the deposition.

Propene reacts with platinum atoms. The excess propene was pumped away at low temperature leaving the organoplatinum compounds. Hydrolysis of this residue with water released propene, propane, 2,3-dimethylbutane, 2-methylpentane, and hexane in decreasing amounts, propene being the major hydrolysis product. These isolated products indicate that a minimum of 1.04 mmol of propene had reacted per 1.00 mmol of platinum. Hydrolysis with deuterium oxide produces propene which is mainly unlabeled. This is behavior similar to that observed with atoms of palladium[4] and nickel,[5] but quite different from that observed with aluminum,[6] chromium,[7] zirconium,[8] the lanthanides,[9] etc., wherein deuterium incorporation is high.

A similar reaction occurs with 1-butene. The excess 1-butene is not isomerized in contact with the organoplatinum compound. Isomerization is observed in a number of other metal atom systems (cobalt atoms[10] are especially effective). However, introduction of hydrogen results in catalytic uptake to produce butane.

Platinum atoms react with 1,5-cyclooctadiene. Extraction of the nonvolatile products with hexane and purification by filtration through a column of alumina leaves a colorless residue. The nmr, infrared, and mass spectra are identical with those described earlier[11] for bis(1,5-cyclooctadiene)platinum(0). This compound was isolated in 64% yield.

The product from platinum atoms and 1,3-butadiene is catalytic for the hydrogenation of the excess butadiene at −78°. After reaction of 400 mol of butadiene per mole of platinum, the hydrogenation reaction was stopped with 40% of the butadiene unreacted. The major product was butane; only small amounts of the isomeric butenes were present. This contrasts with the catalytic properties of the usual platinum catalysts.[12]

Allyl chloride reacts with platinum atoms. The product is a yellow solid which decomposes at 160–170° and is sparingly soluble in chloroform and benzene. This yellow compound reacts with triphenylphosphine to yield $[PtCl(C_3H_5)((C_6H_5)_3P)]$, identified by its mass spectrum and decomposition range 180–190° (lit.[13] 182–188°).

Di-π-allyldi-μ-chloro-dipalladium is reported[14] to hydrolyze at 100° to 1 mol of propene, 1 mol of acrolein, 2 mol of hydrogen chloride, and 2 mol of palladium. When 72.7 mg of the platinum–allyl chloride compound is heated in water for 17 hr at 110°, acrolein, 0.126 mmol of propene, and 0.258 mmol (51.6 mg) of platinum are formed. The 2:1 ratio of platinum to propene and the weight per cent of platinum (71%) indicates that the complex has the formula $[Pt(C_3H_5)Cl]_x$ (calcd, 72% Pt). The platinum–allyl chloride adduct is thought to be the known[13] tetranuclear complex $[PtCl(C_3H_5)]_4$, which is reported to decompose at 173–184°. On the basis of the tentative proposal, the yield is 48%.

Acknowledgment The financial support of the Air Force Office of Scientific Research is acknowledged with gratitude.

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(2) P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, 91, 4440 (1969).

(3) P. S. Skell, L. D. Wescott, Jr., J. P. Goldstein, and R. R. Engel, *ibid.*, 87, 2830 (1965).

(4) P. S. Skell and M. J. McGlinchey, in press.

(5) P. S. Skell and M. J. McGlinchey, in press.

(6) P. S. Skell and L. R. Wolf, in press.

(7) P. S. Skell and D. L. Williams-Smith, unpublished results.

(8) P. S. Skell and S. J. Love, unpublished results.

(9) P. S. Skell, M. J. McGlinchey, and D. L. Williams-Smith, in press.

(10) P. S. Skell and F. A. Fagone, in press.

(11) J. Muller and P. Goser, *Angew. Chem., Int. Ed. Engl.*, 6, 364 (1967).

(12) W. G. Young, *et al.*, *J. Amer. Chem. Soc.*, 69, 2046 (1947).

(13) B. E. Mann, B. L. Shaw, and G. Shaw, *J. Chem. Soc. A*, in press.

(14) R. Huttel, J. Krantzen, and M. Buchter, *Chem. Ber.*, 94, 766 (1961).

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The Structure of α-Cyclobutadienyliron Tricarbonyl Carbonium Ions

Sir:

The very pronounced increase in the stability of a carbonium ion following introduction of an α-organometallic substituent has been recognized for some time but the origin of the stabilization remains obscure. The effect is readily seen in the following three examples: (1) the rate of solvolysis of α-ferrocenylcarbinyl acetate is approximately equal to that of trityl acetate,[1a,b] (2) (benzyl chloride)chromium tricarbonyl solvolyzes 10^5 times faster than benzyl chloride itself,[2] and (3) as we have now found, chloromethylcyclobutadieneiron tricarbonyl solvolyzes at least 10^8 times faster than does benzyl chloride.[3] These data indicate that the cations

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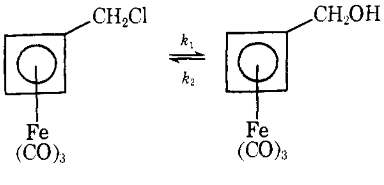
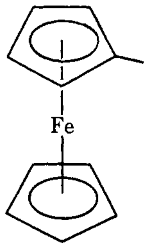
(1) (a) E. A. Hill and S. H. Richards, *J. Amer. Chem. Soc.*, 81, 3483 (1959); 83, 3840, 4216 (1961). (b) For a review of the earlier work in the ferrocene series, see M. Cais, *Organometal. Chem. Rev.*, 1, 435 (1966).

(2) J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometal. Chem.*, 4, 324 (1965); R. Pettit, *Ann. N. Y. Acad. Sci.*, 125, 89 (1965).

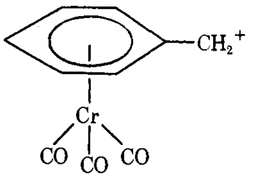
(3) This solvolysis rate was calculated from the rate at which chloromethylcyclobutadieneiron tricarbonyl approaches equilibrium with the alcohol in 5% aqueous acetone. The reaction was monitored by 100-MHz nmr (35°, $k_1 = 1.105 \times 10^{-2}$, $k_2 = 1.520 \times 10^{-2}$). This is a clear



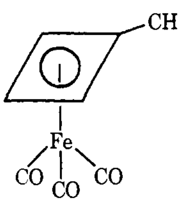
I, II, and III, drawn here as primary carbonium ions, are unusually stable and the question arises as to the nature of the electronic interaction leading to delocalization of the charge. In the case of the ferrocenyl cation



I

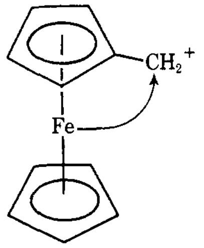


II

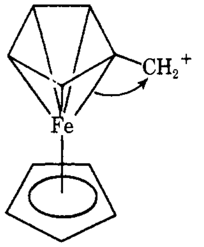


III

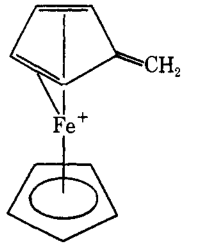
two distinctly different proposals have been suggested: (a) the metal atom moves closer to the exocyclic carbon and directly interacts with it (anchimeric assistance),[1a] structure Ia, and (b) the metal atoms remains roughly symmetrical with respect to the ring and electrons are provided *via* a σ–π interaction resulting in a weakening of the bond between Fe and C$_1$ of the ring (structure Ib),[4] or, in an extreme form of this interaction, structure Ic.[5] Solvolytic and nmr studies have mainly been used to probe the nature of cations but no X-ray structures have been reported. Analogous interactions could also be invoked for explaining the stability of the cations II and III.[2,5] We report here that salts of several cyclobutadienyliron tricarbonyl carbonium ions, IV (R = H), V (R = CH$_3$), VI (R = C$_6$H$_5$), and VII, were isolated as crystalline solids upon treatment of the corresponding carbinols with HBF$_4$ in acetic anhydride followed by precipitation with ether.[6]



Ia



Ib



Ic

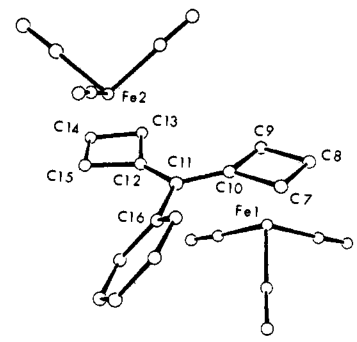
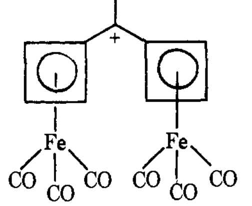
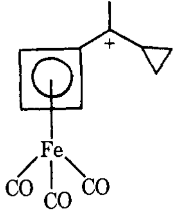


Figure 1. Distances (ångströms) from Fe$_1$ are: C$_7$, 2.04; C$_8$, 2.10; C$_9$, 2.05; C$_{10}$, 2.04; C$_{11}$, 2.85. Distances from Fe$_2$ are: C$_{12}$, 2.03; C$_{13}$, 2.03; C$_{14}$, 2.09; C$_{15}$, 2.03; C$_{11}$, 2.94. Distances in the four-membered rings are: C$_7$–C$_{10}$, 1.47; C$_7$–C$_8$, 1.43; C$_8$–C$_9$, 1.44; C$_9$–C$_{10}$, 1.47; C$_{12}$–C$_{13}$, 1.45; C$_{13}$–C$_{14}$, 1.41; C$_{14}$–C$_{15}$, 1.41; C$_{12}$–C$_{15}$, 1.48. Distances around the central carbon atom are: C$_{10}$–C$_{11}$, 1.39; C$_{11}$–C$_{12}$, 1.41; C$_{11}$–C$_{16}$, 1.47. C–C distances in the phenyl ring range from 1.36 to 1.41 Å, with an average of 1.385 Å. Estimated standard deviations in distances are in the range 0.01–0.02 Å. Angles of twist with respect to the central four-atom plane (C$_{10}$, C$_{11}$, C$_{12}$, C$_{16}$) are: the ring C$_7$–C$_{10}$, 5°; the ring C$_{12}$–C$_{15}$, 8°; the phenyl ring, 43°.

The salts are soluble only in polar solvents such as nitromethane and are deep red materials except for the salt of VII which is yellow. The biscyclobutadienyliron tricarbonyl cations are stable to prolonged exposure to the atmosphere although the monoderivative VII decomposes slowly under these conditions.



IV, R = H
V, R = CH$_3$
VI, R = C$_6$H$_5$



VII

The pertinent results of the X-ray study[7] are given in Figure 1. Details of the data collection, structure solution and refinement, and structural results will be published elsewhere.[8]

The main features which emerge are: (a) the cyclobutadiene rings are very close to being coplanar with the plane formed by the exocyclic carbon and the three carbon atoms to which it is attached (the angles of twist being 5 and 8°), whereas the phenyl ring is twisted 43° from this plane. Thus the main source of stabilization stems from the C$_4$H$_4$Fe(CO)$_3$ moieties rather than from the phenyl ring.[9] (b) The exocyclic carbon lies

indication of the thermodynamic as well as kinetic stabilization of the α carbonium ion. For comparison, a titration experiment in 20% aqueous acetone at 25° gave a half-life of 1.287 × 10^4 sec for (benzyl chloride)chromium tricarbonyl while chloromethylcyclobutadieneiron tricarbonyl was very difficult to follow with a half-life of less than 1.25 × 10^1 sec.

(4) J. C. Ware and T. G. Traylor, *Tetrahedron Lett.*, 18, 1295 (1963); *J. Amer. Chem. Soc.*, **89**, 2304 (1967).

(5) J. D. Fitzpatrick, L. Watts, and R. Pettit, *Tetrahedron Lett.*, 12, 1299 (1966).

(6) The alcohols from which the cations are derived are obtained as follows. For the cation IV, biscyclobutadienyl ketone, obtained following a Friedel–Crafts acylation of cyclobutadiene(carboxyl chloride)iron tricarbonyl with cyclobutadieneiron tricarbonyl was reduced with NaBH$_4$. For V and VI, lithiocyclobutadieneiron tricarbonyl was added to acetylcyclobutadieneiron tricarbonyl and benzoylcyclobutadieneiron tricarbonyl, respectively, and for VII a Friedel–Crafts acylation of cyclobutadieneiron tricarbonyl and cyclopropylcarboxyl chloride was followed by reduction with NaBH$_4$.

(7) Crystals of VI fluoroborate are monoclinic, $P2_1/n$, with a = 14.305, b = 13.430, and c = 11.790 Å, β = 103.44°, and four formula weights per unit cell. Using the 2939 observed reflections of 4178 measured by the stationary crystal–stationary counter technique with Cu Kα radiation, the structure was solved by the heavy atom method. At completion of the refinement by block-diagonal least-squares techniques, using statistically derived weights, the R and weighted R values were 0.063 and 0.047, respectively.

(8) H. D. Simpson and R. E. Davis, manuscript in preparation.

(9) The structures of salts of the cations IV and V are also under investigation by X-ray methods. Although refinement is incomplete as yet, the data indicate structures very similar to that seen in the cation

very nearly in the plane of each cyclobutadiene ring and no significant puckering occurs which would enable the Fe atom to interact more strongly with the exocyclic carbon. (c) The iron atom shows no large displacement from above the center of the cyclobutadiene ring, and the Fe–C$_{11}$ distances are too large (2.85 and 2.94 Å) to support any significant direct metal–exocyclic carbon interaction (the anchimeric effect). The eight iron–ring carbon distances are close to being equal, suggesting the bond energy remains much the same in each case. (d) The carbon–carbon distances of the cyclobutadiene ring remain close to being equal and similar to those in cyclobutadieneiron tricarbonyl itself.[10] This would further suggest that the extreme structure analogous to structure Ic drawn for the ferrocenyl system is not a correct representation.[5, 9]

We conclude that the major interaction leading to stabilization of the cation involves interaction of a filled metal orbital with the four carbon atoms of the cyclobutadiene ring and, through a π–π carbon–carbon interaction, electrons are transmitted to the electron-deficient exocyclic carbon atoms. Anchimeric effects are not involved nor can any one particular iron–carbon bond in the initial cyclobutadieneiron linkage be singled out as being used to provide electrons for the stabilization. By analogy the same kind of stabilization is presumed to occur in the ferrocenylcarbinyl cations and the benzylchromium tricarbonyl systems. Attempts to obtain suitable material to test this are being undertaken.

An additional point of interest concerns the nmr spectrum of the cyclobutadienyl carbonium ions. The nmr spectrum of the cation IV (R = H) at 40° (SO$_2$) consists of sharp singlets at τ 2.74, 4.40, and 4.67 of areas 1:2:4, respectively. The unexpected equivalence of all four ring protons ortho to the point of substitution suggested rapid rotation about the carbon–carbon exocyclic bond. The spectrum shows coalescence at 0°, and at −50° the rotation is apparently stopped[11] for the ortho protons now appear as two doublets each of relative area 2 centered at τ 4.63 and 4.77 (J = 9 Hz); the remaining proton absorptions are unchanged, appearing at 2.77 (s, 1 H) and 4.38 (s, 2 H). Similarly, the nmr spectrum of the methyl derivative V (R = CH$_3$) at 40° consists of three sharp singlets at τ 4.33, 4.76, and 8.28 of relative area 2:4:3, respectively, but on cooling to +15° the spectrum coalesces, and at 10° rotation is halted, the spectrum showing absorptions at τ 4.43 (s, 2 H), 4.66 (d, 2 H, J = 9 Hz), 4.78 (d, 2 H, J = 9 Hz), and 8.30 (s, 3 H).

On the other hand the nmr spectra of the phenyl derivative VI (R = C$_6$H$_5$) and the cyclopropyl system VII show nonequivalent ortho protons in the cyclobutadiene ring at all temperatures up to 50°. Rotation about the exocyclic bond was also not observed previously in other simple alkyl derivatives related to VII.[5] A reasonable explanation for these variations is that the bond order of each exocyclic bond in the biscyclobutadienylcarbinyl cations is considerably lower than that of the monocyclobutadienylcarbinyl cations; the reason the biscyclobutadienylphenyl system VI does not show the rotation at room temperature is possibly due to steric crowding.

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VI. These three salts crystallize with different packing arrangements, in three different space groups, suggesting that the important structural feature of near-coplanarity of the cyclobutadiene rings with the central plane is probably not attributable to packing effects in the crystal.

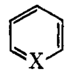
(10) M. I. Davis and C. S. Speed, *J. Organometal. Chem.*, 21, 401 (1970).

(11) Use of an approximative equation (R. J. Karland, M. B. Rubin, and M. B. Wise, *J. Chem. Phys.*, 40, 2426 (1964)) to obtain coalescence temperature rotation rates and the Eyring equation results in the following estimates of the rotational barriers: $\Delta G_{\mathrm{H}}{}^{\ddagger}$ = 13.8 kcal/mol, $\Delta G_{\mathrm{Me}}{}^{\ddagger}$ = 14.7 kcal/mol, $\Delta G_{\mathrm{Ph}}{}^{\ddagger} \gg$ 16.6 kcal/mol (using 50° as a zero-order approximation of the coalescence temperature.)

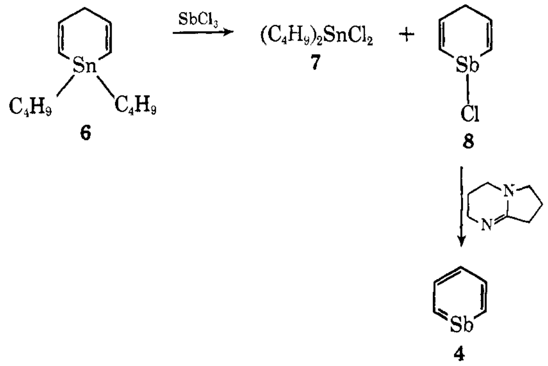
Stibabenzene

Sir:

Multiple bonds to carbon are common for first-row elements but rare outside the first row. A common explanation for the diminished importance of multiple bonds to the heavier atoms is the assumed low strength of such bonds.[1] Our interest in this problem has led us to try to obtain the group V heteroaromatic compounds **1**, **2**, **3**, **4**, and **5**. These compounds would provide a graded series in which carbon is multiply bonded to an entire column of elements and thus should provide detailed information about this bonding as a function of increasing atomic number. The first members of this series, pyridine (**1**), phosphabenzene (**2**),[2] and arsabenzene (**3**),[2] are now available. This communica-



1, X = N
2, X = P
3, X = As
4, X = Sb
5, X = Bi



6 **7** **8** **4**

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(1) To be more correct it has been estimated that single bonds are much stronger than multiple bonds. This may be true but it is necessary to couple this with the kinetic argument that these multiple bonds would be highly reactive in order to explain the rarity of such species. See: K. S. Pitzer, *J. Amer. Chem. Soc.*, 70, 2140 (1948); R. S. Mulliken, *ibid.*, 72, 4493 (1950); D. E. Douglas and D. H. McDaniel, "Concepts and Models of Inorganic Chemistry," Ginn, New York, N. Y., 1965, p 58; R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, New York, N. Y., 1965, pp 3, 8–10, 20.

(2) A. J. Ashe, III, *J. Amer. Chem. Soc.*, **93**, 3293 (1971).