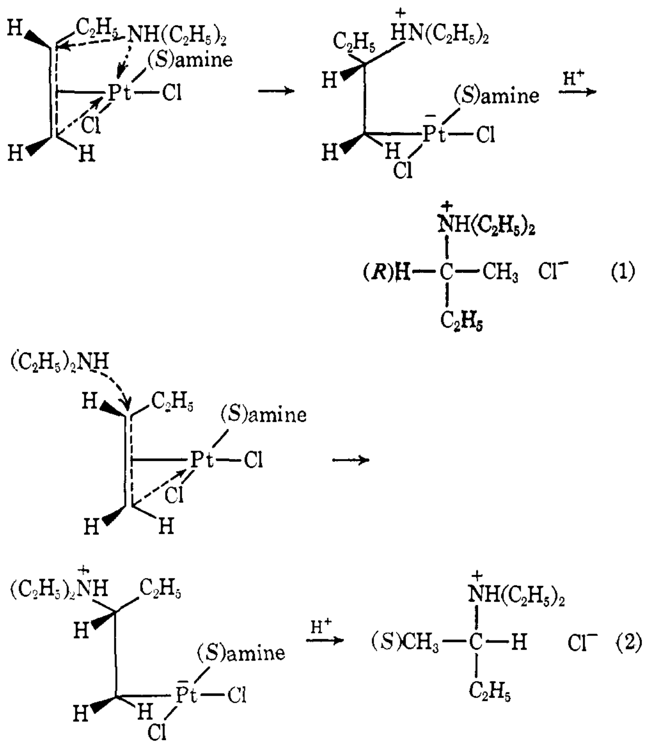
amine with I has been obtained by adding the amine (0.731 g, 0.01 mol) as a 0.2 *M* acetone solution to a stirred ice-cold solution of the complex (4.433 g, 0.01 mol) in the same solvent. The crude alkyl derivative[17] obtained after removal of the solvent was stirred with 37% HCl at room temperature for about 3 hr. The acid hydrolysis gave N,N'-diethyl-*sec*-butylamine hydrochloride in 40% yield, calculated on the starting π complex. The free amine was obtained by means of alkali treatment and purified by gas-chromatographic preparative methods: the identification was made on the basis both of the retention time and of the ir spectrum, compared with those of an authentic sample.

The N,N'-diethyl-*sec*-butylamine obtained by the reaction was the dextrorotatory enantiomer, which has the *S* configuration,[18] with a high optical purity ($[\alpha]^{15}\text{D}$ +85.1°, lit.[19] $[\alpha]^{15}\text{D}$ +89.3°). Scheme I shows a *cis* (eq 1) and a *trans* addition (eq 2) as possible steric paths for the nucleophilic attack. In eq 1 the precoordination of the nucleophile is simply shown as the formation of a pentacoordinated intermediate: it is obvious that the reaction of *any* intermediate containing the nucleophile in *any* given coordination site will yield the same stereochemical result, *i.e.*, the (−)-(*R*)-N,-N'-diethyl-*sec*-butylamine. A *trans* addition will ultimately lead, on the other hand, to the dextrorotatory enantiomer, as has been found.

Scheme I



The reaction of I with ammonia was performed under the same experimental conditions described for the diethylamine reaction. Ammonia, however, was introduced as a gas in the reaction vessel containing the acetone solution of I. Hydrolysis of the reaction product gave in this case *sec*-butylamine as the main product as well as small amounts of other butylamines.[20] The *sec*-butylamine was isolated through preparative gas chromatography and appeared to be the positive enantiomer, $[\alpha]^{15}\text{D}$ +7.56° (lit.[19] $[\alpha]^{15}\text{D}$ +7.80°). This enantiomer has the *S* configuration.[18]

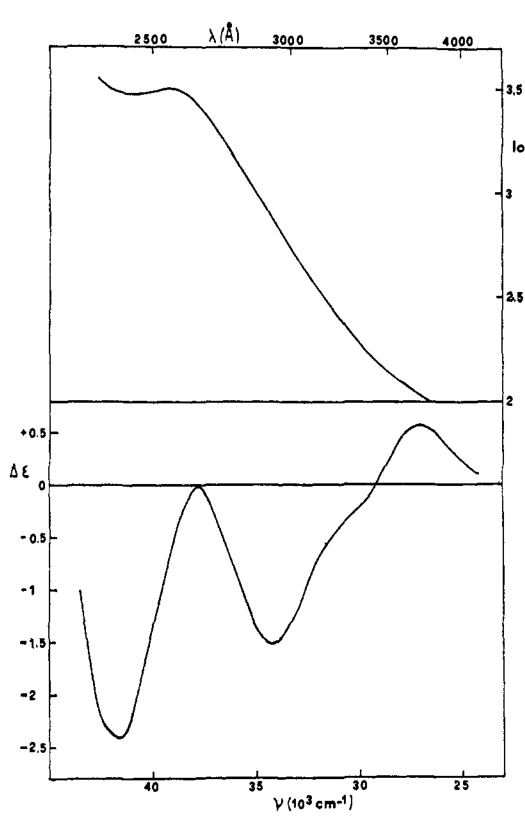


Figure 1. The electron absorption and circular dichroism spectra of complex I in ethanol solution.

These results give straightforward and unambiguous evidence that in the case reported the attack does *not* involve intramolecular rearrangement of an intermediate containing the attacking nucleophile as a coordinated ligand: only the unsaturated substrate has been activated *via* coordination on the metal.

Acknowledgment. This work was performed with the financial support of the Italian Consiglio Nazionale delle Ricerche (CNR).

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configurational assignment: C. Pedone and E. Benedetti, private communication.

[17] The subsequent demolition reaction indicates that the addition product appears of the same type as those obtained in addition reactions of amines with complexes containing α olefins and phosphine donors (see ref 12). It is worth mentioning that in this case stabilizing π ligands are not present. Furthermore the attack direction is different in the two cases. In fact, attack of diethylamine on *cis*-dichloro(1-butene)(tri-*n*-butylphosphine)platinum(II) leads to an equimolecular mixture of N,N'-diethyl-*n*-butylamine and N,N'-diethyl-*sec*-butylamine.

[18] A. Kjaer and S. H. Hanson, *Acta Chem. Scand.*, 11, 898 (1957).

[19] W. Leithe, *Ber.*, 63, 804 (1930).

[20] The multiple alkylation of ammonia in the presence of coordinated olefins has been discussed in a previous paper,[12] where analogous addition reactions with phosphine-containing complexes were reported.

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Received February 24, 1970

Preparation and Structure of a Novel Tetracyanoethylene Complex of Iridium

Sir:

Whereas the reactions of a number of activated olefins with the hydrido complexes $IrH(CO)(PPh_3)_3$,[1]

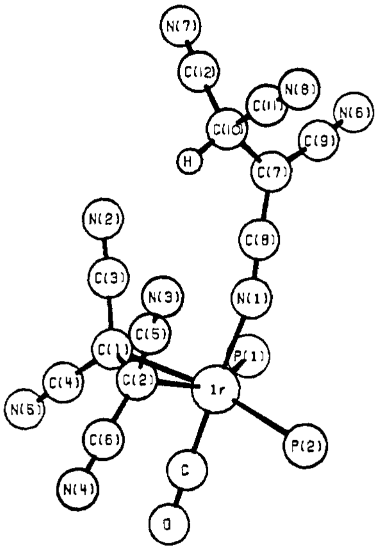


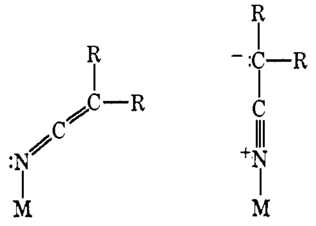
Figure 1. A drawing of the inner coordination sphere about Ir in $Ir(C_6N_4H)(CO)(TCNE)(PPh_3)_2$. Selected bond distances (Å) are: C(1)–C(2), 1.526 (12); C(7)–C(8), 1.394 (13); C(7)–C(9), 1.397 (13); C(7)–C(10), 1.511 (12); C(10)–C(11), 1.467 (14); and C(10)–C(12), 1.488 (15).

$IrH(CO)_2(PPh_3)_2$,[2] and $IrH_3(CO)(PPh_3)_2$[2] (Ph = phenyl) yield the hydrido-π-olefinic complexes IrH(CO)(activated olefin)$(PPh_3)_2$ by displacement of triphenylphosphine, carbon monoxide, and hydrogen, respectively, the reaction of the highly activated olefin tetracyanoethylene (TCNE) with these substances is more complex and gives a novel product.[3]

Addition of a benzene solution of $IrH(CO)_2(PPh_3)_2$ to a fourfold excess of TCNE in benzene at room temperature gives a deep orange solution as bubbles of CO gas are evolved and simultaneously an orange-yellow solid separates. After 0.5 hr of stirring, the solid may be collected and recrystallized from dichloromethane–benzene to give a good yield (70%) of bronze-colored crystals, mp 165–180° dec, whose elemental analysis indicates that the elements of two molecules of tetracyanoethylene per iridium atom are present.[4] *Anal.* Calcd for $C_{49}H_{31}ON_8P_2Ir \cdot {}^1/_2C_6H_6$: C, 59.9; H, 3.3; N, 10.8; P, 5.9; mol wt, 1040. Found: C, 58.7; H, 3.0; N, 10.7; P, 5.9; mol wt, 904 (osmometric in $CHCl_3$). Bands included in the infrared spectrum and their assignments are: 2233 sh ($\nu_{C\equiv N}$), 2220 s ($\nu_{C\equiv N}$), 2168 vs ($\nu_{N=C=C}$ asym), 2080 vs ($\nu_{C\equiv O}$), and 1355 w ($\nu_{N=C=C}$sym). The nmr spectrum shows a singlet at τ 5.8 whose integrated intensity is *ca.* ${}^1/_{30}$ that of the phenyl protons. These data are consistent with the compound being (cyano[dicyanomethyl]keteniminato)carbonyl(tetracyanoethylene)bis(triphenylphosphine)iridium, and an X-ray study establishes this formulation. The crystals belong to the monoclinic system, space group $P2_1/c$, with cell dimensions a = 13.01, b = 16.10, c = 21.74 Å, and β = 94.5°. The observed density of 1.54 g/cm^3 may be compared with that of 1.52 g/cm^3 calculated for four formula units of $Ir(C_6N_4H)(CO)(TCNE)(PPh_3)_2 \cdot {}^1/_2C_6H_6$ per cell. Intensity data were collected on a Picker four-circle automatic diffractometer in the manner previously described.[5] The structure was solved and refined by standard procedures. At the current state of refinement, the conventional R factor is 6.2%.

In Figure 1, it is seen that the geometry about iridium is trigonal bipyramidal with the two P atoms and the TCNE in the equatorial plane. The average Ir–P and coplanar Ir–C distances are 2.40 and 2.18 Å, respectively, and are very similar to those found in $IrBr(CO)(TCNE)(PPh_3)_2$.[6,7] The C of the carbonyl group (Ir–C = 1.79 Å) is at one axial position and the N of the nitrogen-bonded cyano(dicyanomethyl)keteniminato ligand is at the other axial position. The Ir–N(1) distance is 2.02 Å and the Ir–N(1)–C(8) angle is 162°. Formulation of the complex as a cyano(dicyanomethyl)keteniminato compound is assured, both because of the presence of the Ir–N bond and because the bond angles of 110° around C(10) indicate sp^3 hybridization and the attachment of the H atom, originally bonded to Ir, to that carbon atom. The bond angles about C(7) average 120°.

Heretofore little was known of the nature of a keteniminato–transition metal bond even though a few complexes of this type have been previously synthesized.[8] In the valence-bond context, resonance structures such as I and II can be drawn, and the M–N–C bond angle may be indicative of the relative contributions of I and II. The angle of 162° in the present compound suggests to us that the zwitterionic form II is the more important canonical form. With a formal positive charge on the nitrogen atom in form II, we expect the keteniminato ligand to serve as a moderately good π-acceptor function in complexes of low-valence metals, particularly if the R groups are electronegative substituents. The carbon monoxide stretching frequency of 2080 cm^{-1} in the complex reported herein is noticeably higher than the 2055–2065-cm^{-1} range found previously[9] for $IrZ(CO)(TCNE)(PPh_3)_2$ (Z = Cl, Br, I, NCO), and these data imply that the electron density on the iridium atom is less in the keteniminato complex. This condition would be expected to lead to a lengthening of the Ir–CO distance; but unfortunately, a comparison cannot be made with the Ir–CO bond in $IrBr(CO)(TCNE)(PPh_3)_2$, as this bromo complex is disordered.



I II

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(1) W. H. Baddley and M. S. Fraser, *J. Amer. Chem. Soc.*, **91**, 3661 (1969).

(2) M. S. Fraser and W. H. Baddley, in preparation.

(3) A previous mention (ref 1) that $IrH(CO)(TCNE)(PPh_3)_2$ is obtained from $IrH(CO)(PPh_3)_3$ and TCNE is now known to be incorrect.

(4) The X-ray study shows that the crystals contain 0.5 molecule of benzene per atom of iridium.

(5) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(6) J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968).

(7) L. Manojlovic-Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, **47**, 84 (1969).

(8) (a) W. Beck, W. Hieber, and G. Neumair, *Z. Anorg. Allg. Chem.*, **344**, 285 (1966); (b) W. Beck, R. E. Nitzschmann, and H. S. Smedal, *J. Organometal. Chem.*, 8, 547 (1967); (c) S. R. Su, J. A. Hanna, and A. W. Wojcicki, *ibid.*, 21, P21 (1970).

(9) W. H. Baddley, *J. Amer. Chem. Soc.*, **90**, 3705 (1968).

A reasonable reaction path for the herein described synthesis of $Ir(C_6N_4H)CO(TCNE)(PPh_3)_2$ would involve initial formation of a hydrido-π-olefinic complex, followed by a 1,4-addition[8c] to the TCNE to give a coordinatively unsaturated planar iridium(I) complex. That 1,4 addition occurs with tetracyanoethylene instead of the usual 1,2 addition as with unsaturated hydrocarbons is understandable in view of the electronic structure of TCNE, for which calculations[10] have shown a buildup of negative charge on the nitrile nitrogens relative to the olefinic carbon atoms. Thus, transfer of H as hydride is implied and the electrophilic iridium attacks a nitrogen atom to give $Ir(C_6N_4H)(CO)(PPh_3)_2$. Subsequent reaction of this coordinatively unsaturated compound with a second molecule of TCNE would give the product. Allowing for Ir–H addition being 1,4 instead of 1,2, these reaction steps are analogous to those often proposed in the polymerization of olefins as catalyzed by transition metal catalysts, and the structure reported herein is the first to be described of such a model intermediate compound in olefin polymerization.

Acknowledgment. This work was supported by grants from the National Science Foundation.

(10) J. Halper, W. D. Closson, and H. B. Gray, *Theor. Chim. Acta*, 4, 174 (1966).

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Received March 11, 1970

Dynamic Stereochemistry—a Comparator for Electron Impact and Pyrolytic Elimination of Acetic Acid from Acetates[1]

Sir:

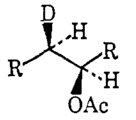
Electron impact induced elimination reactions are demonstrably sensitive to the differences between diastereotopic hydrogens.[2] We now report the utilization of such stereochemically nonequivalent groupings[3] in a study of the 1,2 elimination of acetic acid from 2-butyl acetate and 1,2-diphenyl ethyl acetate which not only uncovers the conformational prerequisites for reaction but also demonstrates that these fragmentations follow a course which parallels their pyrolytic counterparts.[4] The diastereomeric 3-deuterio *sec*-butyl acetates (**1** and **2**)[5] and 2-deuterio-1,2-diphenyl ethyl acetates (**3** and **4**) were prepared as described.[6,7] Table I presents the compounds studied as well as the mass spectral data for loss of acetic acid from these materials.

Table I[a,b]

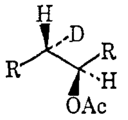
Compd	M − DOAc/M − HOAc	
	70 eV	15 eV
1	25/75	27/73
2	16/84	18/82
3	49/51	50/50
4	24/76	24/76

[a] The spectra were obtained on an MS-902 spectrometer at *ca.* 50° source temperature *via* direct inlet for **3** and **4** and ambient temperature glass inlet for **1** and **2**. [b] The deviations in Table I are *ca.* ±2% (absolute) for the 70-eV runs and ±1% (absolute) for the low-voltage data. The low temperature was attained with a water-cooled source with air and/or water as the coolant. The electron voltages are nominal.

The data in Table I reveal both a stereochemical dependence as well as a greater average loss of deuterated acetic acid from **3** and **4** over **1** and **2**. The latter result most likely derives from the intervention of abstraction from the undeuterated methyl groups in **1** and **2**,[8] in contrast with the C-2 site specificity in **3** and **4**. The mass spectra of 1,2,2-trideuterio- and 2,2-dideuterio-1,2-diphenyl ethyl acetates[9] exhibit no loss of HOAc demonstrating the sole C-2 elimination in **3** and **4**.



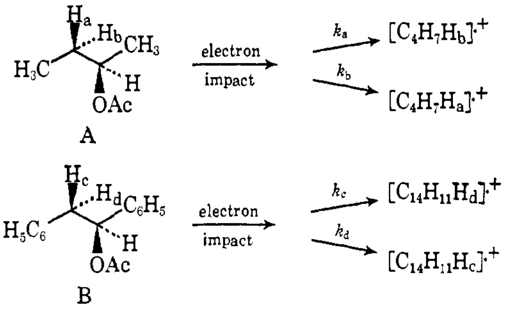
1, R = CH_3
3, R = C_6H_5



2, R = CH_3
4, R = C_6H_5

Chart I exhibits the kinetic relationships for the elimination of the diastereotopic hydrogens from both *sec*-butyl acetate and 1,2-diphenyl ethyl acetate. Our present task is to transpose the data in Table I into quantitative assignments for k_a/k_b and k_c/k_d and thereby into the conformational insights we seek.

Chart I[a]



[a] The rate constants shown represent values averaged over the range of energy states accessible to the reacting molecular ions.

Curtin[6] has previously shown in the case of the pyrolysis of **3** and **4** that k_c/k_d is equal to the square root of the product of the deuterated to undeuterated stilbene in **3** and undeuterated to deuterated stilbene in **4**. Since in the mass spectrometer we may equate the ratio of two ion intensities to the rate constants for the formation of the ions,[10] it will follow that Curtin's analysis[6] may be

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(1) This research has been carried out with the support of a grant from the National Institute of General Medical Sciences.

(2) M. M. Green, *J. Amer. Chem. Soc.*, **90**, 3872 (1968).

(3) K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).

(4) C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

(5) P. S. Skell and W. L. Hall, *J. Amer. Chem. Soc.*, **86**, 1557 (1964).

(6) D. Y. Curtin and D. B. Kellom, *ibid.*, **75**, 6011 (1953).

(7) All deuterated compounds including intermediates were shown to be identical with authentic proteum materials by either melting point and/or vapor phase chromatography.

(8) Earlier work on acetates has demonstrated abstraction from various β positions as well as some 1,3 loss of acetic acid. See: W. Benz and K. Biemann, *J. Amer. Chem. Soc.*, **86**, 2375 (1964); W. S. Briggs and C. Djerassi, *J. Org. Chem.*, **33**, 1612 (1968).

(9) Determined under conditions identical with those for the data in Table I. The compounds were prepared by Grignard reaction of the appropriately deuterated benzyl chloride and benzaldehyde. Monodeuteriobenzaldehyde was prepared as reported previously: D. Seebach, B. W. Erickson, and G. Singh, *ibid.*, **31**, 4303 (1966).

(10) The ion intensities (*e.g.*, M − HOAc/M − DOAc) are related to each other exactly as would be the weight of two products obtained from a single starting material in a unimolecular competition, namely as the