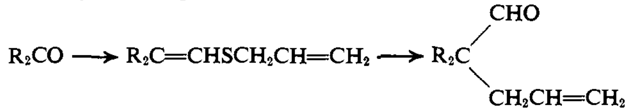
Table I. Conversion of Carbonyl Compounds into Unsaturated Aldehydes by the Wittig Reaction–Thio-Claisen Rearrangement Sequence



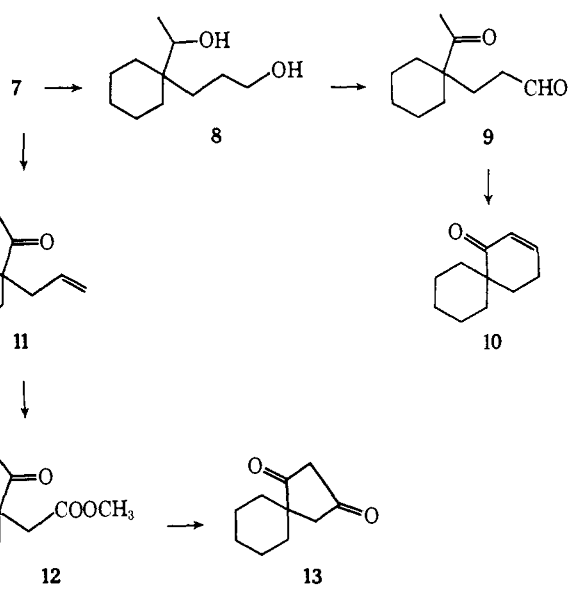
$$R_2CO \longrightarrow R_2C{=}CHSCH_2CH{=}CH_2 \longrightarrow R_2C\begin{cases}CHO\\ CH_2CH{=}CH_2\end{cases}$$

Starting carbonyl compound	Yield of vinyl sulfide, %^{a}	Yield of aldehyde, %^{c}
Cyclohexanone	83	82^d
Cyclooctanone	19^b	72^e
Cyclododecanone	54^b	74^e
Fluorenone	81	43^{f,g}
Norbornanone	65	83^{d,h}
Adamantanone	72	45^f
Camphor	Trace	
Benzaldehyde	83	39^d

[a] Purified by preparative tlc on silica gel; all vinyl sulfides gave satisfactory elemental analyses. [b] Reaction carried out in 10:1 tetrahydrofuran–hexamethylphosphorictriamide. [c] Purified by distillation; the 2,4-DNP derivatives all gave satisfactory elemental analyses. [d] Reaction time 10 min at 190°. [e] Reaction time 2 hr at 190°. [f] Reaction time 2 hr at 210°. [g] Purified by distillation followed by preparative tlc. [h] As a 3:2 mixture of epimers.

reactions. This technique should broaden the scope and utility of the thio-Claisen rearrangement.[9] Table I records the results of a number of mercuric oxide promoted thio-Claisen rearrangements as well as data on the preparation of the requisite allyl vinyl sulfides.

The following transformations illustrate the utility of α-allyl alicyclic aldehydes in the synthesis of spiro compounds using as an example the monocyclic intermediate 7. The individual steps were performed following standard procedures with no attempt at optimization. The diol **8**[2b] was obtained (86%) from **7** by reaction with methyllithium and subsequent hydroboration with disiamylborane.[10] Oxidation of **8**[11] gave keto aldehyde **9**[2b] (45%) which yielded the spiro enone **10**[2] (44%) by treatment with potassium hydroxide in methanol at reflux. The unsaturated ketone **11**,[2] formed in 88% yield from **7** by reaction with methyllithium followed by oxidation,[11] was transformed into the ester **12**[2] in 40% yield by the sequence: (a) ethylene ketalization with ethylene glycol in the presence of methyl orthoformate-*p*-toluenesulfonic acid[12] and (b) oxidative cleavage of C=C to CHO[13] followed by ketal hydrolysis and conversion of the aldehyde to carboxylic acid[14] and methyl ester **12** (CH_2N_2). As previously demonstrated,[15] the ester **12** undergoes facile cyclization to the spiro diketone **13**.



The chain extension, spiro annulation, and mercuric oxide-promoted thio-Claisen rearrangement described above should be of considerable value in synthesis. There is flexibility relative to the ketonic substrate, the allylic grouping introduced (*e.g.*, methallyl instead of allyl), and the reactions used for chain elaboration and cyclization.[16]

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(9) Although the thio-Claisen rearrangement of simple allyl vinyl sulfides has not previously been reported, there is ample precedent for thio-Claisen rearrangements in other systems. See (a) H. Kwart and M. H. Cohen, *J. Org. Chem.*, 32, 3135 (1967); (b) H. Kwart and T. J. George, *Chem. Commun.*, 433 (1970); (c) Y. Makisumi and A. Murabayashi, *Tetrahedron Lett.*, 2449 (1969); (d) L. Brandsma and D. Schuijl-Laros, *Recl. Trav. Chim. Pays-Bas*, **89**, 110 (1970); (e) P. J. W. Schuijl, H. J. T. Bos, and L. Brandsma, *ibid.*, 88, 597 (1969); (f) C. Y. Meyers, C. Rinaldi, and L. Bonoli, *J. Org. Chem.*, 28, 2440 (1963); (g) B. W. Bycroft and W. Landon, *Chem. Commun.*, 168 (1970).

(10) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 1241 (1961).

(11) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

(12) A. Marquet, M. Dvolaitzky, H. B. Kagan, L. Mamlok, C. Ouannes, and J. Jacques, *Bull. Soc. Chim. Fr.*, 1822 (1961).

(13) R. Pappo, D. S. Allen, Jr., R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, 21, 478 (1956).

(14) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(15) B. D. Akehurst and J. R. Bartels-Keith, *ibid.*, 4798 (1957).

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Preparation and Structure of $[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2][BF_4]\cdot CH_2Cl_2$, an Unusual Iridocycle

Sir:

Considerable attention has been given recently to the oxidative addition reactions[1] of coordinatively unsaturated transition element compounds. In view of its reactivity the d^8 system, $IrCl(CO)(PR_3)_2$, has been of special interest.[2] Herein, we report the preparation and structural determination of *trans*-$[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2][BF_4]\cdot CH_2Cl_2$, I, a novel species formed when the addendum is the π-aromatic cation, $[C_3(C_6H_5)_3]^+$.

Addition of triphenylcyclopropenium tetrafluoroborate to a methanolic solution of *trans*-$IrCl(CO)(P(CH_3)_3)_2$ and recrystallization of the product from a CCl_4–CH_2Cl_2 mixture yielded intense purple crystals of the complex I. *Anal.* Calcd for $IrC_{29}H_{35}OBF_4Cl_3P_2$: C, 41.10; H, 4.17; Cl, 12.58; P, 7.32. Found: C, 40.25; H, 4.06; Cl, 13.20; P, 7.12. Infrared spectrum (KBr pellet): ν(C–O) = 2060 cm^{-1}.

trans-$[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2][BF_4]\cdot CH_2Cl_2$ crystallizes in the orthorhombic space group $P2_12_12_1$

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(1) J. P. Collman and W. R. Roper, *Advan. Organometal Chem.*, 7, 53 (1968), and references therein.

(2) See, for example, L. Vaska, *Accounts Chem. Res.*, 1, 335 (1968); A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1562 (1969); J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, 7, 1298 (1968).

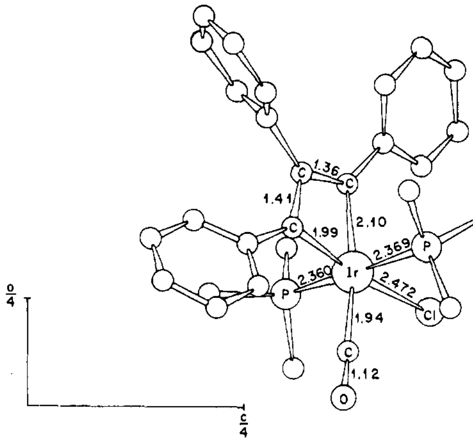

Figure 1. The $[(C_3(C_6H_5)_3)IrCl(CO)(P(CH_3)_3)_2]^+$ ion as viewed along the crystallographic *b* axis. Standard deviations are as follows: Ir–P, Ir–Cl, 0.005 Å; Ir–C, 0.015 Å; C–C, 0.02 Å.

with unit cell dimensions $a = 9.808$ (1), $b = 17.758$ (2), $c = 19.971$ (3) Å; $Z = 4$; $D_{\text{calcd}} = 1.61$ g cm^{-3}; $D_{\text{obsd}} = 1.62$ g cm^{-3}. The moving-crystal, moving-counter technique and Cu Kα radiation were used to collect intensity data ($2\theta_{\text{CuK}\alpha} \leq 140°$). The structure was solved using standard heavy-atom techniques and refined to a conventional R factor of 0.060 for the 3257 reflections whose intensities were greater than two times their estimated standard deviations.

Solution of this structure affords a singularly significant fact: the cyclopropenium ring is opened by and adds oxidatively to $IrCl(CO)(P(CH_3)_3)_2$ to form the product, I. In this molecule the iridium(III) ion has a distorted octahedral environment formed by two trans phosphine groups, a chlorine atom, carbon monoxide, and two carbon atoms of the propenium fragment (Figure 1). An interior C–Ir–C angle of 64.5 (3)° represents the greatest angular distortion from idealized octahedral geometry in the complex. Both of the Ir–Cl and Ir–C(O) distances are long since they are trans to a σ-bonded carbon atom. A trans lengthening of similar magnitude was found for Ir(III)–Cl bonds in $[Ir(CO)_2Cl_2(CH_3)]_2$[3] and the benzylacetophenone complex, $IrCl_2(C_{15}H_{13}O)((CH_3)_2SO)_2$,[4] where the chlorine atom is trans to a methyl and methylene group, respectively. The two iridium–carbon bonds within the iridocycle differ in length by 0.11 Å which is presumably due to the dissimilar trans influence of the CO and Cl groups. Mason and coworkers have noted an analogous asymmetry in metal–carbon bond lengths arising from different trans ligands in the π-allyl derivatives $(\pi\text{-}CH_3C_3H_4)Pd(Cl)(P(C_6H_5)_3)$[5] and $[(\pi\text{-}C_3H_5)_2RhCl]_2$.[6]

The metallocyclic portion of the molecule is essentially planar (disregarding the substituent phenyl groups) and the two iridium–carbon bond lengths are within the range expected for an Ir(III)–C(sp^2) distance when there is no appreciable dπ–pπ interaction. An average value of 1.385 (15) Å was found for the two carbon–carbon distances in the propenium fragment, which is very nearly equal to that determined (1.373 (5) Å) for the uncomplexed cyclic ligand in $(Ph_3C_3)(ClO_4)$.[7] The transannular distances of 2.61 (Ir–C) and 2.12 Å (C–C) are dictated mainly by the stereochemistry of a planar four-membered ring system and indicate little or no bonding interaction. Inasmuch as there is no evidence for a significant π interaction between the carbon and iridium atoms, the two π electrons associated with the original $(C_3Ph_3)^+$ species appear to remain localized on the propenium group.

To our knowledge this is the first authenticated example of the oxidative addition of a metal ion across a carbon–carbon bond. We draw attention to the striking similarity between this complex and the intermediate recently postulated[8] for the valence isomerism of cubane and its derivatives. Other metal-atom-induced cleavages of three-membered ring systems are known, such as the formation of the cyclopropane derivative,[9] $[PtCl_2(C_3H_6)]_4$, and the reaction[10] of $C_3H(C_6H_5)_3$ with $PdCl_2(C_6H_5CN)_2$ to give a π-allylic derivative of palladium(II). Coordinatively unsaturated d^{10} complexes might also be expected to react with $(C_3Ph_3)^+$, and studies along these lines are in progress.

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(3) N. A. Bailey, C. J. Jones, B. L. Shaw, and E. Singleton, *Chem. Commun.*, 1051 (1967).

(4) M. McPartlin and R. Mason, *ibid.*, 545 (1967).

(5) R. Mason and D. R. Russell, *ibid.*, 26 (1966).

(6) M. McPartlin and R. Mason, *ibid.*, 16 (1967).

(7) M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, 88, 198 (1966).

(8) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, 92, 3515 (1970).

(9) S. E. Binns, R. H. Cragg, R. D. Gillard, B. T. Heaton, and M. F. Pilbrow, *J. Chem. Soc. A*, 1227 (1969).

(10) P. Mushak and M. A. Battiste, *J. Organometal. Chem.*, 17, P46 (1969).

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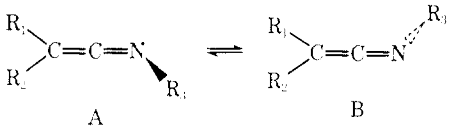
Ketenimines. Geometry and Barriers to Racemization

Sir:

In continuation of our studies on barriers to configurational interconversion in cumulenes,[1,2] we wish to report on the geometries and barriers to racemization of the ketenimines Ia and Ib.



Ia, R_1 = phenyl; R_2 = isopropyl; R_3 = phenyl
Ib, R_1 = methyl; R_2 = isopropyl; R_3 = phenyl

In analogy with carbodiimides,[2] ketenimines can be expected to have a linear C=C=N moiety and dihedral angles of 90° between the C and N substituents (*e.g.*, R_1 and R_2 in I). A ketenimine with different substituents R_1 and R_2 should be chiral, and in such a compound an isopropyl substituent should have diastereotopic methyl groups which might be differentiated by nmr.

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(1) R. Kuhn, B. Schulz, and J. C. Jochims, *Angew. Chem.*, 78, 449 (1966).

(2) F. A. L. Anet, J. C. Jochims, and C. H. Bradley, *J. Amer. Chem. Soc.*, 92, 2557 (1970).