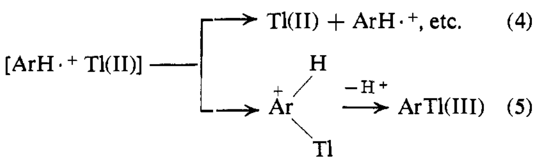
gests that such processes may be more widely operative with other substrates than commonly believed. It represents a viable alternative to the formulation of Tl(III) invariably as a two-electron oxidant, as in the recently described oxidative coupling of phenols.[7]

(b) The formation of arene cation radicals with TTFA may implicate them as common intermediates in the thallation process, *e. g.*

$$\mathrm{Tl(III)} + \mathrm{ArH} \rightleftharpoons [\mathrm{ArH\ Tl(III)}] \quad (3a)$$

$$[\mathrm{ArH\ Tl(III)}] \rightleftharpoons [\mathrm{ArH}\cdot^{+}\mathrm{Tl(II)}] \quad (3b)$$



$$[\mathrm{ArH}\cdot^{+}\,\mathrm{Tl(II)}] \longrightarrow \mathrm{Tl(II)} + \mathrm{ArH}\cdot^{+}\text{, etc.} \quad (4)$$

$$[\mathrm{ArH}\cdot^{+}\,\mathrm{Tl(II)}] \longrightarrow \overset{+}{\mathrm{Ar}}(\mathrm{H})(\mathrm{Tl}) \xrightarrow{-\mathrm{H}^{+}} \mathrm{ArTl(III)} \quad (5)$$

The transient colors observed on mixing arenes with TTFA suggest the initial formation of charge-transfer complexes (eq 3).[8] Aromatic substitution can then proceed by collapse of the cage species (eq 5), or the arene cation radical can be observed after diffusive separation (eq 4).[9]

(c) Tl(III) allows the generation of a variety of metastable arene cation radicals for esr study under *static* conditions. Herefofore, the one-electron oxidant, cobalt(III) trifluoroacetate, has been employed in a rapid mixing flow method, which is costly and much less convenient.[10] Furthermore, the lines of the spectra are broader due to the concomitant formation of the paramagnetic Co(II) species. Co(III) and Pb(IV)[11] are not suitable oxidants for esr studies of reactive arene cation radical in a static system.

Acknowledgment. We wish to thank the National Science Foundation for financial support and Mr. John Powers for TTFA and helpful discussions.

(7) M. A. Schwartz, B. F. Rose, and B. Vishnuvajjala, *J. Amer. Chem. Soc.*, **95**, 612 (1973).

(8) Low-temperature studies indicate that the absorption maxima with different arenes vary in the same way as those of the corresponding tetracyanoethylene–arene complexes (J. W. Powers, unpublished results).

(9) (a) The esr studies do not *prove* that these processes are related by a common intermediate, but it is the most economical explanation. (b) We could find no evidence that the disproportionation in eq 2 is reversed in trifluoroacetic acid. Thus, various mixtures of Tl(III) and Tl(I) trifluoroacetates afforded no paramagnetic species whose esr spectrum could be observed at various temperatures.

(10) R. M. Dessau, S. Shih, and E. I. Heiba, *J. Amer. Chem. Soc.*, **92**, 412 (1970); *J. Chem. Phys.*, **57**, 1200 (1972).

(11) *Cf.* R. O. C. Norman, D. Allara, and B. C. Gilbert, *Chem. Commun.*, 319 (1965).

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Stereochemistry of Methoxypalladation of 2-Butenes

Sir:

Unfortunately, the suggestion[1] that the mechanism of the Wacker oxidation of olefins involved cis stereochemistry in the rate-determining hydroxypalladation step has been generally accepted and assumed to apply to all the similar reactions in which nucleophilic attack on olefins coordinated to palladium(II) and platinum(II) take place. The cis hydroxypalladation mechanistic suggestion was based primarily on kinetic results, but the data are also consistent with trans stereochemistry for the addition. Thus, the stereochemical path of the methoxypalladation and methoxyplatination of chelating diolefins, which was demonstrated to take place trans in every case,[2] was regarded as anomalous.

In order to explain this assumed anomaly, it was suggested[3–5] that the reaction of the bicyclic chelating diolefins followed the trans stereochemical path for steric reasons. On the basis of an incorrect structural assignment to the 1,5-cyclooctadiene oxypalladation product,[6] it was also suggested[3] that this addition, contrary to the stereochemical path reported originally,[2] took place to give the cis addition product; X-ray structural determinations have verified the original stereochemical assignments, however.[7] The trans stereochemistry has also been attributed either to the inability of the chelating diolefins to rotate 90° from the position perpendicular to the square plane of the metal complex into a position which would favor cis addition by metal and a ligand attached to it,[8] or to the fact that methanol does not coordinate to the metal prior to addition.[9] There is increasing evidence, however, that when a nucleophile such as acetate,[10] chloride,[11] or amine[12] is not coordinated to palladium prior to attack, the addition stereochemistry is trans, even with simple monoolefins.[13]

In the course of a study designed to explore the synthetic utility of the palladium(II)–copper(II) Wacker-type catalyst for the conversion of methanol solutions of monoolefins to β-methoxy esters in the presence of carbon monoxide, the carbonylation of *cis*- and *trans*-2-butene was carried out. In this way we have been able to determine the stereochemistry of the methoxypalladation reaction since, although the intermediate oxymetallation product is unstable, and cannot be isolated, it can be trapped by carbon monoxide "insertion," a reaction which has been demonstrated to proceed with *100% retention at the carbon bearing the palladium.*[14]

The results of the catalytic carbonylation of *cis*- and *trans*-2-butene (Table I) show that in the initial stages of the reaction, stereospecific trans methoxypalladation is observed, yielding exclusively the *threo*- and *erythro*-β-methoxy esters, respectively. In the later stages of the reaction cis–trans isomerization of both butenes becomes increasingly important such that trans methoxypalladation to the cis–trans mixtures yields both erythro and threo products. The rate of methoxypalladation of *cis*-2-butene is approximately three times faster than that of the trans isomer.

(1) (a) P. M. Henry, *J. Amer. Chem. Soc.*, **86**, 3246 (1964); (b) *ibid.*, **88**, 1595 (1966).

(2) J. K. Stille and R. A. Morgan, *ibid.*, **88**, 5135 (1966).

(3) P. M. Henry, *Advan. Chem. Ser.*, No. 70, 151 (1968); *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14**, F17 (1969).

(4) R. F. Heck, *Fortschr. Chem. Forsch.*, 16, 221 (1971).

(5) M. Green and R. I. Hancock, *J. Chem. Soc. A*, 2054 (1967).

(6) C. B. Anderson and B. J. Burreson, *Chem. Ind.*, 620 (1967).

(7) (a) W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 310 (1966); (b) C. Panattoni, G. Bombieri, E. Forsellini, B. Crociani, and V. Belluco, *ibid.*, 187 (1969).

(8) B. L. Shaw, *Chem. Commun.*, 464 (1968); *Amer. Chem. Soc., Div. Petrol. Chem. Prepr.*, **14**, F17 (1969).

(9) F. R. Hartley, *Nature (London)*, **223**, 615 (1969).

(10) P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 7305 (1972).

(11) P. M. Henry, *J. Org. Chem.*, 37, 2443 (1972).

(12) A. Panunzi, A. De Renzi, and G. Paiaro, *J. Amer. Chem. Soc.*, **92**, 3488 (1970).

(13) P. M. Henry, *Accounts Chem. Res.*, 6, 16 (1973).

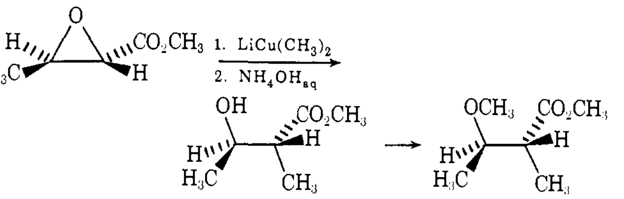
(14) L. F. Hines and J. K. Stille, *J. Amer. Chem. Soc.*, **94**, 485 (1972).

Table I. Catalytic Carbonylation of *cis*- and *trans*-2-Butene[a]

		Products[b]							
		Methyl 3-methoxy-2-butanecarboxylate			Dimethyl 2,3-butanedicarboxylate			Olefin isomerization	
Olefin	Time, hr	% yield	% threo	% erythro	% yield	% *dl*[c]	% meso[c]	% cis	% trans
cis-2-Butene	2	1.4	100	0				100	0
	8	6.7	100	0				85	15
	100	33	87	13	1	60	40	23	77
trans-2-Butene	2	0.7	0	100				0	100
	8	1.9	0	100				5	95
	100	19	40	60	1	100	0	20	80
cis-2-Butene[d]	100	0			3	0	100	100	0
trans-2-Butene[d]	100	0			20	100	0	0	100

[a] 50 mmol of olefin, 2.8 mmol of $PdCl_2$, 100 mmol of $CuCl_2$, 75 ml of methanol, 2 atm of CO at 28°. [b] % yield ± 1%, determined by glc and based on olefin. Isomer distribution ±1%, determined by glc. [c] Identified by hydrolysis to the corresponding acids (R. P. Linstead and M. Whalley, *J. Chem. Soc.*, 3722 (1954)). [d] 100 mmol of sodium acetate added to the reaction mixture.

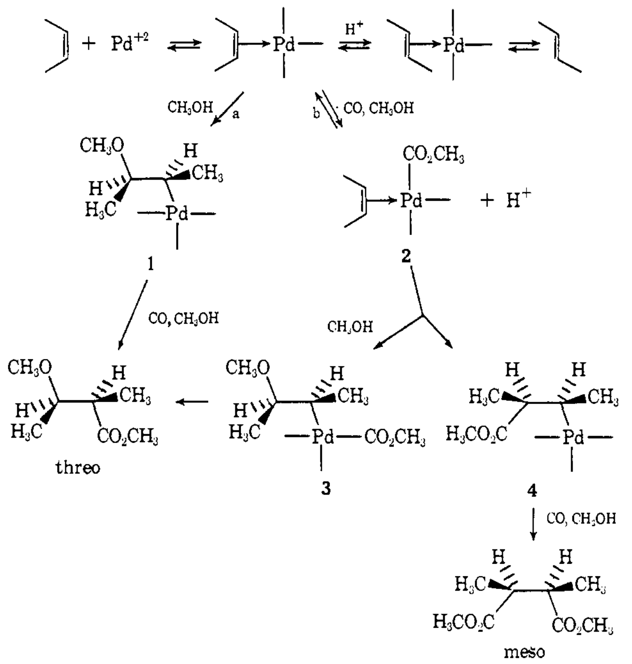
The erythro and threo isomers were identified by the independent synthesis of *threo*-methyl 3-methoxy-2-butanecarboxylate.[15]



Formed coincidentally with the methoxy esters, although in relatively smaller amounts, are substituted succinic esters. *cis*-2-Butene gives a mixture of diesters, meso and *d,l* pair, while *trans*-2-butene yields only the *d,l* enantiomers. By the addition of sodium acetate, conditions which preclude prior isomerization of the olefins are obtained, the diesters are the exclusive products, and the dicarbonylation is stereospecifically cis. The carbonylation of *trans*-2-butene, which is at least seven times faster than that of the cis isomer, gives exclusively the *d,l*-succinic ester while *cis*-2-butene gives only the meso diastereomer.

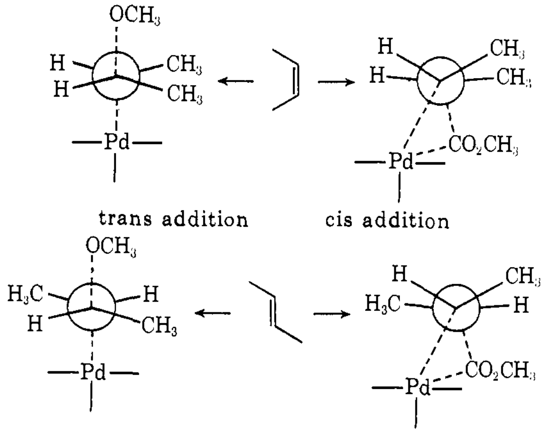
These results are consistent with the mechanism shown in Scheme I for *cis*-2-butene.

Scheme I



Several aspects of this mechanism deserve comment. The cis–trans isomerization reaction appears to be acid catalyzed as isomerization does not occur in the early stages of the reaction or under buffered (sodium acetate) conditions. The *threo*-β-methoxy ester could be readily obtained from the carbonylation of the intermediate product **1** resulting from trans methoxypalladation of the *cis*-2-butene. The olefin–palladium carboxylate complex **2** is a plausible common intermediate to both the β-methoxy ester and the diester. Trans attack of uncoordinated methanol solvent could give the σ-bonded complex **3** which undergoes carbon monoxide insertion and reaction with methanol also to give the *threo*-β-methoxy ester. Alternatively, **2** may undergo a cis addition of palladium and coordinated carboxylate to yield the σ-bonded complex **4**, carbonylation of which gives the observed meso diester.

The faster rate of the conversion of *cis*-2-butene to β-methoxy ester relative to *trans*-2-butene is consistent with this mechanism which requires formation of a more stable π complex for the cis isomer[16] and greater relief of steric repulsion in the transition state for the trans addition to a cis olefin. By contrast, cis addition of coordinated carboxylate ligand and palladium to *cis*-2-butene to form diester requires a transition state generating greater steric crowding than that observed for the trans isomer.



The relative rate data, showing that the rate of methoxypalladation is greater for the cis isomer while the rate of carbomethoxypalladation is greater for the

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(15) R. W. Herr, D. M. Wieland, and C. R. Johnson, *J. Amer. Chem. Soc.*, 92, 3813 (1970).

(16) F. R. Hartley, *Chem. Rev.*, 73, 163 (1973).

trans isomer, also strongly suggest that **4** is not an intermediate in the formation of *both* β-methoxy ester and diester products. Although S_N2 displacement of palladium by nucleophile has been demonstrated in acetic acid systems[10] and postulated for alcoholic systems,[17] it is clear that β-methoxy ester and diester products are best explained by two distinctly different intermediates arising from the rate-determining step (formation of the Pd–C σ-bonded complex).

The effect of added acetate to this system is quite remarkable in that it can change the course of the reaction completely, and either β-methoxy ester or diester can be obtained at will. Several explanations are possible. If paths a and b each are exclusively responsible for the formation of β-methoxy ester and diester, respectively, sodium acetate may enhance the formation of intermediate **2** by base catalysis. Also, acetate ion may influence the rates of the reactions occurring by the different pathways by coordination to palladium, thereby changing the structures of the intermediate complexes and thus their activity.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[17] O. L. Kaliya, O. N. Temkin, N. G. Mekhryakova, and R. M. Flid, *Dokl. Chem.*, **199**, 706 (1971).

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Evidence for Structurally Different $C_7H_7^+$ Ions. An Electron Impact Study of Benzyl Phenylacetate

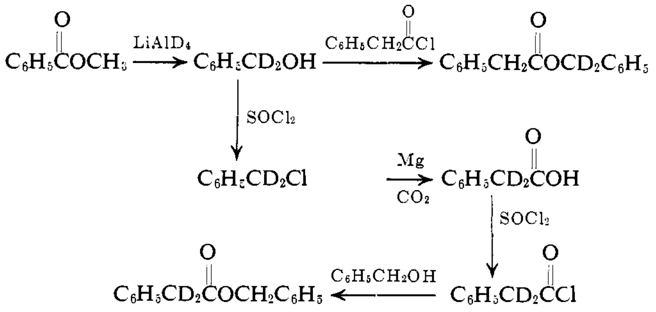
Sir:

The structure of the $C_7H_7^+$ ion formed from various precursors has interested mass spectrometrists for over 15 years.[1–6] Indeed the ring expansion of the ion when formed from benzyl-type derivatives and the subsequent decomposition routes are among the more interesting examples of bond migrations in organic chemistry.

In most systems studied, usually by isotopic labeling, the $C_7H_7^+$ ion has ring expanded to form a tropylium ion, and those ions with sufficient energy to further decompose are both completely H–D and carbon scrambled. As a contrast to the usual simple losses of hydroxyl or halogen to form $C_7H_7^+$, Meyerson[7] has examined the mass spectra of diphenylmethane and bibenzyl. Deuterium labeling studies seem to indicate that the symmetrical bibenzyl forms $C_7H_7^+$ ions with an energy distribution similar to that of other simple benzyl derivatives: the C_7 species is best described as a tropylium ion formed by random insertion of hydrogen into the carbon skeleton.[8] Diphenylmethane, on the other hand, apparently forms a tropylium ion *via* a different energetic pathway—1,2 insertion [*i.e.*, the hydrogen (deuterium) atoms on the methylene group insert onto adjacent carbon atoms].

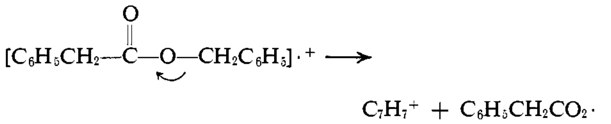
In an effort to further elucidate this structural problem, and to explore the possibility of generating two structurally and energetically different $C_7H_7^+$ ions from different parts and by different pathways within the same molecule, we have examined the mass spectrum of benzyl phenylacetate and its d_2 and d_4 isomers. The synthetic route is outlined in Scheme I.

Scheme I

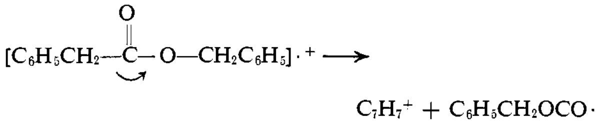


The low-temperature mass spectra of benzyl phenylacetate (I), benzyl-α-d_2 phenylacetate-d_2 (II), benzyl-α-d_2 phenylacetate (III), and benzyl phenylacetate-α-d_2 (IV) were obtained at 70 eV.[9] The relative intensities of selected ions are shown in Table I.

As expected, the $C_7H_7^+$ ion dominates the spectra of benzyl phenylacetate. In the d_4 species, this peak shifts cleanly to $C_7H_5D_2^+$. The two dideuterated esters, III and IV, show that the C_7 ion is formed by two different pathways.



$$[C_6H_5CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2C_6H_5]^{\cdot +} \longrightarrow C_7H_7^+ + C_6H_5CH_2CO_2\cdot \quad (1)$$



$$[C_6H_5CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2C_6H_5]^{\cdot +} \longrightarrow C_7H_7^+ + C_6H_5CH_2OCO\cdot \quad (2)$$

The presence of metastable peaks at 36.3 and 37.9 amu in the mass spectra of III and IV confirms these processes. The C_7 moiety appears to be formed more easily by cleavage of the benzyl–oxy bond (eq 1) than by cleavage within the phenylacetate portion of the molecule, if one assumes equal decomposition rates for the reactive C_7 ions (*vide infra*).

As expected, the total ion current within the C_7 ions from III and IV is the same, relative to that carried by the molecular ions, and the amounts of ion current carried by $C_7H_7^+$ and $C_7H_5D_2^+$ ions are reversed in these two esters.

The distributions of the deuterium label found within the C_5 ions from II are quite similar to those found by

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[1] P. N. Rylander and S. Meyerson, *J. Amer. Chem. Soc.*, **78**, 5799 (1956).

[2] P. N. Rylander, S. Meyerson, and H. M. Grubb, *ibid.*, **79**, 842 (1957).

[3] S. Meyerson, P. N. Rylander, E. L. Eliel, and J. D. McCollum, *ibid.*, **81**, 2606 (1959).

[4] K. L. Rinehart, A. C. Buchholz, G. E. Van Lear, and H. L. Cantrill, *ibid.*, **90**, 2983 (1968).

[5] A. S. Siegel, *ibid.*, **92**, 5277 (1970).

[6] M. K. Hoffman, manuscript submitted for publication.

[7] S. Meyerson, H. Hart, and L. C. Leitch, *J. Amer. Chem. Soc.*, **90**, 3419 (1968).

[8] The data are not nearly as conclusive as one might have expected, and the actual situation may perhaps be more complicated than the interpretation implies. See ref 7; also see below.

[9] The data here reported were obtained from direct probe samples at a source temperature of 100° using an AEI MS9 mass spectrometer. Spectra obtained at higher temperatures differed primarily in that they exhibited less intense molecular ions. The relative ratios of the C_7 and C_5 species remained essentially unchanged.